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Materials of Construction *for* Shipboard Waste Incinerators

Report of
The Committee on Materials of
Construction for Shipboard Incinerators

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D.C.
1977

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PREFACE

The study upon which this report is based was requested by the U. S. Navy and the U. S. Coast Guard to respond to their need for complying with legislation which prohibits polluting the ocean within the coastal regions. One alternative for compliance is storing the shipboard waste for ultimate disposal at land-based facilities or dumping far out at sea. Another is directly processing wastes on board the ship. The Navy and Coast Guard have decided to pursue the latter alternative, and it is to this problem that this study of material for shipboard incinerators is addressed.

Incineration of wastes in land-based facilities presents no serious material problem since there is no limitation to the size and weight of such incinerators. Standard commercial ceramic materials should be adequate to withstand conditions for land-based incinerators. However, for shipboard, the weight and size of incinerators are limited and bulky ceramics are excluded. These restrictions on weight and size dictate a light-weight system and in particular the use of an incinerating chamber which is light and small. These criteria call for a metallic or light-weight ceramic liner.

The high operating temperature of incinerators and the large quantities of aggressive species as chlorine, sulfur, and sodium, challenge the existing materials technology. It was for this reason that the Navy and the Coast Guard decided to convene a panel of experts under the aegis of the National Academy of Sciences. This panel was asked to consider the potential performance of materials together with any modification in design which would be necessary to achieve reliable performance.

The panel was convened by the National Materials Advisory Board (NMAB) which is an operating unit of the Commission on Sociotechnical Systems of the National Research Council. Members of the panel, together with their areas of technical contribution follow:

Mr. Eugene C. Bailey, John Dolio and Associates, Inc. (Incineration of Metropolitan Solid Waste in Power Boilers)

*Mr. Walter K. Boyd, Battelle Memorial Institute (Corrosion and Materials Selection)

Prof. Ivan B. Cutler, University of Utah (Ceramic Materials)

Mr. Richard B. Engdahl, Battelle Memorial Institute (Incinerator Technology)

Prof. Robert H. Essenhigh, Pennsylvania State University (Flames and Fuel)

Dean Earnest F. Gloyna, University of Texas at Austin (Pollution Control and Sanitary Engineering)

Mr. Edwin Myskowski, Fairchild Industries (High Temperature Materials)

Dr. Fred S. Pettit, Pratt and Whitney Aircraft (High Temperature Corrosion Theory and Turbine Experience)

Prof. Roger W. Staehle, Ohio State University, Chairman (Corrosion)

**Dr. Craig S. Tedmon, General Electric Research and Development Center (High Temperature Corrosion)

Dr. William Tessin, Florida Atlantic University (Ship Design and Operation)

This committee met with experts who contributed information and perspectives from available scientific and technological sources. Their contributions are gratefully acknowledged. These participants were:

C. M. Adema, David W. Taylor Naval Ship Research and Development Center
R. Alliegro, Norton Company
J. L. Boyland, Marquardt Company
R. B. Burden, Jr., Thermal Engineering Company
D. Clark, Thiokol Corporation
S. Dapkunas, David W. Taylor Naval Ship Research and Development Center
J. Gangler, National Aeronautics and Space Administration
R. Hasselman, Lehigh University
P. Lakomski, Thiokol Corporation
F. K. Lampson, Marquardt Company
C. Marks, Vent-o-Matic Incinerator Corporation
E. Nolan, General Electric Company

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*Mr. Boyd was a consultant to the committee. In this connection he participated especially in the preparation of the chapters on the corrosion of materials and met with the committee at regular meetings.

**Dr. Tedmon was an original member of the committee but later had to resign. He was replaced by Dr. Pettit.

M. Raupuk, David W. Taylor Naval Ship Research and
Development Center
M. Rossetti, Arthur D. Little Company
J. Santoleri, Trane Thermal Corporation
P. D. Sierer, Jr., David W. Taylor Naval Ship Research and
Development Center
H. Soman, 3M Corporation
W. van Hees, David W. Taylor Naval Ship Research and
Development Center
T. Vasilos, Avco Corporation
W. Wheatfall, David W. Taylor Naval Ship Research and
Development Center
R. C. Whitaker, Marquardt Company
R. J. Wolfe, David W. Taylor Naval Ship Research and
Development Center
S. V. Wyatt, Naval Ship Engineering Center
L. Yerkovich, Huntington Alloys
S. R. Zerrip, David W. Taylor Naval Ship Research and
Development Center

The first meeting of the committee was held on 18-19 February 1975. Subsequent meetings were held approximately once per month and the final meeting was held 4-5 March 1976. As the work of the committee progressed, several important ideas became clear. First, the performance of materials depends critically upon the design and operation of the incinerators. The implicit environmental conditions in incinerators are sufficiently aggressive to exclude virtually all materials so that careless or nonstandard operations could easily destroy even the best material. As a result, the committee decided to broaden its view of reliability. This report was expanded to include the broad set of factors which are closely interrelated with incinerator performance. The final report is more of a materials-design text.

A second important realization involved the possibly broader application of the technology of small volume incinerators to commercial uses. Since much of the information in this report had never been synthesized, the expanded treatment serves the anticipated application to a broader constituency than the original objective to serve only the Navy and the Coast Guard.

A previous NMAB report, "Materials for Wet Oxidation Processing Equipment (Shipboard)," (NMAB-312), reviewed materials of construction for the wet oxidation of shipboard waste. This was a brief study requested by the Office of the Director, Defense Research and Engineering, U. S. Department of Defense. However, as the concern for processing shipboard wastes has extended to include a broader range of materials, the wet oxidation process is not suitable, and multifunctional incinerators become more desirable.

The early incinerators considered by the Navy and the Coast Guard were the less complex vortex and pot types. However, these can handle only fluid wastes and are not capable of handling the more complex wastes including solids. The primary objective of the study is the development of multifunctional incinerators which can handle all shipboard wastes.

I wish to acknowledge a number of important contributions to the final report. First, members of the committee contributed various chapters and subsections according to their respective areas of expertise. These chapters were successively improved over the final 6 months of committee work. Improved versions of these drafts were refined by reviews from other members of the committee and benefited greatly therefrom. The committee met on 4-5 March 1976 to review the final draft. The draft was then reviewed by Mrs. D. C. Andrews from the English Department at The Ohio State University and this version was edited technically by the committee chairman.

In a volume such as this, there are inevitably differences in style among the contributors and as appropriate to the different subjects. While the editor extensively modified the text in the interests of brevity and coordination among chapters, many inconsistencies in style remain. However, further editing to achieve a monlithic style seemed unnecessary. A perceptive reader will note also some inconsistencies in the units. In particular, there are some odd temperatures which resulted from transforming °F to °C. But these small awkwardnesses are hopefully forgiveable.

I wish to thank my own staff, Mrs. Antoinette Biggert, Mrs. Carol Davis and Mrs. Catherine Ward, for their assitance through phases of my participation in the work of this committee. I wish particularly to thank Mrs. Sue Morrisson, from NMAB, who typed the entire manuscript with great care and competence. In editorial matters, I was assisted by Mr. B. Miglin and Mr. L. Littleton.

Mr. W. K. Boyd from Battelle is acknowledged for his extensive contributions over the tenure of the committee as a consultant although he was not appointed originally. His broad knowledge of corrosion processes was invaluable.

Messrs. Paul Schatzberg, George Wacker, and Dr. Irvin Kramer of the U. S. Navy and Messrs. Thomas Scarano and James White of the U. S. Coast Guard, the principal liaison representatives from the sponsoring agencies, were particuarly helpful in providing critical comments and in supplying important data from their organizations.

Finally, I wish to acknowledge especially the work of Donald G. Groves of the National Materials Advisory Board-National Research Council-National Academy of Sciences professional staff who coordinated the work of this committee. His energetic efforts and stimulating comments contributed greatly to the effectiveness of this committee.

Roger W. Staehle
Chairman

NATIONAL MATERIALS ADVISORY BOARD
COMMITTEE ON
MATERIALS OF CONSTRUCTION FOR SHIPBOARD INCINERATORS

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ROGER W. STAEHLE, Professor and Director, Fontana Corrosion Center, The Ohio State University, Columbus, Ohio

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IVAN B. CUTLER, Professor, Ceramic Engineering, Department of Materials Science and Engineering, College of Engineering, University of Utah, Salt Lake City, Utah

RICHARD B. ENGDAHL, Fellow, Environmental Research, Battelle-Columbus Laboratories, Columbus, Ohio

ROBERT H. ESSENHIGH, Professor of Fuel Science, Combustion Laboratory, The Pennsylvania State University, University Park, Pennsylvania

EARNEST F. GLOYNA, Dean, Engineering, University of Texas at Austin, Austin, Texas

EDWIN MYSKOWSKI, Fairchild Statos Division, Manhattan Beach, California

FREDERICK S. PETTIT, Materials Engineering Research Laboratory, Pratt and Whitney Aircraft Corporation, Middletown, Connecticut

WILLIAM TESSIN, Chairman, Department of Ocean Engineering, Florida Atlantic University, Boca Raton, Florida

Liaison Representatives

PAUL SCHATZBERG, Senior Research Chemist, Pollution Abatement Division, U. S. Naval Ship Research and Development Laboratory, Annapolis, Maryland

IRVIN KRAMER, Materials Department, U. S. Naval Ship Research and Development Laboratory, Annapolis, Maryland

GEORGE WACKER, Head, Metal Physics Branch. David W. Taylor Naval Ship Research and Development Center, Annapolis, Maryland

THOMAS SCARANO, Commandant (GDET), Office of Research and Development, U. S. Coast Guard, Washington, D. C.

JAMES WHITE, Commandant (GDET), Office of Research and Development, U. S. Coast Guard, Washington, D. C.

Special Advisor on Corrosion

WALTER K. BOYD, Manager, Corrosion and Electrochemical Technology Section, Battelle-Columbus Institute, Columbus, Ohio 43201

NMAB Staff

DONALD G. GROVES, Staff Engineer

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CHAPTER 1.0

EXECUTIVE SUMMARY WITH CONCLUSIONS AND RECOMMENDATIONS

The development of incinerators for shipboard use is implied by provisions in the Water Quality Act of 1972 which requires that certain wastes not be dumped overboard in the oceans within coastal regions after 1980. The requirements of this act imply that most wastes generated on ships must be reduced to simple, non-contaminating chemical species before they are released.

The shipboard wastes to be incinerated consist primarily of human wastes, solid waste, garbage, and waste oil sludge. Incineration of such wastes in land-based facilities is performed in commercial or municipal systems which usually are not subject to restrictions of space and weight.

The design of incinerators for shipboard operation poses substantially different problems from those posed by land-based units. Problems include (a) limitations of weight, (b) limitations of size, (c) the reliability and lifetime of systems or key components without extensive intermediate repair, (d) the level of training of operative personnel, and (e) the limited availability of repair techniques for unique materials. These problems combine to produce circumstances that press existing candidate materials of construction beyond their capacity to perform economically and reliably.

This study was requested by the U.S. Navy and the U.S. Coast Guard to assess the nature of the materials problems associated with the development of reliable shipboard incinerators. The committee viewed the materials problem broadly. It considered metallic and ceramic materials, variations of composite constructions, changes in design which could solve many of the problems with incinerator materials, special problems with combustion flames as they influence materials behavior, and problems of reliability associated with auxiliary equipment.

The sponsors advised the committee that reliability was the dominating criterion.

The committee was requested by the sponsors to assess relative costs of alternative materials systems, but this assessment was not made because of uncertainties in both fabrication techniques and performance.

An important part of assessing the performance of materials is defining the environment. This is particularly important in the complex circumstances of an incinerator designed to minimize volume and weight. The current understanding of environmental conditions is summarized in Section 1.1. With that as a basis, the performance of candidate materials is summarized in Section 1.2 according to the range of conditions over which they may be expected to perform reliably. Conclusions and recommendations are presented.

Since the performance of materials is only one part of the general problem of reliability, the committee considered critical questions of reliability, maintainability, and safety. These considerations with appropriate conclusions and recommendations are given in Section 1.3. Finally, since the technology of small incinerators is not mature, a substantial amount of additional work is needed. Future work is recommended in Section 1.4.

1.1 Operational Factors Affecting the Performance of Materials

The critical factors influencing the performance of materials are temperature, chemical environment, wall inpingement by flames or particles, and operating procedures.

1.1.1 Temperature

Much of the problem with materials arises from the high temperatures required to maintain stable flames and to destroy odors. The minimum temperature required to stabilize the flame at the low combustion limit is about 1200°C; and to allow for temperature or concentration fluctuations without flameout, a temperature of at least 1300°C should be sought. The generally accepted method of destroying odor involves maintaining the temperature above about 800°C for at least 0.5 second.

The maximum wall temperatures permitting materials to perform reliably are substantially lower than these two flame temperatures. For low alloy steels, the maximum temperature is about 290°C, while for highly alloyed materials, the maximum temperature is ~ 980°C. For ceramic materials, the maximum possible temperature is ~ 1100°C. With air- or water-cooled furnace walls, these operating temperatures can be reduced for metallic liners to as low as about 540°C (air-cooled) or 180°C (water-cooled).

The outlet temperature for the incinerator system must be less than about 340°C to be compatible with the exhaust system of the ship. These lowered temperatures can be achieved by diluting with air.

1.1.2 Chemical Environment

The chemical environment is determined by the materials which enter the incinerator: human waste, garbage, rubbish, waste oil, salty flush water, fuel. While a wide range of contaminants has been identified, those which are present in relatively large quantities and accelerate corrosion are chlorine, sulfur, and sodium. The aggressiveness of the resulting environments may be accelerated by the formation of low-melting salts, and by alternating oxidizing and reducing conditions.

1.1.3 Wall Impingement

The liners of the incinerator may be degraded when the flame, particles, or unevaporated spray impinge on the walls.

Flame impingement can produce local overheating which, at a minimum, causes distortion of metal liners and erosion of ceramic walls, and at worst, consumes or collapses the wall. The rate of consumption may be accelerated if the local atmosphere is reducing. Flame impingement on refractories is usually not so damaging unless the surfaces are soft. However, the possible damage by flame impingement on ceramic walls needs more study. Impacting particles may adhere to the surface of the wall if they are hot enough to be sticky; if they are hard, they may erode the surface. Spray condensation typically causes localized cooling and the resulting thermal stresses cause distortion and cracking.

1.1.4 Operations

The life of materials is usually reduced by cyclic variations in thermal and chemical conditions. Normal daily cycling, associated with periodic operation of the incinerator, causes more rapid degradation than operating at constant temperatures. The degradation is also increased with the severity of the chemical environment. Very rapid thermal transients produce thermal shock and consequent spalling of ceramic materials.

When the lower temperature—corresponding to shutdown conditions—is below the condensation temperature of the flue gases, the resulting aqueous solutions are likely to contain acid-forming species such as HCl and H_2SO_4 which accelerate general corrosion or stress-corrosion cracking. Consequently, the lifetime of the system will be extended if minimum temperatures in the furnace or gas passages are maintained above the condensation temperature.

To reduce the frequency of inevitable on/off operation, holding tanks and refuse storage tanks should be as large as possible so that the period of incinerator operation can be lengthened.

To reduce the potential for thermal shock on startup, the burner should be programmed to reach high load in stages. The reverse procedure should also be used on shutdown both to purge the chamber of combustible waste gases and to control cooling.

Rapid thermal transients can be caused by two upset conditions. Flameout from fuel supply failure will cause rapid cooling, and overheating will be caused by either blockage of the sewage supply or by a rapid injection of combustible materials.

A serious hazard of operation can be associated with the removal of deposited solids. When an accumulation of solids has to be mechanically removed, careless raking out may damage the liner. Specially designed tools and methods are recommended for removal of deposits.

1.2 Performance of Candidate Materials

1.2.1 Conclusions

1. The environment within an operating incinerator chamber is highly aggressive because of the high temperature and the presence of corrosive combustion products such as sulfates and chlorides. Further, the conditions of operation greatly influence the performance of materials. The following conclusions apply to metallic liners.

a. For designs with water-cooled walls and temperatures rigidly controlled between 150°C minimum and 290°C maximum, plain carbon steels are satisfactory. The relatively high lower limit is required because of the aggressiveness of the condensed water as it leaches chemicals from deposits when the incinerator is shut down.

b. For air-cooled systems operating within the temperature range of 290°C to 600°C, austenitic steels such as types 309 and 310 are acceptable materials provided, as with the low alloy steel liner, the minimum temperature is maintained above 150°C.

c. For incinerators operating in the range of 600°C to 760°C where molten salts or ash may be present, only highly alloyed materials can be used. Candidate alloys in order of preference are those having a composition of ~50 - ~50 nickel-chromium (Inconel-671); the 60-30 nickel-chromium (Inconel-690); the ~28 - 51 chromium-cobalt (Haynes-150); and possibly the ~22 - 22 - ~40 nickel-chromium-cobalt (Haynes-188).

d. For temperatures of 760°C and above, the lives of metallic liners will be limited. The only metallic alloy material which may be acceptable in this regime is one having an approximate 50-50 nickel-chromium composition. This alloy perhaps can be used to 980°C with temperature excursions to 1100°C, but this capacity needs further confirmation. The use of MCrAlY ("M" is, for example, Co or Ni) coatings could improve the performance of such liners.

2. For wall temperatures of 600°C and above, ceramics appear to be acceptable liner materials. The candidate materials in order of preference for chemical reactivity and with these maximum recommended

operating temperatures are: SiC (18% Si_3N_4) (980°C); Mullite ($3Al_2O_3 . 2SiO_2$) (980°C); castables (60 to 97% Al_2O_3) (760°C); rigidized aluminum silicate fibers of over 60% alumina content (760°C); and aluminum silicate blankets for backup insulation only.

3. Above 600°C, the choice between metallic and ceramic materials depends on the failure mechanisms which may be implicit in the operation of the incinerator liner; in particular, corrosion for metals and thermal shock for ceramics.

4. The available information indicates that a service life of 10,000 hours is attainable with existing materials if they are operated within the conditions specified for satisfactory performance.

1.2.2 Discussion

Materials performance data for operational prototype incinerators are limited. Laboratory evaluation of materials of construction under simulated incinerator operating conditions is in progress. A substantial amount of applicable data is available from the following sources: municipal incinerators, water-wall incinerators, gas turbines, and stationary power plants. Degradation mechanisms for metallic materials involve acidic attack at temperatures below 150°C due to condensation of corrosive species as well as oxidation and hot corrosion at higher temperature.

Fifty years of operating experience with fossil fuel power boilers and more recent experience with water-wall incinerators demonstrate that the maximum safe operating temperature for carbon and low alloy steels under anticipated shipboard incinerator environments is 290°C.

In benign environments, the austenitic steels can be used to temperatures as high as 980°C. For shipboard incinerators, these steels should not be used above 600°C for the following reasons:

- In the presence of chloride salts, they suffer severe intergranular oxidation above 650°C.
- Long time exposures at temperatures exceeding 600°C can produce a sigma-phase along grain boundaries which can cause materials embrittlement.
- In certain grades, carbide precipitation may increase the susceptibility to high-temperature oxidation and low-temperature stress-corrosion cracking.

Like the carbon steels, the austenitic stainless steels suffer rapid degradation at low temperatures in the presence of acid-chloride deposits.

For shipboard incinerators, ferritic stainless steels of the Fe-26Cr-1Mo type appear to have only limited applicability in view of their metallurgical instabilities over the temperature ranges required.

Where resistance to both high temperature oxidation and molten-salt-induced attack is required, gas turbine and stationary power plant experience with residual oil has shown that alloys must contain at least 30 percent chromium. In addition, the refractory metal content (Mo, W, V) must be kept as low as possible owing to the tendency to cause catastrophic oxidation.

Ceramic materials have been shown to resist high temperature corrosion induced by molten deposits. The main shortcoming of ceramic materials is their inherent brittleness and susceptibility to damage by thermal shock. A second undesirable feature is their relatively high weight per unit area of the finished construction compared to metallic systems.

1.2.3 Recommendations

Full-scale life tests of the most promising metallic and ceramic materials should be begun as soon as possible aboard ship. These liners should be instrumented so as to define operating conditions and failure mechanisms.

It appears unwarranted to pursue a major alloy development for this application since there are extensive data available for materials of interest. However, it is recommended that additional data be generated for the following material properties.

1. The upper temperature limits of nickel, chromium, cobalt alloys such as Inconel-671, Inconel-690, and Haynes-150.

2. The long-time metallurgical stability of weldments such as those composed of Inconel-671.

3. The thermal shock characteristics of ceramics under long-time cyclic operating conditions.

1.3 Reliability, Maintainability, Safety

1.3.1 Conclusions

1. Incinerators are not critical to a ship's overall mission. However, they should be reliable and easy to maintain, and any malfunction should not interfere with the mission of the ship. The Navy and Coast Guard consider that acceptable reliability can be defined in terms of one allowable system failure in 60 ten-hour operating cycles. Similarly, maintainability can be arbitrarily defined as a maximum repair time of five hours. If these objectives can be achieved, the reliability is 0.98; the resulting mean time between failures is then 500 hours. The information on materials performance

summarized in section 1.2 suggests that the liner materials should be able to meet this objective.

2. Safe operation means the avoidance of detonations or uncontrolled fires. These events result from malfunction of the fuel supply; accidentally introduced ordnance or other explosives; paints, solvents and fuels in closed container; or methane accumulations from stored sewage.

1.3.2 Discussion

If the remainder of the incinerator system is marginally designed, then a special effort to develop superior liner materials is unwarranted. The committee identified numerous operating and design circumstances which could improve the incinerator system.

1.3.3 Recommendations

1. The probability and conditions for incinerator detonations and uncontrolled fires should be clearly defined and appropriate operating controls included in the design.

2. Controls for incinerator operation should be designed to minimize temperature excursions and impingement of flames on the liners.

3. Careful attention should be given to the design of auxiliary equipment so that it is not less reliable than the liner materials.

1.4 Future Studies and Applications

1.4.1 Conclusions

Increasing legal and social pressures to reduce pollution suggest greater use of incinerating equipment not only in naval but also in municipal and commercial applications. The small volume incinerator systems developed for shipboard applications will be useful in commercial applications. Identification of problems in development and operation of shipboard incinerators will be valuable in the development of improved units. With respect to the development of improved shipboard units as well as the technology of small volume and high performance incinerators, the following specific conclusions pertain:

1. Many of the promising metallic and ceramic materials for use as incinerator chamber liners have been investigated or are now under study.

2. Burner rig tests have proved useful in rating candidate materials, and results from these studies correlate well with the limited service performance. However, no one testing procedure is adequate in view of the complex circumstances of operation. As candidate materials are refined, more sensitive predictive tests will be needed as well as good programs of proof testing of liners in operating incinerators.

3. Techniques for the fabrication and repair of liners require extensive study.

4. In order to assure the reliability and long life of small volume incinerators, some design concessions will be required to reduce the severity of the thermal and chemical conditions.

1.4.2 Discussion

The environment in an incinerator combustion chamber is hostile because of the combination of high temperature and corrosive molten salt deposits. Laboratory tests must simulate such operating conditions. The burner rig test was developed by the Navy to provide a means of evaluating candidate metallic materials. As a starting point, urine was burned with fuel and the combustion products impinged on metal test coupons at 760°C. At this temperature, eight alloys exhibited corrosion rates low enough to warrant consideration for liner application.

While the 760°C test temperature was useful, the performance of candidate metals at temperatures above and below this point needs to be investigated since actual service temperatures will depend on incinerator design. Owing to the complexity of conditions in incinerators, there is no method of predicting behavior at possible lower and higher average temperatures (650°C or 870°C) on the basis of data obtained at 760°C. Another unknown factor is the effect of brief temperature excursions due to system malfunction. Such malfunctions could raise temperatures to 980°C or higher with resultant melting of ash deposits and consequent acceleration of corrosion.

The fabrication of metal liners will require the use of weld materials which may be subject to long-term aging effects. The metallurgical aging of the weld metal would further degrade the properties of the weld deposit and increase the probability of service failure. Additional weld repairs might be required during the lifetime of the liner. At present, because fabrication and repair procedures for both metallic and ceramic liner materials are not well defined, potential problems exist.

Because of the complexity of the severe environment, no simple tests can be used to define all of the boundary conditions. Specific areas for study include temperature limits; high, low, and ambient temperature reactions between combustion products and liner materials; and effects of normal operational cycling.

Very little is known about the effects of design changes on performance of liner materials. Design optimization can reduce the severity of the local environment with consequent improvement in performance of liner materials.

1.4.3 Recommendations

Studies are recommended in the following areas:

1. Burner rig testing should be extended to include temperatures of 650°C and 540°C and excursions to 980°C.

2. Ash deposits should be further studied to determine elemental compositions, chemistry, melting point, and reactivity with liner materials at high, low, and ambient temperatures.

3. Fabrication and repair procedures for candidate metallic and ceramic liner materials should be developed.

4. Cycling effects (frequency, range, and rate) on liner materials should be investigated.

5. Ameliorative effects of introductions such as clay, calcia, magnesia as well as possibly deleterious effects of lead, zinc, and silver contaminants should be investigated.

6. Life testing of a nickel, chromium, cobalt alloy liner such as Inconel-671, under normal operating conditions should be conducted (see section 1.2.3).

7. Design optimization studies should be an important objective of future work.

CHAPTER 2.0

INTRODUCTION

2.1 The Problem of Shipboard Waste

Until recently, waste disposal was not an issue of serious concern in ship design and operation. Wastes were indiscriminately disposed of both at sea and on land. Two factors have dramatically changed this situation. First, media converage of oil spills made the public aware of the damage done to the oceans by accidental spillage. Second, the environmental movement in the 1960's focused popular interest on the pollution of air, land, and sea by municipal, industrial, and residential patterns of waste disposal. Concern for the environment eventually took the form not merely of public interest expressed in all media, but also of new laws and regulations designed to curb pollution, both on land and at sea.

In addition to sanitary wastes, the most obvious component of shipboard waste, the trash produced in the course of day-to-day operations, must be disposed of: cans, bottles, food wastes, oil, and the like. Trash presents problems under all conditions, but when produced aboard ship, it requires special techniques of disposal to assure both that the environment is protected and that the ship's normal operations are not hindered.

2.1.1 Legislative and Regulatory Developments

The current Navy and Coast Guard programs for the development of shipboard waste incinerators are part of a larger effort to reduce vessel waste discharges to the environment. In turn, these efforts in marine environmental protection at the Federal level are part of a nationwide effort to improve and preserve the water, air, and land resources of the United States. This goal was promulgated by the Federal Water Pollution Control Act Amendments of 1972 (1972 FWPCA) [1] which states in part:

> The objective of this Act is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters. In order to achieve this objective it is hereby declared that...

> (1) it is the national goal that the discharge of pollutants into the navigable waters be eliminated by 1985;
>
> .
>
> .
>
> .
>
> (6) it is the national policy that a major research and demonstration effort be made to develop technology necessary to eliminate the discharge of pollutants into the navigable waters, waters of the contiguous zone, and the oceans.

This Act and related prior Federal laws are the basic enabling legislation for the Navy and Coast Guard programs in marine environmental protection, including the development of shipboard waste incinerators.

The accomplishment of the objectives and goals of the 1972 FWPCA at the Federal level were reaffirmed by Executive Order 11752 (2):

> It is the purpose of this order to assure that the Federal Government, in the design, construction, management, operation, and maintenance of its facilities, shall provide leadership in the nationwide effort to protect and enhance the quality of our air, water, and land resources...

Shipboard waste incinerators are currently being developed to dispose of sewage, waste oils, and solid waste. Most of these units are components of total vessel management systems, and are intended to dispose of the various types of waste either singularly or in combination. Legislation, standards, and regulations for each waste have necessitated vessel waste management systems in general, and shipboard incinerators in particular.

With regard to shipboard sewage, the 1972 FWPCA (3) states in part:

> ...the Administrator...shall promulgate Federal standards of performance for marine sanitation devices...which shall be designed to prevent the discharge of untreated or inadequately treated sewage into or upon the navigable waters from new and existing vessels...

Pursuant to this requirement, the Environmental Protection Agency (EPA) issued performance standards for marine sanitation devices which, in part, set forth limitations on no-discharge and discharge devices, and established the effluent quality standards for discharge devices. The EPA standards [4] state:

> (1) In freshwater lakes, freshwater reservoirs or other freshwater impoundments whose inlets or outlets are such as to prevent the ingress or egress by vessel traffic..., marine sanitation devices... installed on all vessels shall be designed and operated to prevent the overboard discharge of sewage, treated or untreated, or of any waste derived from sewage...
>
> (2) In all other waters,... marine sanitation devices installed on all vessels shall be designed and operated to either retain, dispose of, or discharge sewage. If the devices has a discharge,... the effluent shall not have a fecal coliform bacterial count greater than 1000 per 100 milliliters nor visible floating solids...

Subsequent to the issuance of EPA's performance standards and in accordance with the provisions of the 1972 FWPCA, the Coast Guard promulgated certification procedures and design and construction requirements [5] which:

> ...prescribe regulations governing the design and construction of marine sanitation devices and procedures for certifying that marine sanitation devices meet the regulations and standards of the Environmental Protection Agency...to eliminate the discharge of untreated sewage from vessels...

With regard to the discharge of oil to the environment, Congress indicated in the 1972 FWPCA [6] that:

> ...it is the policy of the United States that there should be no discharges of oil...into or upon the navigable waters of the United States, adjoining shorelines, or into or upon the waters of the contiguous zone.
>
> .
>
> .
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>
> The discharge of oil...into or upon the navigable waters of the United States, adjoining shorelines, or into or upon the waters of the contiguous zone in harmful quantities...is prohibited...

The Environmental Protection Agency has defined harmful discharges of oil [7] as those which:

> (a) violate applicable water quality standards, or
>
> (b) cause a film or sheen upon or discoloration of the surface of the water or adjoining shorelines or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines...

Regulations for the implementation of the EPA standards and certification procedures for shipboard oil/water separators are currently being formalized by the Coast Guard.

Efforts being undertaken to abate the discharge of vessel-generated solid waste are based on the Refuse Act of 1899 [8] which states in part:

> It shall not be lawful to throw, discharge, or deposit... either from or out of any ship, barge, or other floating craft of any kind, any refuse matter of any kind or description whatever... into any navigable water of the United States or into any tributary of any navigable water from which the same shall float or be washed into such navigable water...

In addition, the Solid Waste Disposal Act of 1965 [9] states:

> The purposes of this Act therefore are -
>
> (1) to initiate and accelerate a national research and development program for new and improved methods of proper and economic solid waste disposal...

This review of the legislative and regulatory developments affecting the discharge of shipboard wastes highlights the major legislative and regulatory events which serve as the basis for Navy and Coast Guard programs in marine environmental protection. A more complete compendium of applicable Federal and state legislation may be found in the literature [10].

2.2 Institutional Responses to the Problems of Shipboard Waste

In response to this growing awareness of environmental damage caused by improper waste disposal at sea and to specific legislative and regulatory requirements, the maritime community formed the Maritime Information Committee Panel on Treatment and Disposal of Sanitary Wastes. Its goal was to find an acceptable way to dispose of wastes at sea; the Panel's comprehensive report, issued in 1971 [11], identifies the issues and poses solutions.

The Navy and Coast Guard developed methods to deal with solid wastes as well as sanitary wastes by preparing specifications for an incinerator or solid waste disposal unit for operation by shipboard personnel [12]. The report, "Summary of Coast Guard Experience with Shipboard Wastewater Sludge Incinerators," discusses their activities in this area.

The formation of the Committee on Materials of Construction for Shipboard Incinerators of the National Materials Advisory Board of the Commission on Sociotechnical Systems (National Research Council) and its review of disposal systems and equipment represents an important development in the recognition of the problem and in efforts to solve it.

2.3 Objectives and Scope of the Committee's Activities

The Committee on Materials of Construction for Shipboard Incinerators was formed to meet the following objectives as stated in its charge:

> The objective of this in-depth study will be to determine the optimum materials of construction for shipboard incinerator systems to be used on board U. S. Navy and U. S. Coast Guard ships. The study will delineate those factors which are most critical in the selection of an incinerator system. The study will also delineate those factors which are most critical in the selection of an incinerator material. Since the incinerators can be of several different configurations and employ different operating principles, the recommendations will address materials of construction suitable for the various types. Space and weight restrictions inherent in the shipboard environment, reliability, maintainability, safety and life-cycle cost, will be major considerations. In addition, problem areas requiring further study will be identified.

The Committee thus aimed to identify a reasonable course of action for the development of materials of construction for shipboard incinerators. It assessed available materials, identified work required to develop materials not currently available to meet objectives, and considered modifications in design to improve the performance of materials.

The use of incinerators on shipboard poses a problem substantially different from that of land-based units. Such differences are associated primarily with (1) limitations of weight; (2) limitations of size; (3) reliability and lifetime without intermediate repair; (4) level of training of operating personnel; and (5) limited availability of high technology repair techniques. These requirements combine to produce circumstances which press existing candidate materials beyond their capacity to perform economically and reliably.

In general, a satisfactory materials design system for shipboard incinerators must meet two opposing requirements: minimum weight and volume; and maximum resistance to especially aggressive environments resulting from operation at sea. The Committee had therefore to consider a broad set of options in materials, design, and operation. While the Committee did not directly address design and operation, it was necessary to identify options therein which would favor the reliable performance of materials.

This study has thus incorporated more than considerations of materials. It considers flames, reliability of auxiliary systems, and emissions of particulates. Since the report concludes that there are some uncertainties in the performance of materials in the uncertain environments of incinerators, we have considered procedures for undertaking experimental programs. Also, important principles of materials stability have been identified as a guide for materials and design specialists.

2.4 Approaches to Treatment

There are two general approaches to treatment of ship-generated wastes:

1. total retention in storage tanks aboard the ship and subsequent discharge to wastewater treatment or solid residue handling facilities, or

2. processing of wastes in the ship with overboard discharge of residuals.

Total retention is practical only for a low volume of waste (about one to two gallons/man-day) [13]. This situation occurs on small vessels where toilet wastes are stored and shower and lavatory facilities are non-existent. In nearly all other situations, the amount of sewage produced daily is about 6 to 30 gallons/man-day, and there is also a considerable amount of bilge waste, ballast water, oily wastes and solids wastes. Because of the large space required to store such wastes, it is necessary to consider onboard treatment and discharge of acceptable effluents.

Various onboard treatment systems must be developed to meet current discharge standards. Acknowledged candidate processes are: (1) maceration-chlorination; (2) biological treatment; (3) physico-chemical treatment;

(4) evaporation; and (5) incineration. Each process has certain advantages and disadvantages; efficiency of the system depends on the character of the waste and the mission of the vessel. Each of these options is discussed briefly below. But for large naval vessels, only incineration is a practicable process.

2.4.1 Maceration-Chlorination

This process consists of cutting the solids into small pieces without removing them from the waste and sewage. The device used for this operation is commonly called a comminutor or macerator. The effluent is chlorinated prior to discharge. This device has little or no effect on the biochemical oxygen demand (BOD) or suspended solids content and could have some difficulty meeting new standards proposed by the Federal government when applied to inland or coastal waters [14].

An additional difficulty with the macerator-chlorinator is that it does not sufficiently reduce particle size to allow for effective disinfection. It is very difficult to disinfect wastewater effectively when it contains large fecal particles. Other difficulties are created by the variable unit of usage, which affects the retention time in the unit.

2.4.2 Biological Treatment

Activated sludge bio-disks or some modification thereof are sometimes considered as components of a candidate process for treating shipboard sanitary wastes. This process may entail primary sedimentation, or the entire waste may be mixed with an active mass of bacteria and aerated for a period of time before final settling and discharge as effluent. The retention time in the aeration tank is related to the concentration and biodegradability of the waste. Much of the settled sludge is returned to the aeration tank to maintain the desired concentration of mixed liquor (bacterial mass). Excess mixed liquor containing active biological and primary settled sludge is removed from the system as required. Retention times usually vary between four and eight hours.

Activated sludge plants are effective for wastewater treatment on land, and can usually produce a high quality effluent. However, they require considerable technical control. Ship systems may become excessively large and subject to slow startup. Therefore, their use seems to be limited to large vessels.

2.4.3 Physico-Chemical Treatment

Physico-chemical systems are used mainly in intermediate and small-size vessels where space, power, and maintenance facilities are generally limited. Heeney, et al. [13] evaluated a three-stage system which consisted of:

1. separation of solids from liquids by screen filtration;
2. carbon adsorption to remove dissolved and colloidal solids;
3. chlorination to reduce coliform content.

This sequence was selelected because of its simplicity, flexibility, and low power requirements. Using a synthetic waste considered typical of shipboard sewage, removal efficiencies of 88 percent to 92 percent were obtained. BOD reductions were 86 percent to 95 percent, and it was concluded that the overall system design was feasible.

2.4.4 Evaporative Waste Treatment

Treatment of liquid wastes by evaporation has as its objective the reduction of the volume of wastes. This is accomplished by boiling off excess water and venting the steam to the atmosphere. The degree of concentration attainable depends on the use of fresh water or salt water for flushing toilets. Vessels using fresh water can have their wastes concentrated to about 12 percent solids by weight, while wastes from seawater-using ships can be concentrated to approximately 36 percent solids by weight. This increased percentage is attributed to the dissolved solids normally present in seawater. It is possible to obtain higher concentrations, but this tends to cause pumping difficulties when the evaporator is drained and cleaned.

Assuming that the density of the solids is similar to that of water, the liquid wastes from vessels using fresh water can be reduced by a factor of 12 if the incoming wastes contain approximately 1 percent solids. Since seawater normally contains 3.5 percent solids, the wastewater should have about 4.5 percent solids. Therefore, the volume is reduced by a factor of 8. An evaporator with a 100 gallon (378.5 liters) working volume can collect 1200 gallons (4.542 kiloliters) of sewage before it must be drained of sludge if fresh water is used in toilets, or 800 gallons (3.028 kiloliters) if seawater is used. Assuming a sewage production of 20 gallons (75.7 liters) per man per day, the fresh water system can handle a vessel with 60 men with one draining per day.

Evaporators require considerable energy to raise the temperature of the sewage from ambient to 100°C and to supply the latent heat necessary for conversion of liquid water to steam. Suspended solids have very little influence on the boiling point or the latent heat. However, dissolved salts such as urea or sodium chloride (NaCl) tend to elevate the boiling point and thus increase the energy requirement for the evaporation of the wastewater. Since urine is 2.5 percent urea by weight and the average daily excretion of urine is about 0.30 gallon per man per day, the influence of urea should not be significant. In the case of systems using seawater, the high dissolved solids content (3.5 percent) would slightly raise the boiling point.

Odor problems have frequently been associated with evaporators. The presence of small amounts of gases and vapors which have been expelled from feces and urine in the boiling process may cause odors. These gases and vapors are generated by simple release from the solids due to physical agitation or mechanical breakup in the boiling process, by steam distilling of vapors along with boil-off of water, or by actual chemical decomposition due to heating [15]. Synergistic effects and the sensitivity of the human sense of smell enhance the recognition of the presence of odors at very low concentrations.

A low-temperature catalytic vapor treatment system might be used to control the odors emanating from the evaporator. The vapor is mixed with adequate amounts of air and passed through a suitable catalyst bed at 180-205°C. This system has been tested in the U.S. Navy vessel MONOB and reportedly passed a series of Navy tests wherein no objectionable odors or deterioration of the catalyst bed were apparent during the year of operation [15].

2.4.5 Incineration

Incineration can be used for eliminating refuse, sludge, and wastewater. Furthermore, incineration provides the greatest volume reduction in the least space. The parameters which are most important in the incineration process are: moisture, volatiles, inerts, and calorific value. Moisture can be reduced in the sludges or solid components by physical-chemical-biological dewatering techniques. These techniques include thickeners, vacuum filtration, and centrifuges in conventional wastewater treatment and evaporators in treatment of shipboard wastes. Volatile and inert materials affect the calorific or BTU value of sludge. This calorific value depends on the relative concentrations of different compounds. For sewage solids, this value is usually considered to be 10,000 BTU/pound of volatile solids.

Because of space and weight limitations, incinerators would normally be considered useful in ships with 400 or more men. These units have a rated capacity of 200 to 500 pounds per hour of wastes and until recently were used as little as possible, mainly for the destruction of classified material. Existing incinerators often produce dirt in operation and lead to air pollution; they also require excessive manual labor. Considerable engineering effort has been directed toward correcting these difficulties by modification of existing equipment and installation of new devices for air pollution control.

Figure 2.1 is a schematic view of a typical multifunctional shipboard incinerator. Such an incinerator is capable of handling both liquid and solid wastes. Sewage enters a specific point at the lower left side and solid materials are introduced at the middle of the right side. Various grates are employed to preburn the solid materials. Figure 2.2 is a schematic view of sequential functions involved in excess air multifunctional incinerators. Important auxiliary functions also are shown togehter with approximate temperature.

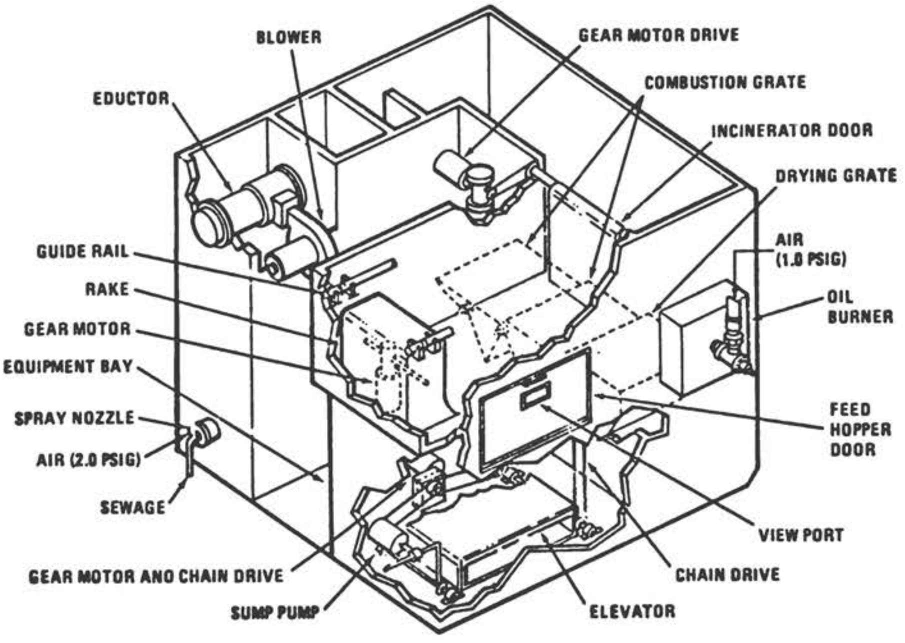


FIGURE 2. 1 Schematic View of Arrangements of Multifunctional Incinerator for Handling Solid and Liquid Wastes [16].

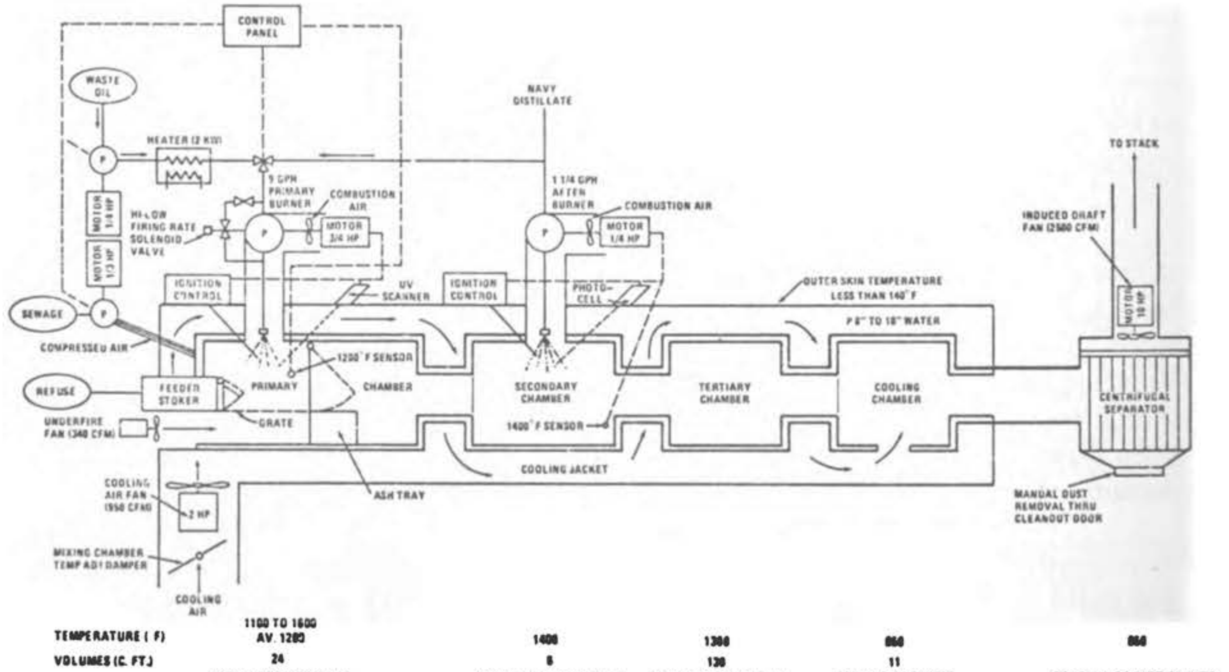


FIGURE 2. 2 Schematic View of Functions for Multifunctional Incinerators Indicating Auxiliary Systems, Temperatures and Sequence of Events [16].

2.5 Conditions Imposed Upon Shipboard Incinerators

The specific conditions of operations and the sizing expected for shipboard incinerators are summarized by the following excerpts from specifications developed by the Navy for shipboard incinerators [12].

1. The units should be capable of processing a minimum of 1100 pounds per day with a capability of scaling up to 10,000 pounds per day of the following:

Waste Material	Percent
Wood	8.0
Paper	27.9
Glass and Ceramics	0.9
Cloth	2.8
Metal	1.7
Rubber	0.3
Plastic	0.5
Composite	0.6
Other	1.8
Garbage	55.5

In addition, the unit should be capable of processing a minimum of 160 pounds per day of dewatered sewage of 0.5 to 15 percent solids by weight in a salt water medium. This capacity should be capable of scaling up to 1400 pounds or 3200 pounds per day of sewage with 0.5 to 2 percent solids by weight in a fresh water plant.

The unit should also be capable of processing a minimum of 800 pounds per day with a capacity of being scaled up to 5600 pounds per day of waste oil containing 75 percent oil and 25 percent water.

2. Size and weight restrictions are critical on shipboard applications:

a. The weight cannot exceed 10,000 pounds (4540 kilograms)

b. The system must be designed for a working space of 64 square feet (5.94m^2) by 7 feet high (2.1m).

3. Additional general requirements:

a. The equipment should be designed for minimum operating attention and should not require manual stoking or manual ash removal.

b. The equipment should be designed to operate continuously or intermittently.

c. The system should remain safe and sanitary and should not create offensive odors or unsanitary conditions.

d. The system should not be easily damaged by small metal or other durable objects.

e. The unit should be capable of attachment to a steel deck.

f. The stack emissions produced by incineration should meet applicable requirements of the Environmental Protection Agency or other standards established by the Navy. Further, the particulate emission shall be measured by procedures described in "Specifications for Incinerator Testing at Federal Facilities" or any amendments thereafter.

g. The density of any emissions from the unit should not exceed one on the Ringelmann Scale or the Smoke Inspection Guide for a period or periods aggregating more than 3 minutes in any one hour or be of such opacity as to obscure an observer's view to an equivalent degree.

h. The incinerator exhaust gas should not exceed the temperature of 345°C.

i. The incinerator should be designed to operate safely.

j. The unit should be subject to the following analyses previews:

- Failure modes and effects
- Maintenance engineering
- Design
- Effects of storage, packaging, transportation, handling, and maintenance
- Failure data and development of correction action
- Demonstrated capacity for reliability and maintainability that will not compromise the availability of the ship.

REFERENCES

1. Federal Water Pollution Control Act Amendments, P. L. 92-500, 33 USC 1151 et seq., Sec. 101. (a), (18 October 1972).
2. "Prevention, Control, and Abatement of Environmental Pollution at Federal Facilities," Federal Register, Vol. 38, No. 243, Executive Order 11752, pp. 34793-97, (19 December 1973).
3. Federal Water Pollution Control Act Amendments, P. L. 92-500, 33 USC 1151 et seq., Sec. 312. (b)(1), (18 October 1972).
4. "Marine Sanitation Device Standards of Performance," Federal Register, Vol. 41, No. 20, 40 CFR 140, Sec. 140.3(a), pp. 4452-54, (29 January 1976).
5. "Certification Procedures and Design and Construction Requirements for Marine Sanitation Devices," Federal Register, Vol. 40, No. 21, Sec. 159.1, 33 CFR 159, pp. 4621-30, (30 January 1975).
6. Federal Water Pollution Control Act Amendments, P. L. 92-500, 33 USC 1151 et seq., Sec. 311. (b)(1) and 311. (b)(3), (18 October 1972).
7. "Discharge of Oil," Federal Register, Vol. 36, No. 228, Sec. 110.3 and 110.4, p. 22487, (25 November 1971).
8. Refuse Act of 1899, Section 407 of the Rivers and Harbors Appropriations Act of 1899, 33 USC 401-413, (1899).
9. Solid Waste Disposal Act, P. L. 89-272, (20 October 1965).
10. Pollution Abatement Plan, Naval Sea Systems Command U. S. Navy, Washington, D. C., (1974).

11. "A Synthesis of Current Information on Treatment and Disposal of Vessel Sanitary Wastes," Maritime Research Information Systems Report, Maritime Information Committee, National Research Council-National Academy of Sciences, Washington, D. C. (July 1971).

12. Singerman, H. H., Head Pollution Abatement Division, NSRDC, Letter (with enclosures) to members of the NMAB Committee on Materials of Construction for Shipboard Incinerators, (February 1975).

13. Heeny, J. M., Neverill, R. B., and Krug, E. K., Development and Evaluation Report: Physical Chemical Marine Sanitation System, Project No. 15020 HJL, Prepared for the Office of Research and Monitoring, Environmental Protection Agency, Washington, D. C., (1974).

14. Librizzi, W., Evaluation of Macerator-Chlorinators, (Unpublished Report), Edison Water Quality Laboratory, Environmental Protection Agency, Edison, NJ, (1971).

15. Glueckert, A. J. and Saigh, P. A., Onshore Treatment System for Sewage from Watercraft Retention Systems, Project No. 68-03-0221, Prepared for the Office of Research and Development, Environmental Protection Agency, Cincinnati, OH, (1974).

16. Wacker, G. and Wheatfall, W. L., "Corrosion Problems Associated with Shipboard Waste Incinerator Systems," Submission for Proceedings of the 1976 Tri-Service Corrosion Conference, Philadelphia, PA, (26-28 October 1976).

CHAPTER 3.0

SHIPBOARD WASTES: COMPOSITION AND DEFINITION

3.1 Introduction

The composition of wastes processed in incineration systems constitutes a major part of the aggressive environment in which materials of construction must operate. Chemical species which must be considered in evaluating the performance of materials arise from human wastes, non-human wastes, and carrier fluids such as seawater.

Subsequent sections which consider the performance of materials must compare the test environments with those which would be produced by the processing of wastes described in this chapter.

A precise description of all waste materials is not possible owing to the various modes of operating ships and the commercial or political influences which control non-human wastes. The mix of paper, wood, polymers, and glass used for packing will change as the economic climate and the availability of materials change. The composition of human wastes, on the other hand, is relatively well-known.

An important consideration in assuming environmental influences is the sometimes catastrophic effects of small amounts of contaminants. For example, small amounts of vanadium cause catastrophic acceleration of high temperature corrosion processes. Such small amounts are not analyzed in some cases. Thus, "typical" compositions given herein are exemplary only. Development of high performance incineration systems should give close attention to the presence of small amounts of aggressive chemical species.

Shipboard wastes consist of liquid wastes and solid wastes. The liquid wastes include sewage and waste oils; the solid wastes include the refuse or solid debris which is generated during normal vessel operation.

3.2 Waste Sources and Characteristics

3.2.1 Sewage

For this application, sewage is defined as the combination of feces, urine, and paper, plus whatever diluent or flush medium is used.

Daily per capita generation data for feces, urine, and paper are presented in Table 3.1.

TABLE 3.1 Primary Waste Material Generation

	Wet Weight		
Material	Pounds per Capita per Day	Grams per Capita per Day	Percent Solids (by weight)
Feces[a]	0.13 - 0.55	60 - 250	15 - 35
Urine[a]	1.4 - 4.1	615 - 1845[b]	4 - 6[c]
Paper[d]	0.01 - 0.04	5 - 20	--------

[a] Data from reference 1

[b] Assuming specific gravity = 1.025 and production rate of 0.16 to 0.48 gallon/capita/day (0.6 to 1.8 liters/capita/day)

[c] Calculated from data in reference 1 and mean production rate of 0.32 gallon/capita/day (1.2 liters/capita/day).

[d] Data from reference 2

The quantity and composition of human feces may vary, depending on diet, activity, and physiology. The approximate daily per capita wet weight production is 0.13 to 0.55 pound (60 to 250 grams). Fecal matter contains food residues, the remains of bile and intestinal secretions, cellular substances from the body, and bacterial cell masses in large amounts up to 25 percent of the weight of the feces. The water content of feces ranges between 65 to 85 percent, and the pH may vary from 6.9 to 7.7. Data on the approximate constituent composition of feces are presented in Table 3.2

The average daily per capita production of urine is 0.16 to 0.48 gallon (0.6 to 1.8 liters). The specific gravity of urine varies with volume, since the amount of solute is relatively constant. For the volume above, the specific solids content is approximately 4 to 6 percent by weight. The approximate composition of urine is presented in Table 3.3.

The paper associated with human body wastes is assumed to be of a cellulose base. From the limited data available, the average daily per capita use of paper is 0.01 to 0.04 pound (4 to 20 grams). [2].

In weight and volume, the major component of sewage is the flushing fluid used as a carrier for the feces, urine, and paper. The flushing medium normally used onboard vessels is either potable water or seawater. Seawater may consist of whatever type of water the ship is operating on—fresh, brackish, or ocean water.

TABLE 3. 2 Composition of Feces

Constituent	Milligrams per Capita per Day
Bulk	50,000 - 350,000
Dry Matter	23,500 - 35,000
Electrolytes	
Aluminum	0.0428 - 2.9
Arsenic	0.071 - 8.27
Calcium	100.0 - 1,180
Chloride	14.97 - 35.65
Cobalt	0.0001 - 1.40
Copper	1.020 - 2.638
Iron	4.6 - 100.0
Lead	0 - 400
Magnesium	107 - 252
Manganese	1.283 - 8.556
Molybdenum	2.0 - 4.0
Nickel	0.0856 - 10.0
Phosphorous	506.2 - 1700
Potassium	291 - 1037
Sodium	116 - 122
Tin	0.5 - 32.09
Zinc	4.135 - 10.27
Nitrogen Compounds	11,070 - 14,580
Total Fat	1,000 - 7,000

Source: Reference 1

TABLE 3. 3 Composition of Urine

Constituent	Milligrams per Capita per Day
Solids	55,000 - 70,000
Electrolytes	
Aluminum	0.049 - 0.112
Arsenic	0 - 0.091
Bicarbonate	35.0 - 840
Bromine	0.840 - 7.70
Calcium	43.0 - 581.0
Chloride	7,600 - 15,000
Chlorine	2,800 - 12,600
Copper	0 - 0.049
Fluoride	0.30 - 7.0
Iodine	0.007 - 0.490
Iron	0.02 - 1.1
Lead	0.004 - 0.15
Magnesium	29.4 - 307.0
Manganese	0.007 - 0.098
Nickel	0.140 - 0.280
Phosphorous	700 - 1,600
Potassium	1,120 - 3,920
Selenium	0 - 0.140
Silicon	14.0 - 420
Sodium	1,750 - 6,580
Sulfur, Total	357 - 3,400
Tin	0.0091 - 0.0175
Zinc	0.110 - 0.500
Ammonia	300 - 1,100
Nitrogen, Total	1,000 - 21,000
Urea	14,000 - 35,000

Source: Reference 1

No data are available on the composition of typical shipboard potable water. However, from a corrosion/materials standpoint, potable water may not be a major concern. On the other hand, seawater as a diluent is considered a major factor for corrosion and materials selection. The approximate composition of seawater is presented in Table 3.4; Table 3.5 presents data on the major salts remaining after the evaporation of seawater [3].

TABLE 3.4 Composition of Seawater

Ions	Chemical Form in Ocean	Amount (percent o)[a]
Chloride	Cl^-	19.353
Sodium	Na^+	10.76
Sulfate	$SO_4^=$	2.712
Magnesium	Mg^{++}	1.294
Calcium	Ca^{++}	0.413
Potassium	K^+	0.387
Bicarbonate	HCO_3^-	0.142
Bromide	Br^-	0.067
Strontium	Sr^+	0.008
Boron	H_3BO_3	0.004
Fluoride	F^-	0.001

[a] Percent o = parts per thousand by weight

Source: Reference 3

TABLE 3.5 Major Salts Remaining After The Evaporation of Seawater

Chemical Compound	Formula	Amount (percent o)[a]
Sodium chloride	$NaCl$	27.21
Magnesium Chloride	$MgCl_2$	3.81
Magnesium sulfate	$MgSO_4$	1.66
Calcium sulfate	$CaSO_4$	1.26
Potassium sulfate	K_2SO_4	0.86
Calcium Carbonate	$CaCO_3$	0.12
Magnesium Bromide	$MgBr_2$	0.08

[a] Percent o = parts per thousand by weight

Source: Reference 3

The second major variable with regard to diluent or flush medium is the daily per capita use. This parameter varies as a function of type of fixture (commode vs. urinal), type of collection system (standard gravity drainage vs. reduced volume collection), and the number of uses for each fixture per day. For the standard gravity collection system, shipboard flusometers are normally set to produce 4 gallons (15 liters) per flush for a commode and 1 gallon (3.8 liters) per flush for a urinal. With a reduced volume collection system (vacuum or pumped), these values decrease to 0.4 gallon (1.5 liters) per flush for a commode and 0.13 gallon (0.5 liter) per flush for a urinal. Fixture usage rate is assumed to be 4 urinations and 1 defecation per capita per day, and the average daily per capita production of body wastes (urine, feces, and paper) is taken as 0.5 gallon (1.9 liters). Using these data, the daily per capita generation of sewage can be calculated. These rates are listed in Table 3.6. It will be noted that the use of a reduced volume flushing system significantly decreases the amount of sewage produced.

TABLE 3.6 Sewage Generation

	Volume[a]		Weight[b]	
Collection System	Gallons per Capita per Day	Liters per Capita per Day	Pounds per Capita per Day	Kilograms per Capita per Day
Standard[c]	8.5	32.2	70.8	32.2
Reduced Volume[d]	1.4	5.3	11.7	5.3

[a] 4 urinations and 1 defecation per capita per day; 0.5 gallon (1.9 liters) of body waste per capita per day; standard collection, 4 gallons (15 liters) per flush for commode, 1 gallon (3.8 liters) per flush for urinals; reduced volume collection, 0.4 gallon (1.5 liters) per flush for commodes, 0.13 gallon (0.5 liter) per flush for urinal.

[b] Assume 1 gallon (3.785 liters) = 8.33 pounds (3.785 kilograms)

[c] Standard commodes and urinals with gravity collection

[d] Special commodes and urinals with vacuum or pumped collection

Source: Reference 4

3.2.2 Waste Oil

In the context of this study, waste oils are defined as the petroleum-based products collected from bilge water oil/water separators which are used to treat bilge waters. These waste oils may include fuel oil, lubricating oils, and petroleum-based solvents. Based on limited data, waste oil generation may be in the range of 800 pounds (363 kilograms) per day for a 320 man vessel, with a water content up to 25 percent by weight [5].

3.2.3 Solid Wastes

Solid wastes from normal vessel activities include trash, rubbish, garbage and inert materials. The average shipboard solid waste production rate is approximately 3 pounds (1.4 kilograms) per capita per day. Table 3.7 shows data on the composition of typical shipboard solid wastes.

TABLE 3.7 Solid Waste Composition

Material	Pounds per Capita per Day	Grams per Capita per Day	Percent of Total
Wood	0.25	113.40	8.2
Paper	0.93	421.84	30.6
Ceramic	0.02	9.07	0.7
Cloth	0.08	36.29	2.6
Metal	0.52	235.87	17.1
Rubber	0.01	4.54	0.3
Plastic	0.01	4.54	0.3
Other	0.08	36.29	2.6
Garbage	1.14	517.09	37.6
TOTAL	3.04	1379.91	100.0

Source: Reference 6

Garbage is the largest single component, accounting for approximately 38 percent of the total solid wastes. The moisture content of the various types of solid wastes varies considerably, with estimates of up to 10 percent for trash (wood and other), 50 percent for rubbish (paper, cloth, rubber, plastics), and 70 percent for garbage.

Table 3.8 presents data on the representative heat values for sewage, oil, and solid wastes. The heat values are presented on the basis of dry weight of combustible solids. The heat value of oil is taken as the lower heat value of petroleum-based products representative of those that would be present in bilge waters. The heat value datum for solid wastes has been estimated on an equivalent ash-free basis.

TABLE 3.8 Heating Values of Wastes

Material	Combustibles Percent	Ash Percent	BTU/Pound (Dry Weight)
Raw Sewage Solids[a]	70	30	10,000[b]
Oil[c]	---	---	17,500 - 18,500[d]
Trash, Rubbish, Garbage	100	0	10,000[b]

[a] Feces, urine and paper

[b] Per pound of dry combustible solids

[c] Waste oil may contain up to 25 percent water by weight

[d] Lower heat value at constant pressure on water-free basis [4].

3.2.4 Detergents

Synthetic detergents, as well as natural detergent soaps, can be expected in both the kitchen and the shower wastewaters. These detergents will lower the surface or interfacial tension of water; increase its ability to wet substances in which they come in contact; emulsify grease and oil; peptize or deflocculate colloids; induce floatation of solids and give rise to foams; and may create other problems. A high-foaming detergent system may contain, on a solid product basis, 10 to 30 percent organic actives. Additives and their proportions may include: amide foam stabilizers, 3 to 6 percent; sequestering and building polyphosphates, 25 to 40 percent; corrosion-protecting silicates, 5 to 7 percent; soil-suspending carboxymethylcellulose, 0.5 to 1 percent; diluent sodium sulfate, 15 to 25 percent; water, 6 to 15 percent; and other additives [7].

3.3 Effects of Pre-Treatment Techniques on Waste Characteristics

As discussed earlier, vessel-generated wastes include sewage, waste oils, and solid waste. In the foregoing discussion, the properties and composition of the various wastes in their natural state were delineated as they may affect incineration. However, aside from the normal variation in waste characteristics, the methods of treatment prior to incineration may affect waste characteristics.

3.3.1 Solid Wastes

Presumably, no treatment would be provided for solid wastes prior to incineration. But, variations in waste properties may result from packaging in plastic bags, natural compaction, and biodegradation of the putrescible materials. For all practical purposes, solid wastes should be discharged to the incinerator in their natural, collected state.

3.3.2 Waste Oils

Treatment of bilge wastes is accomplished in oil/water separators. These systems usually employ physical separation techniques, and produce two liquid by-products—waste oils with some entrained water and discharge water with some entrained oil. The oil/water ratio of the effluent, compared to the oil/water ratio of the influent, is thereby greatly reduced; however, the chemical characteristics of the oil fraction are not changed significantly.

3.3.3 Sewage

Of the vessel wastes being considered for disposal by incineration, sewage may receive the greatest degree of pre-treatment by a number of waste management systems. These systems might include:

- reduced-volume collection using fresh or seawater for the diluent followed by direct incineration;
- treatment of sewage by physical/chemical or biological means with overboard discharge of the treated effluent and incineration of the by-product waste solids;
- substitution of oil-flush for water-flush with physical separation of oil and waste products, and incineration of the separated waste products; and
- treatment of combined non-oil wastewater (sewage, galley waste, laundry, shower, etc.) by physical/chemical or biological means with overboard discharge of the treated effluent and incineration of the by-product waste solids.

With reduced-volume collection of sewage, the effects of pre-treatment are minimal and consist mainly of particle size reduction by maceration. Since minimum volumes of diluent are used, the resulting concentration of waste materials would be significantly higher than that produced by a gravity collection system (possibly by an order of magnitude). In addition, since potable or seawater may be used as the diluent, it is possible that sea salts may be present together with waste solids.

Another method of sewage disposal consists of processing the waste stream through physical/chemical or biological systems. With this approach, most of the dissolved solids will be discharged overboard with the treated effluent. Thus, the waste solids discharged to the incinerator will have a lower concentration of dissolved solids than the waste from, for example, a reduced-volume collection system. On the other hand, various chemicals may be added, such as aluminum sulfate, ferric chloride and polyelectrolytes, to aid in solid-liquid separation. These chemical precipitates would remain with the separated solids and be discharged to the incinerator. In addition, it is probable that seawater would be used as the diluent with this type of system. As such, sea salts in the water portion of the sewage sludge would be processed through the incinerator.

With a recirculating sewage system using oil as the flush medium, human body wastes are separated from the oil due to differences in specific gravity. The oil is recirculated and the separated wastes may be incinerated. In this method, the wastes discharged to the incinerator consist essentially of undiluted feces, urine, and paper. Thus, the concentration of wastes would be even greater than that produced by a reduced-volume collection system. In addition, varying amounts of the oil flush medium may be discharged with the waste materials.

The focus of this discussion has been on the disposal of sewage only. However, under certain circumstances, it may be desirable to process a combined waste stream of sewage, galley, laundry, and shower wastewaters through physical/chemical or biological systems. The impact of these treatment processes on the composition of the waste sludge is the same as discussed above, namely, a decrease in dissolved waste solids, and the possible presence of chemical precipitates and sea salts. Additionally, contaminants from the non-sewage wastewater sources would be part of the sludge by-product, including food scraps, detergents, soap, hair, and the like. In general, the waste solids from a combined wastewater system can be expected to be significantly different in composition from those produced by a system which processes sewage only.

REFERENCES

1. Bioastronautics Data Book, NASA Report No. SP-3006, P. Webb, editor, pp. 215-222.

2. Ligman, K., Hutzler, N., and Boyle, W., "Household Wastewater Characterization," Paper No. 10372, Proceedings of ASCE, J. Environ. Engrg. Div., pp. 208-209, (Feb. 1974).

3. Myers, J. J., Holm, C. H., and McAllister, R. F., Handbook of Ocean and Underwater Engineering, pp. 1-7, McGraw-Hill Book Co., New York, NY, (1959).

4. Marks, L. S. and Baumeister, T., Standard Handbook for Mechanical Engineers, 7th Edition, pp. 7-23, McGraw-Hill Book Co., New York, NY, (1967).

5. Wyatt, S. V. and Kemezis, R. J., "Reliability and Maintainability Requirements for Shipboard Incinerators," Procedings of the 1976 Annual Reliability and Maintainability Symposium, p. 189, (1976).

6. Johnson, R. J. and Bourn, W., "Technology Available for Treating Shipboard Generated Solid Waste," Paper No. VIII/3, Symposium on Prevention of Pollution from Ships, International Nickel Company, Acapulco, Mexico, (March 1976).

7. Fair, G. M., Giar, J. C., and Okun, D. A., Water and Wastewater Engineering, Volume 2, John Wiley and Sons, Inc., New York, NY, (1968).

CHAPTER 4.0

COMBUSTION CHARACTERISTICS OF WASTES DURING COMBUSTION

4.1 Introduction

The combustion characteristics of wastes greatly influence selection of the materials of construction. The combustion products determine the atmospheres—oxidizing, reducing, etc.—to which the materials will be exposed. The temperatures of combustion determine the thermal stresses on the walls. These temperatures also determine the state—dry, sticky, fluid—of inorganic ash constituents in the wastes; the aerodynamic flow pattern strongly influences the probability of deposition and/or sedimentation of such constituents on the walls or floor with the attendant potential for corrosive attack. The nature of the wastes may also determine whether they are to be grate-fired or suspension-fired.

These characteristics are not only important in the selection of construction materials but also in design. Clearly, the problems of design and materials selection cannot be separated. A detailed review of incinerator design principles is out of place in this report whose prime emphasis is materials; at the same time, however, some overview of salient combustion characteristics is necessary. No suitable reference text is available to provide such an overview, particularly for waste materials.

Incineration is a complex combustion process involving reaction kinetics, combustion aerodynamics, and heat transfer. The complexity is aggravated by the nature of the waste, or "fuel," whose composition is usually imprecisely known and often subject to major fluctuations. Basic texts on combustion [1-5] are not fully relevant to the problem of solid wastes. Beer and Chigier [6] address the problem of combustion aerodynamics, providing some valuable qualitative insights into general combustor configurations, but they do not deal specifically with incinerators. Hottel and Sarofim [7] include a section on heat transfer in furnaces, but not in incinerators. Other standard texts on heat transfer [8, 9] do not even treat the problem of furnaces.

Engineering-oriented texts on furnaces [10-13] treat kinetics, fluid flow, and heat transfer only superficially since they were written with different objectives. Only Thring [14] includes adequate discussion of these topics, but this work is not oriented towards waste incineration (though includes some discussion of solid bed kinetics) and it lacks the advances of the last 15 years. Air pollution texts and handbooks [15-18] similarly lack, for the most part, an in-depth review of these fundamental topics; Starkman [19] is one exception. Liptak [20] includes one chapter which briefly discusses design with reference to the significance of kinetics and aerodynamics. The only text or handbook on design which relates to incineration and is based on fundamental considerations is the Shell Afterburner Systems Study handbook [21]. This text is restricted to afterburners.

Only Corey!s text [22] is specifically concerned with incineration, but not with quantitative design from fundamentals. More useful in that respect is Niessen's Systems Study of Air Pollution From Municipal Incinerators [23]. Mention should also be made of a recent publication, Combustion Fundamentals for Waste Incineration [24], but this is concerned exclusively with thermodynamic equilibria and has no bearing on the kinetic, aerodynamic, and heat transfer aspects of incineration.

One reason for this near total absence of texts on fundamentals of waste incineration is the paucity of fundamental information in the first place. This stems largely from the lack of economic incentive in the past to obtain good combustion during incineration; research in progress in the late 1960's under the stimulus of air pollution control was almost totally abandoned when it was though that recycling might be a better method of controlling solid wastes. Consequently, only a little fundamental information on waste combustion is available in the literature (such as the ASME Incinerator Conference papers [25]). This presentation is therefore drawn mainly from other research sources and adapted where possible.

Incinerator designers are presumed to be familiar with the literature on general kinetics, aerodynamics and heat transfer, and with means of applying these principles to incinerators where possible. Materials specialists, however, cannot be assumed to have this background. This section thus offers a brief, mainly qualitative overview of the fundamental principles to provide context for the materials specialist. Once these principles are understood, the texts noted above may be useful as reference sources for specific topics.

4.1.1 Scope of the Problem

The design can only be as good as the information available. Where research results are missing, the designer has to guess. Three basic sciences are primarily involved in combustion research: reaction kinetics, heat transfer, and combustion aerodynamics. Material properties also affect design in two ways: through the properties of the fuels themselves and through the construction materials of the combustor (the primary concern of this report.) Developing design data requires experiments of increasing complexity and sophistication. One research scheme is illustrated in Figure 4.1. It emphasizes that knowledge of the basic sciences by themselves is not enough; it is also necessary to know how different basic sciences interact. Application of fundamental research results to an engineering or commercial system therefore requires care.

This section, whose scope is partially indicated by Figure 4. 1, briefly covers such other factors as atomization and burner construction. One particular aspect of combustion behavior unique to incineration is treated in detail. This is the need to satisfy, almost simultaneously, two mutually exclusive temperature requirements. This need is at the core of the materials problem. The first requirement is to generate temperatures in some part of the flame in excess of roughly 1250°C to maintain ignition (flame holding) and to accelerate burn-out. The second conflicting requirement aimed at favoring materials is to maintain the combustion chamber walls at temperatures less than or substantially less than those in the flame-holding flame ball.

Peak flame temperatures in practice tend to lie between approximately 1400°C and 1900°C. Wall temperatures should be as low as possible, with maximum temperatures near 1100°C depending on such factors as wall material and waste components. With chlorides present, which greatly accelerate corrosion, the value may have to be as low as approximately 800°C.

These two conflicting requirements, in part, determine the design and operation. Specifically, sufficient heat must be extracted from the flame gases (thermal loading) so that they are cooled at the flue to roughly wall temperature without affecting flame stability. The gases are cooled by the addition of high excess air and/or water (this latter can be a natural component of some of the liquid wastes). Such cooling in turn increases the required volume for the combustion chamber, and hence the space needed for the incinerator (remembering that space on board ship is at a premium). At the same time, the atmosphere adjacent to the walls should normally be oxidizing rather than reducing. However, this is not easily achieved at all points, even at high overall excess air. If sulfur is significantly present, the preferred method of cooling may be water rather than air to suppress SO_3 formation. Water, however, may introduce problems of salt emissions. Overcooling can also create undesirable odors: a typical rule of thumb is that odor destruction requires oxidation at a temperature in excess of about 800°C for a period exceeding 0. 5 second. Destroying odors can therefore impose a critical constraint on designs for cooling.

The behavior is largely determined by the gas mixing pattern. A poor pattern can upset the flame, locally overheat the walls, and generate reducing atmospheres at localized areas of the walls. Unstable flame patterns can produce alternate oxidizing and reducing conditions which accelerate corrosion. A poor pattern can also cause liquid or sticky particulates to precipitate onto the walls and, from bypass, permit escape of combustibles (sometimes including smoke) even with high excess air.

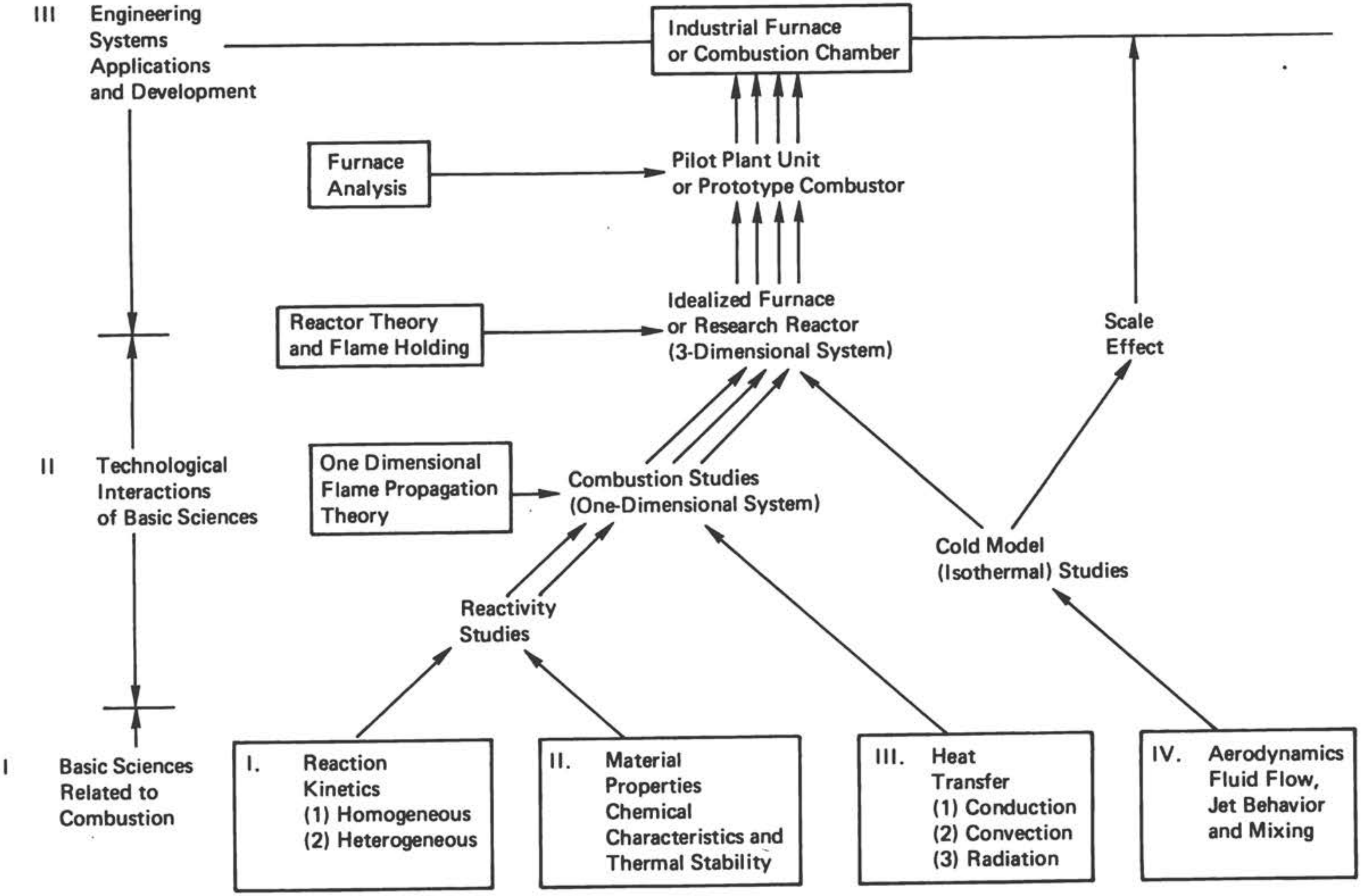


Figure 4.1 Schematic to Illustrate the Relationship Between Basic Sciences Related to Combustion and the Engineering Applications of Combustion Theory.

The results of a poor mixing pattern can be offset by increasing the size of the combustion chamber. Size is otherwise determined largely by reaction kinetics as a function of fuel and waste phase—solid, liquid, or gas.

Local, internal behavior is therefore controlled mainly by the aerodynamic mixing pattern and the rates of reaction (Section 4. 3. 2) and varies substantially from system to system and from one waste to another. Fortunately, certain overall constraints provide a common framework within which virtually all incinerable waste—and also all fossil fuels—can be considered. These constraints are considered below.

4. 2 External Heat and Mass Balance: Stoichiometry

4. 2. 1 Generation Considerations

The simplifying aspects of the combustion of fossil fuel and organic materials derive from two facts: (1) that all organic materials of all phases (solid, liquid, or gas) require approximately one cubic foot of cold air for combustion for every 100 BTU of heat released; and (2) that the air required generally outweighs the fuel by a substantial margin. The heaviest component of material flowing through the combustion chamber is always nitrogen from the air. The ballasting effect of the nitrogen means that all flame temperatures and combustion limits are roughly the same, as a first approximation, whatever the material being burned (but see Figure 4. 2). The addition of other attemperating materials, such as water, likewise has an effect in proportion to the weight added, and independent of the material being burned or incinerated.

If materials are burned or incinerated in a fully adiabatic enclosure, the products of combustion (POC) emerge at the adiabatic flame temperature. The maximum adiabatic flame temperature, which is theoretically obtained at zero excess air, can be taken as about 2000°C. Achieving such a temperature in practice is virtually impossible because of the diluting effect of excess air and the heat losses through the wall, and because of the complex kinetic effects of firing wastes. If excess air dilution is great enough, particularly if coupled with thermal loading of the flame (from wall loss or from usefully heating stock in a furnace), the POC temperature can be brought down as low as desired. In a boiler, for example, the final POC temperature into the stack may be 150°C to 200°C. Such heavy thermal loading, however, can only be allowed on the tail gases: in an upstream section of the flame, sometimes referred to as the flame ball, the temperature must always exceed about 1200°C (about 1350°C to allow a margin for safety) if the flame is not to extinguish. As there is always some thermal loading, the flame ball or peak temperature generally lies in the range from 1400°C to 1900°C as already indicated.

The problem in incinerator design then derives from the need to reduce the temperature of the flame gases to some acceptable level, to be specified by the materials selection, without interfering with flame stability.

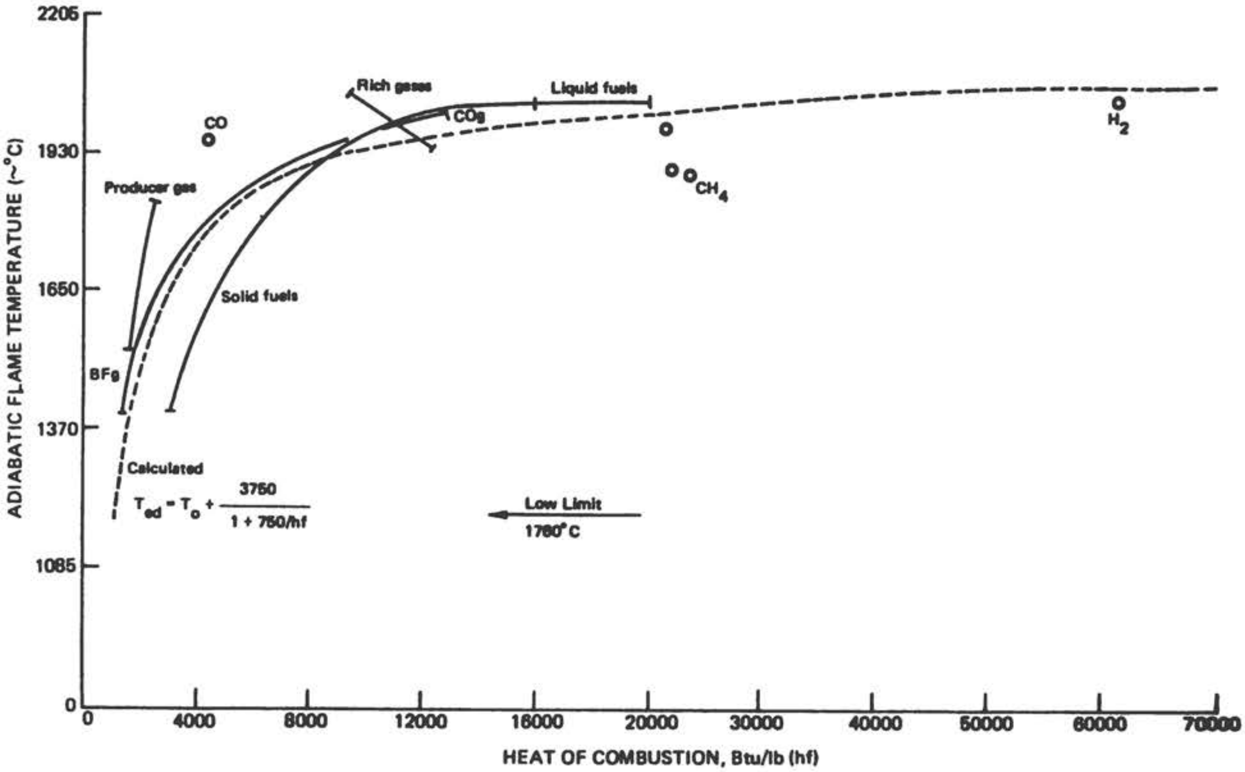


Figure 4.2 Variation of Adiabatic Flame Temperature With Heat of Combustion

This problem also occurs in other circumstances; in a boiler, for example, the POC temperature leaving the combustion chamber to enter the convection section must be below the fusion point of any ash from the fuel to prevent or reduce adhesion and possibly corrosion. In practice, this can mean temperatures ranging from 1650°C to 800°C with the final drop to 150°C to 200°C taking place in the convection section. In boilers, the cold walls provide substantial thermal load to aid in reducing the temperature. With incinerators that are not raising steam, this source of thermal load is absent; the main source is excess air and/ or water. If the incinerator has a double shell to eliminate ultimate wall losses, the problem is that much more severe.

These considerations, therefore, dictate certain aspects of design. If the primary heat source is either waste or fresh oil (grate firing must be considered as a special case), only a fraction of the attemperating water or excess air can be allowd through the stabilizing flame ball; the balance must be injected into the hot gases (that can be still burning) downstream of the flame stabilization section. The attemperating water may be assumed to carry the waste to be incinerated, a condition which further limits design. With a separately stabilized flame, reaction is maintained downstream as the combustible waste is added, but the reaction rate falls sharply with temperature. A typical rule is to require 0.5 seconds at 800°C (generally stated for odor, as mentioned above, but applicable to many other materials). This means that temperature must be maintained above 800°C while the waste is reacting; only afterward can the final temperature be lowered if lower POC temperatures are required.

4.2.2 Combustion Temperatures and Limits

The starting point for flame temperature and limit calculations is the simple balance between the heat released from one unit of fuel and the sensible heat going into the relevant products of combustion. If the stoichiometric air required for any fuel is G_s (weight air/weight fuel), at E percent excess air, the POC weight is $[1 + G_s\ (1 + E\%/100)]$. If h_f is the heat of combustion of the fuel, $\bar{C}_p$ is the average POC specific heat, and T_{ad} is the subsequent adiabatic flame temperature, then a heat balance yields

$$h_f = [1 + G_s\ (\frac{1 + E\%}{100})]\ \bar{C}_p\ (T_{ad} - T_o) \tag{4.1}$$

where T_o is the ambient temperature. In evaluating this expression, we can first invoke the approximate relation that one cubic foot of cold air is required per 100 BTU (3.75 MJ/cubic meter); so $h_f/100$ cubic feet are required for fuel of calorific value h_f, for h_f in FPS units. Converting into pounds of air by multiplying by the air density (0.073 pound per cubic foot) we get

$$G_s = \frac{h_f}{1370} \tag{4.2}$$

Rosin and Friedlander [26] have determined G_s for a wide range of fuels. Statistically, they find a more accurate expression is

$$G_s = \frac{\left(\frac{h_f + B}{s}\right)}{A} \tag{4.3}$$

where values of A, B, and specific gravity, s, are as given in Table 4.1. Values of h_f range from 1000 BTU per pound (blast furnace gas to 61,000 BTU per pound—hydrogen—2.3×10^6 to 1.4×10^8 J/kg). For the most part, the term B/s in Table 4.1 is a correction term, with values of A in the region of 1370 (liquid fuels are somewhat higher).

TABLE 4.1 Relation Between Heat of Combustion (h_f) and Stoichiometric Air Requirements (G_s) and Common Fuels

$$h_f/G_s = A/(1 + B/s.h_f)$$

Fuel	Heat of Combustion h_f (BTU/lb)	A	B	Specific Gravity s	BTU per Cubic Foot
Solid fuels	<10,000	1375	890	(1)	------
	>10,000	1375	1000	(1)	------
Liquid fuels	18,000	1637	4233	(1)	------
Gaseous fuels					
Blast furnace gas	1000 - 1500	1749	0	1.0	90 - 115
Producer gas	1250 - 4000	1596	0	0.9	90 - 300
Blast furnace gas + coke oven gas	1500 - 8000	1302	-210	0.75 ± 0.25	90 - 450
Medium BTU gases	8000 - 14000	1275	-320	0.45 ± 0.05	300 - 500
Carbon Monoxide	4,368	1780	0	0.97	341
Hydrogen gas	61,035	1780	0	0.07	343
Methane	23,863	1386	0	0.55	1067

Source: Reference 26

In these expressions, it is generally the net or lower heating value (LHV) that is used for h_f, but the difference between lower and upper heating values is generally not significant. The difference between the higher and lower heating values (or gross and net calorific values) at constant pressure is obtained by subtracting 1030 BTU per pound of water generated in the combustion from the higher or gross value (Defined by ASTM: D-407).

When evaluated from Equation 4.2 or 4.3, G_s ranges from about unity for blast furnace gas to 13 or 14 for liquid fuels, and 44.5 for hydrogen. Dry solid wastes and related organics have heats of combustion in the region of 8000 BTU per pound to 10,000 BTU per pound, so G_s is in the region of 6 or 7. Particularly with high excess air, the air tends to outweigh the fuel. Thus, in Equation 4.1 the unit is often neglected to a first approximation, so

$$T_{ad} = T_o + (h_f/G_s\,\overline{C}_p)/(1 + E\%/100). \qquad (4.4)$$

Using the approximation of Equation 4.2 that (h_f/G_s) is approximately constant, we obtain the result that the adiabatic flame temperatures are also approximately constant. At zero excess air, $T_{ad} \simeq 1370/\overline{C}_p$. An appropriate value of $\overline{C}_p$ is 0.38 (including dissociation), yielding approximately 2000°C for the adiabatic flame temperature, substantially independent of fuel type.

This calculation is only approximate and breaks down at low calorific values. The results of more accurate calculations are summarized in Figure 4.2 for the fuels listed in Table 4.1. The dotted line, as a fair average of the data plotted, is given, for T in degrees C, by

$$T_{ad} = T_o + 2120/(1 + 750/h_f)\ (^\circ\text{C}). \qquad (4.5)$$

Over the range of calorific values of 5000 to 60,000 BTU per pound (12 to 140 MJ/kg), the adiabatic flame temperature lies roughly between approximately 1800°C to 2050°C.

The effect of excess air is indicated by Equation 4.4 to an approximation. If the system is still adiabatic, the final temperature is still known as the adiabatic flame temperature, with a maximum value, $T_{ad,\ max}$, at zero excess air (assuming 100 percent combustion efficiency). Equation 4.4 can therefore be written

$$T_{ad} - T_o = (T_{ad,\ max} - T_o)/(1 + E\%/100) \qquad (4.6a)$$

or somewhat more accurately

$$T_{ad} - T_o = (T_{ad,\ max} - T_o)/[1 + (E\%/100)/(1 + 1/G_s)] \qquad (4.6b)$$

This is illustrated for the approximation of Equation 4.6a in Figure 4.3.

The effect of a thermal load, such as a wall loss, is similar. It is best related to a percent of input. If the wall loss is ω percent of input, a factor $(\omega\%/100)\,h_f$ is added to the right side of Equation 4.1. Factorizing, the wall loss is seen to be equivalent to reducing the fuel calorific value by the same percentage. The effect on the adiabatic temperature is to change it to a gas exit (POC) temperature, T_g, given by

$$T_g - T_o = (T_{ad} - T_o)(1 - \omega\%/100) \qquad (4.7)$$

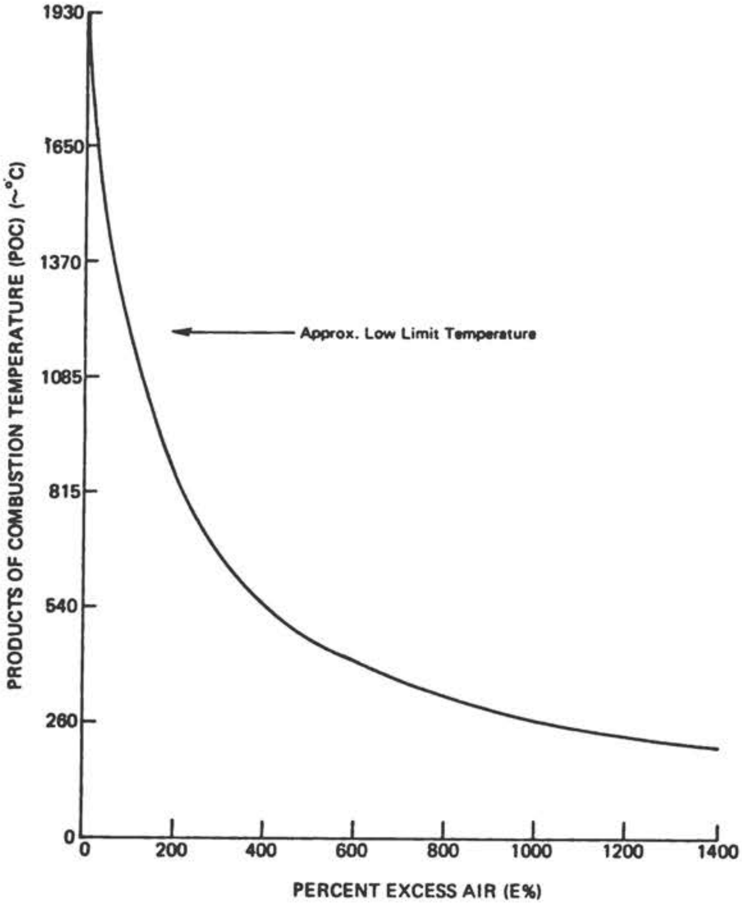


Figure 4. 3 Variation of POC Temperature with Percent Excess Air. [33]

4. 2. 3 Combustion Limit Requirements for Organic Fuels

Combustion of any fuel requires, naturally, a mixture of fuel and oxidant. If the oxidant is in exact theoretical proportion to oxidize all the fuel to final stable oxidants (generally carbon dioxide—CO_2—and water vapor for organic fuels) the fuel and oxidant are said to be in stoichiometric proportion. This is the parameter G_s introduced in Section 4. 2. 2. If the mixture ratio is non-stoichiometric, it means that either the fuel or the air is in excess. If the oxidant or air-to-fuel ratio is then G, the "equivalence ratio" (ϕ) is then defined as the normalized fuel-to-air ratio, given by

$$\phi = (1/G)/(1/G_s) = G_s/G \tag{4.8}$$

In terms of excess air (positive or negative), the equivalence ratio is inversely proportional to the excess air percent, thus

$$\phi = 1/(1 + E\%/100) \tag{4.9}$$

If either the air or the fuel is in sufficient excess, combustion cannot be sustained, and the flame extinguishes. These are known as the "combustion limits." The limit with excess air is known as the lean or lower limit. The limit with excess fuel is the rich or upper limit. Since we require complete combustion, the limit of concern is almost invariably the lean or lower limit.

The lower combustion limit causes problems in flame stability. This complex problem in real systems is frequently simplified by treating multiple jet or swirled jet flames (vortex combustors) as having two flow regions: a region of uniform mixing near the burner of the supply jets, and a downstream region in "plug" or "piston" flow in which the combustion is completed. The extent to which this is an over simplification is discussed in numerous articles [27, 28] (see also Section 4.3.4). It will nevertheless serve us to illustrate the stability problem.

The key to flame stability is the region of uniform mixing. This may be conveniently referred to as the stabilizing flame ball. There are two requirements for stability. First, this flame ball must by dynamically stable, which is to say that there is an ignited region that does not move in spite of a flux of gases in and out. Second, the flame must satisfy combustion limit requirements. Dynamic stability is conferred by a proper construction of the mixing pattern, and thus generally (or invariably) requires a region of "backmix flow" in which hot gases move up-stream against the mean direction of flow. This backmix aids distribution of fresh fuel and oxidant throughout the flame ball and/or provides heat of ignition for the fresh fuel. A good mixing pattern can be upset by additional jets in the wrong place or in the wrong direction, such as injection of waste streams for incineration. On the other hand, well designed injection can aid mixing.

The combustion limit requirement is based on a simple heat balance [27]. Inside the flame ball, only part of the fuel is burned before the products flow out of this mixing region into the plug-flow region downstream where combustion is completed. As the partly burned products flow out, they carry out heat. Since the fuel and oxidant are supplied cold, there is a net removal of heat from the flame by the flowing gases, and this heat must be balanced by the heat liberated in combustion if the temperature of the flame ball is to be maintained. If the heat loss exceeds the heat gain, the temperature of the flame ball gases will steadily drop until the flame suddenly extinguishes.

The precise moment and temperature of extinction depend on a number of factors such as the firing rate, the size of the flame ball, the thermal load from the walls, and the nature of the fuel. For our purposes, however, we may use a simple "rule," first proposed in 1911 by Burgess and Wheeler [29] similar to the stoichiometry rule described above. For many gases, the product of mole percent concentration at the low limit (p_L%) and the heat of combustion in kcal/mole (ΔH) is approximately 1100. A better expression includes the molecular weight (M)

$$p_L \times \Delta H = 910 + 54.5\,(M)^{1/2} \tag{4.10}$$

The original approximation corresponds to saying that the amount of heat going into one mole of air at the low limit is about the same for all fuels, and produces about the same temperature. This is about 1200°C with a spread of ± 95°C. It corresponds to about 50 BTU/cubic foot of the fuel/air mixture (1.86 MJ/m^3).

In an intensely mixed flame with a flame ball, as described above, only about two-thirds of the fuel is generally burned in the flame ball, with the balance burned downstream. Consequently, the mixture entering the flame ball must have the potential of reaching about 1550°C, if it burns fully, to reach the limit of 1200°C at two-thirds combustion. As the intensity of mixing is reduced, however, the potential maximum temperature can be allowed to drop from 1540°C to 1200°C.

These limits provide a basis to estimate the effect of waste stream addition into the flame ball. There can be two effects: dilution and additional thermal load. The major effect is usually dilution. Low limits may be determined experimentally by increasing the excess air until the limit is obtained. This limit generally corresponds to approximately 100 percent excess air. If the excess oxygen in the air at the low limit is replaced by inerts such as nitrogen, the low limit is unaffected. The oxygen concentration in the incoming mixture would be reduced to about 10 or 11 percent by such replacement if the dilution is equivalent to 100 percent excess air and if the mixture burns completely in the flame ball. If there is only two-thirds combustion in the flame ball, the permitted dilution is much less, and the oxygen concentration in the equivalent mixture must be 15 percent to 16 percent. If the added diluent has an appreciably higher specific heat than the oxygen it replaces in the calculation, then the permitted oxygen level must be higher still.

In summary, therefore, if a waste stream is to be injected directly into the flame ball, the oxygen concentration of the effective mixture must be checked before combustion to make sure that it will not affect flame stability. It also follows that any solids will be heated to something between

1200°C and 1980°C. If this would result in melting or vaporization of salts or other compounds, the combustion gases must be kept off the cold wall until the materials have re-solidified. Unfortunately, this may only be possible if the aerodynamic mixing pattern permits by-pass, which can create additional problems in the loss of unburned hydrocarbon.

If the waste is injected into the downstream region of the flame, the loading can be as high as desired since this does not affect flame stability. Moreover, if gases are to exhaust at temperatures below the softening points of the solid particulates present, then the maximum upper range for exhaust would be approximately 500°C to 800°C. This cooling cannot be achieved by wall loss; it has to be achieved by substantial excess air and/or waste stream addition, with the bulk of either added downstream of the flame ball. This is simple in principle but can be remarkably difficult in practice because of the difficulty of mixing two gas streams in the time and space available: substantial striation can occur, and the hot gas stream and cool added stream can survive with little mixing through the combustion chamber into the stack which may then by grossly overheated in parts. If the diluent stream is air, local overheating is the main problem. If the diluent stream is waste, however, an additional problem occurs: the time and temperature may be too short and too low to destroy the waste. This provides another constraint on the degree of dilution even if the mixing is well done.

4.2.4 Combustion Intensity, Combustion Volume, and Incinerator Capacity

The size of an incinerator for any specified firing rate is principally determined by the rate of chemical reaction of the fuel and other combustibles. Reaction must be completed within the combustion chamber. Obviously, the total reaction time must therefore be less than the residence time of the combustion gases in the combustor. Clearly, the less reactive the fuel and/or wastes, the larger the combustion chamber must be for a given firing rate. Likewise, if a chamber is fired at capacity with a reactive fuel or waste, the introduction of a less reactive fuel or waste requires a reduction in firing rate, which means reduced capacity. In normal circumstances, this is not a problem since the same fuel is used, with specifications kept between determined limits. However, when waste is fired by itself, or with added fuel, and if the waste is the main fuel, the "fuel specifications" can sometimes vary wildly, usually with periodic opportunity for upset conditions which can result in unwanted emissions. Even if the waste, as a secondary fuel, is added to a stably burning fuel or flame, it can still cause problems if there are significant interactions between the waste components and the fuel. Chlorides notably tend to affect gas-phase reactions, in many cases acting as reaction inhibitors. Consequently, the effective reactivity of the supporting fuel is reduced, thus requiring a drop in firing rate or capacity of the unit.

Additional factors that can critically affect behavior are as follows:

1. There is no uniform residence time in the combustor for all fuel and oxidant elements supplied; there is always a distribution of residence times, and the shorter residence times may determine the allowable design limit.

2. Groups of particles differ so in temperature and composition that there is no single reaction time; there is a distribution of reaction times, and the longer reaction times may have to be selected to match the shorter residence times to reduce emissions to permissible levels.

3. Any significant dilution requirements to meet maximum permitted gas exit temperatures will reduce the average residence time because of increased volume flow through the combustor, and will increase reaction times because of reduced temperatures.

The remaining variable that can permit continued operation without unwanted emissions is the firing rate, which may have to be reduced if dilution is increased, thus reducing incinerator capacity.

The problem is thus sufficiently complex that design of any combustion chamber from first principles is at present impossible. What may be used to determine approximate sizes and quantities is combustion intensity, based on past experience. Combustion intensity is defined as the average thermal loading rate per unit volume of the combustion chamber. It is obtained by determining the BTU supply rate from all combustible sources, and dividing by the combustion chamber volume (V_c). Formally:

$$I = F \cdot h_f / P\, V_c \left(\frac{\text{BTU}}{\text{ft}^3\ \text{hr atm}} \right) \tag{4.11}$$

where I is the combustion intensity, F is the fuel and waste supply rate, h_f is the effective calorific value of the combined fuel and waste streams, and P is the absolute pressure in atmospheres (which can be assumed always to be unity in this context). A simple analysis dating from 1925 [30] (see also [27]) then yields the approximate relation between I and the stipulated mean combustion time (t_c), the excess air (E%), and the mean flame temperature ($\overline{T}_f$)

$$I = K\, (T_o/\overline{T}_f)/t_c \tag{4.12}$$

where

$$K = \rho_o\, h_f\, [1 + G_s\, (1 + E\%/100)] \tag{4.13}$$

and where ρ_o is the standard temperature pressure (STP) density of air, and G_s is the air/fuel stoichiometric relationship for the dry, inert-free (DIF) fuel (or waste). Since G_s is typically 8 to 10 even for DIF wastes, and E% is typically large to keep down the temperatures, the constant K can be written approximately as $[\rho_o h_f/G_s (1 + E\%/100)]$. Using the relation mentioned above that $(h_f/100)$ is the cubic feet of cold air required for combustion, $(\rho_o h_f/100)$ is therefore the weight of air and is thus equal to G_s. We then have reduced Equation 4.12 to

$$I = \frac{100}{(1 + E\%/100)} \times \frac{T_o}{T_f} \times \frac{1}{t_c} \tag{4.14}$$

Again, a reminder is due that if excess air (E%) goes up, the mean flame temperature (T_f) goes down, but the combustion time (t_c) increases more than proportionately. The permitted combustion intensity therefore drops, and from Equation 4.11 the firing rate must be reduced in proportion.

Typical values of combustion intensity for all fuels are listed in Table 4.2 [27, 31]. For solid wastes fired on a grate, combustion intensities are listed in Table 4.3 (bottom line) [31] for the top five Incinerator Institute of America (IIA) Waste type Categories [32] (defined in Table 4.4).

Notable in the values in the tables is the range of combustion intensities of roughly eight orders of magnitude (Table 4.2) for all fuels. At the lower combustion intensities, this represents the distinction between intensity based on flame volume and intensity based on furnace volume, with many lower intensity systems having flame volumes one-tenth or one-hundredth of the combustion volume (particularly using gas). The balance of the range in intensities is due to ranges in combustion time (t_c) for the different fuels. Combustion time can be as low as 10^{-5} seconds for gas in a detonation, up to 1 second for normal pulverized coal combustion, and 10^2 to 10^3 seconds for solid lumps on grates. By contrast, a large rise in excess air from zero to 400 percent is only a factor of 5 change in $(1 + E\%/100)$; a large drop in average flame temperature from 1650°C to 540°C is only a factor of 3 in $(T_o/\overline{T}_f)$. Reactivity, controlling t_c, is clearly the sensitive factor.

Further examination of the tables, especially Table 4.3, however, reveals that practical systems, particularly incinerators, are likely to have combustion intensities lying between 10^3 and 10^5 BTU/ft^3 hr atm, even if stabilizing (oil) flames are required. They may have combustion intensities at 10^6 but occupy only 10 percent of the combustion volume. The stabilizing flame will be at low excess air and high temperature. In a system, for example, with 400 percent excess air overall, and the average flame temperatures close to 820°C (and maybe exiting at 540°C), combustion times (matched by residence times) lie in the range of 10^{-1} to 10 seconds (from Equation 4.14). This is likely to bracket most operating conditions.

TABLE 4.2 Comparisons of Combustion Intensities Obtained with Different Fuels

Combustion Intensity (Btu/hr cu ft atm)	Fuel Type		
	Gas	Liquid	Solid
4×10^9	Mullins theoretical upper limit		
10^9			
10^8	Longwell bomb (80% combustion) (Special research reactor)	Liquid fuel rockets	
10^7	Premixed gas burners (intensity defined on flame volume)	Ram jet Gas turbines using pressure atomized oil	Solid fuel rockets
10^6	Premixed or turbulent diffusion gas flames with intensity defined on furnace volume	Medium fuel oils (pressure and air atomized)	Pulverized fuel (experimental for MHD). Also cyclone burners alone (excluding radiant chamber)
10^5		Heavy fuel oils (air and steam atomized)	
10^4		Household oil burners	Pulverized fuel and stoker firing (industrial)
10^3			
10^2	ALL FUELS - for drying and baking ovens		

NOTE: The industrial furnace operations can be taken as being at one atmosphere. The gas turbines are normally pressurized operation.

Source: Reference 27

TABLE 4.3 Estimated Values of Waste Factor (K) and of Combustion Intensities (I)

Waste Type	0	1	2	3	4
Logarithmic Waste	13	13	10	8	----
Factor (K_L)	13	1 13	10	8	-----
Ash % (A)	5	5	5	5	5
Moisture % (M)	10	25	50	70	85
Heat of Combustion (B) BTU/lb	8500	7000	4500	2500	1000
Auxiliary Fuel BTU/lb	----	----	----	1500	3000 to 8000
Average Volumetric Reaction Rate ($\bar{R}_V$) lb/hr cu. ft.	4.53	4.53	3.06	2.17	1.41
Waste Factor (K)	4.33	4.33	3.33	2.67	2.0
Combustion Intensity (I) BTU/cu. ft. hr.	38,500	31,750	13,750	5425	1405

Source: Reference 31

The above discussion applies generally to all combustors, including grate-fired units. Grate-fired units, with solids on grates, are covered by Equation 4.14 because grate firing of organic solids (coal, wood, waste, etc.) is primarily a gasification process, and the main combustion volume to be sized is above the grate. For grate-fired units, an additional expression is available [31] relating the firing rate, F, the combustion intensity, I, and the area firing density, F_A (lb/sq ft hr):

$$F_A = C \times (I \times h_f)^{2/3} \times F^{1/3} \qquad (4.15)$$

where C is a dimensionless incinerator "constant" that depends on the proportional dimensions of the combustion chamber and has a value near unity. Typical values of F_A range from 10 to 50 pounds per square-foot-hour, equivalent to 10^4 to 5×10^5 BTU/square-foot-hour (3×10^4 to 1.5×10^6 watt/m^2).

TABLE 4.4 Incinerator Institute of America (IIA) Classification of Wastes to be Incinerated

Classification of Wastes		Principal Components	Approximate Composition (% by Weight)	Moisture Content (%)	Incombustible Solids (%)	Btu Value/lb of Refuse as Fired	Btu of Aux. Fuel per lb of Waste to be included in Combustion Calculations	Recommended Min Btu/hr Burner Input per lb Waste
Type	Description							
0*	Trash	Highly combustible waste, paper, wood, cardboard cartons, including up to 10% treated papers, plastic or rubber scraps; commercial and industrial sources	Trash 100%	10	5	8500	0	0
1*	Rubbish	Combustible waste, paper, cartons, rags, wood scraps, combustible floor sweepings; domestic, commercial, and industrial sources	Rubbish 80% Garbage 20%	25	10	6500	0	0
2*	Refuse	Rubbish and garbage; residential sources	Rubbish 50% Garbage 50%	50	7	4300	0	1500
3*	Garbage	Animal and vegetable wastes, restaurants, hotels, markets; institutional, commercial and club sources	Garbage 65% Rubbish 35%	70	5	2500	1500	3000
4	Animal Solids and organic wastes	Carcasses, organs, solid organic wastes; hospitals, laboratories, abattoirs, animal pounds, and similar sources	100% Animal and human Tissue	85	5	1000	3000	8000 (5000 primary) (3000 secondary)
5	Gaseous, liquid or semi-liquid wastes	Industrial process wastes	Variable	Dependent on predominant components	Variable according to wastes survey	Variable according to wastes survey	Variable according to wastes survey	Variable according to wastes survey
6	Semi-solid and solid wastes	Combustibles requiring hearth, retort, or grate burning equipment	Variable	Dependent on predominant components	Variable according to wastes survey	Variable according to wastes survey	Variable according to wastes survey	Variable according to wastes survey

*The above figures on moisture content, ash, and Btu as fired have been determined by analysis of many samples. They are recommended for use in computing heat release, burning rate, velocity, and other details of incinerator designs. Any design based on these calculations can accommodate minor variations.

Source: Reference 32

4.2.5 Effects of Waste Addition Organic Fuels Combustion

The possible effects of the addition of waste to organic fuels combustion have already been indicated. A summary will suffice here. Four effects are common: heat additions by combustible components; increased thermal loading of the flame by incombustible components (solids or liquids); volume expansions of liquids that form vapors and that reduce residence time; and adverse catalytic effects inhibiting combustion and/or aiding smoke formation. Reduced reactivities for any reason can overload the incinerator. Briefly:

1. Combustible (dry ash-free) components can be easily included in any simple calculation by addition of thermal input rates. Air requirements increase roughly in proportion (at one cubic foot, cold, per 100 BTU). If the excess air is maintained at the same percentage level, the POC temperatures are essentially unchanged on account of the DIF waste components. Figure 4.3 illustrates the variation in adiabatic flame temperature with excess air, which is also effectively the POC temperature at zero wall loss. This graph was constructed from the available heat chart [33].

2. The increased thermal loading of the flame, which occurs when inerts other than air are added, has a substantially similar effect to excess air. The specific heats of many solids are about the same as that of air at the lower temperatures on a weight basis (0.25 to 0.30 BTU/pound degree F over the temperature range of interest, neglecting dissociation), unless the solid liquifies, sublimes, and/or vaporizes. However, as a first approximation, the effect can be considered about equal to those of excess air on a weight basis. Water has more effect: approximately 1000 BTU/pound latent heat of vaporization, plus the sensible heat rise at a specific heat of 0.5, or roughly twice that of air. The loadings at approximately 800°C and 1650°C are therefore approximately 1750 and 2500 BTU/pound water. However, one pound of oil at 18,000 BTU/pound exceeds the loading of an equal weight of water by a factor of 7 to 10. By comparison, one pound of oil requires roughly 15 pounds air, and thermal loadings of 1700 to 2500 BTU due to excess air correspond to roughly 30 percent and 22 percent excess air—not extreme amounts. Excess air is thus frequently a greater thermal load than is water. If water alone is used to bring a stoichiometric oil flame down from approximately 1650°C to 1200°C, between 3.5 and 4 pounds water per pound fuel oil is theoretically required. Figure 4.4 illustrates the compromise between added water and reduced excess air to maintain a given exit gas temperature (T_g).

3. Liquids (mainly water) that form vapors expand the volume. When other factors are corrected, the remaining effect is to reduce the residence time in the combustion chamber. The specific volume of steam at boiling point is 26.8 cubic feet per pound which would be equivalent to about 20 cubic feet per

pound water if it could be reduced to 16°C without condensing. The stoichiometric air at the same temperature is about 180 cubic feet, so water at a ratio of one pound per pound of oil would increase the POC volume by roughly 10 percent, thus reducing the residence time by the same percentage. Clearly, this is not a dominant effect.

4. The chemical effect of waste components is potentially significant, but the details are complex, only partially understood, and out of place here. The possible adverse effects are inhibition of reaction and enhancement of smoke formation.

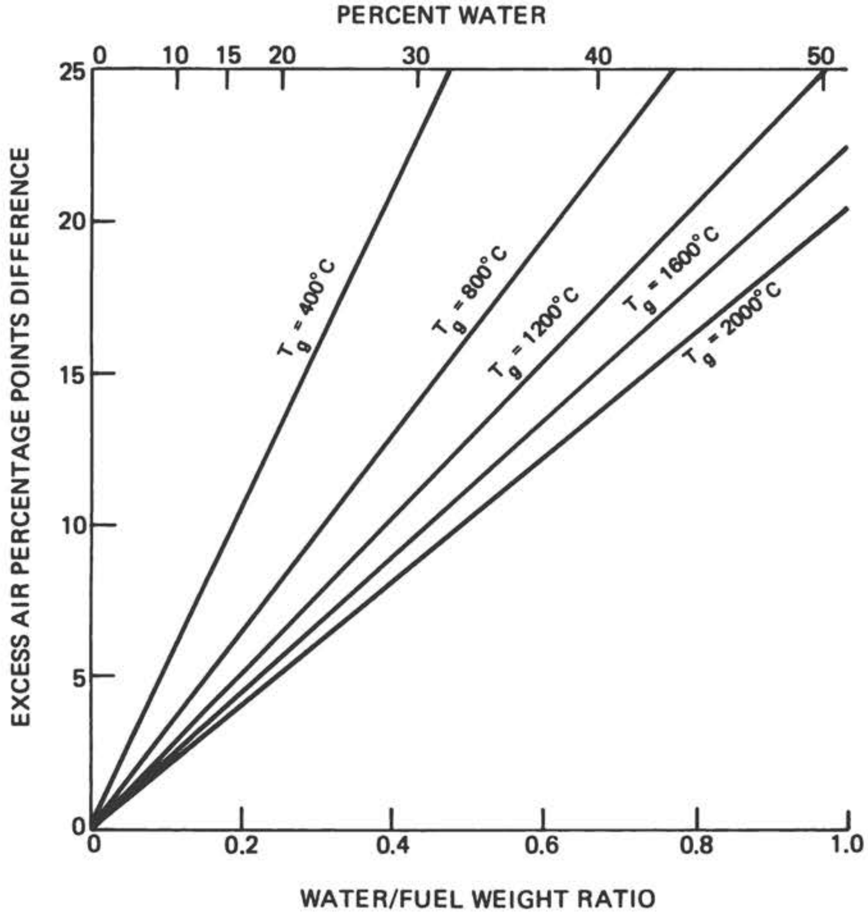


Figure 4.4 Required Percentage Point Drop in Excess Air to Offset Thermal Loading of Water [52].

Note: T_g = Exhaust or gas exit temperature.

4.3 Internal Characteristics of Combustion Chambers

4.3.1 General Characteristics

Internally, the combustion chambers combine reaction, flow, and heat transfer. A full mathematical description is extremely complex and out of context in this report (see references 1-9, 14, 21, 27, 28 and references quoted in those texts). What follows is an essentially qualitative description of certain key characteristics of combustion in incinerators.

4.3.2 Generalized Reaction Kinetics

1. Organic solids on a grate start combustion by heating up, drying out, and pyrolyzing. This process first evaporates water out of the solid and then thermally decomposes the solid into combustible volatiles that escape into the space above the bed, and leave a residue of char or coke on the grate. The pyrolysis is generally mildly endothermic, so that heat has to be supplied. Certain plastics, however, are found to change from mildly endothermic to substantially exothermic if they are pyrolyzed at high temperatures. As a consequence, the pyrolysis becomes exothermic, heat is released, and the temperature continues to escalate. Even if the incinerator is shut down, the exothermic heat of pyrolysis maintains a thermal supply into the system that continues to raise the temperature. This is known technically as a thermal explosion system. If this reaction is not prevented, the grate may overheat and be destroyed.

In normally well-behaved systems, the solid material can be fed onto the grate from on top (overfeed), from underneath the bed (underfeed), or from the side (side- or crossfeed). The material then behaves essentially as described above: initial pyrolysis is followed by combustion and gasification, but with significant variations depending on the feed. In general, as the particles move through the bed, they first dry, then pyrolyze, and then start to react. However, with overfeed, the particles move against the direction of the underfire combustion air. The gaseous products resulting from drying, pyrolysis, and reaction are carried into the higher levels of the bed. With the underfeed system, the drying and pyrolysis products are carried up into the reaction zone, instead of into the drying and pyrolysis zone as with top feed. In the case of crossfeed, the products of pyrolysis, etc., interact with the other zones to some extent, but the products more frequently escape to the gas phase above the bed, with less further interaction in the bed itself.

These differences can strongly affect the nature of the products going into the overbed zone, and hence, potentially, the nature of the reactions in the gas phase of the bed. The gas phase above the bed is where generally 70 to 90 percent of combustions take place when materials of cellulosic origin, such as paper, are being incinerated. Even with coal, the overbed region is still the source of 50 to 60 percent of the combustion.

The time required to pyrolyze the material is an important parameter. In the absence of better data, it can be taken as roughly proportional to the square of a linear dimension of the particle, with a proportionality constant of about 100 cgs units. The pyrolysis time for a one centimeter particle would therefore be about 100 seconds (i.e., one to two minutes).

In simple incinerators, the feed is generally from the top or from the side, and more particularly from the top if the system is periodically batch-fed. Although there are certain differences in behavior, nevertheless the following description of the top feed (overfeed) will suffice to illustrate the typical process in a burning solid bed. As the particles descend through the bed, after drying and pyrolyzing in the upper levels, they move farther down into a zone where they meet rising combustion products that originate even deeper in the bed. If the bed is deep enough (and it generally is), then by about the middle of the bed the products of reaction emanating from below have no oxygen left, with the result that the main reaction occurring in the middle sections of the bed is gasification; that is to say, reaction of char (left by the pyrolysis) with CO_2 to form carbon monoxide . In general, as the bed depth increases, the proportion of carbon monoxide in the gas reaching the top of the bed increases, although this is a function of the overall temperature.

Below the gasification zone in the bed, then, is the combustion zone. In this zone, all the oxygen of the underfire air is used up and, in the process, most of the heat released is carried upwards by the combustion products into the upper levels of the bed. This is necessary to maintain the upper levels of the bed at a temperature where the gasification reactions will continue at a respectable pace, typically about 1100°C to 1300°C. If too little underfire air is used, the gasification reactions will become very slow or stop altogether, and there will be mainly carbon dioxide leaving the top of the bed moving into the gas phase above. This can, in fact, produce a deleterious effect on the burnout of volatiles because of the excessive dilution in the gas phase by the inert CO_2. This means that a minimum underfire air rate is required, although in some particular furnaces overfire air infiltrates into the bed in sufficient quantity to maintain the reaction at the necessary rate. On the other hand, too high a velocity tends to lift ash into the overbed space, where it can be difficult to remove to prevent pollution. Gasification rates are typically in the range of 5 to 50 pounds per square-foot-hour, with air rates in the range 10 to 100 pounds per square-foot-hour for gasification.

A simple mathematical model has been developed for this overfeed system. The model is in broad agreement with the actual behavior. The behavior can also be described in terms of the concentrations of gases in the rising combustion products stream, as illustrated in Figure 4.5. At the grate level, air comes in with 21 percent oxygen. As the gases rise in the bed the oxygen is consumed, falling to near zero level within a few inches above the grate (typically, 2 to 5 particle diameters). At the same time, the carbon dioxide builds up to reach a peak at about the level where the oxygen has vanished. Above that point, if the temperatures are high enough, the carbon dioxide is converted back to carbon monoxide which increases from that point on. The processes in the bed are therefore in part drying, in part pyrolysis, in part combustion, and in part gasification.

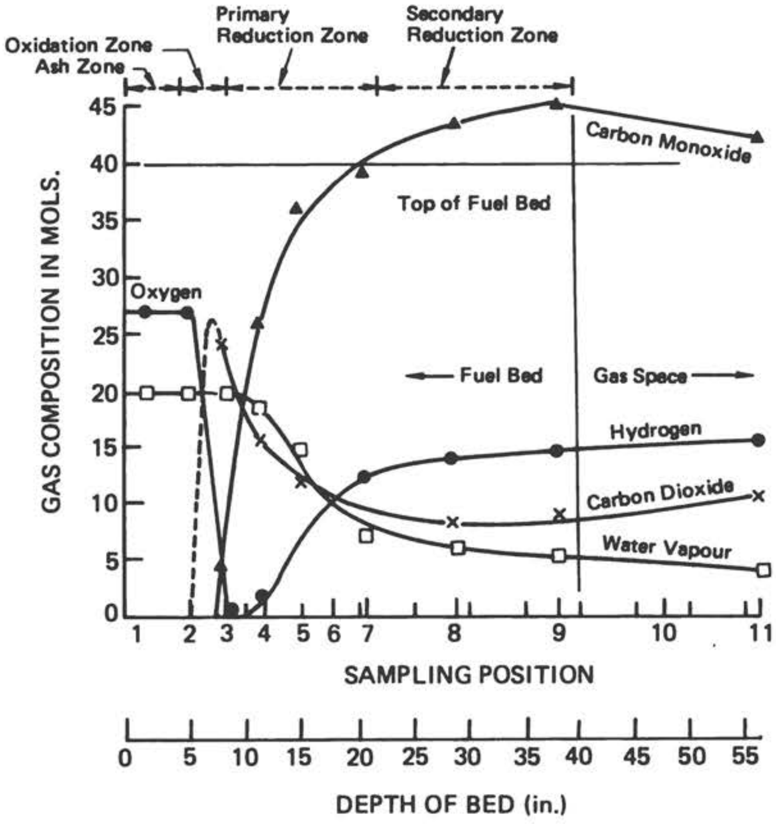


Figure 4.5 Composition of Gases in the Fuel Bed of a Gas Producer. Basis, 100 Mols. of N_2, Anthracite or Coke [10].

2. <u>Homogeneous gas and vapor phase combustion</u> takes place either above a pyrolyzing and gasifiying fuel bed, or simply inside a combustion chamber into which the fuel components are injected. At its simplest, the reactions can be described by overall equations, which, however, only describe fuel that mostly turns into carbon dioxide and water vapor. These equations are perfectly accurate as an overall description, but do not cover the details of moving from reaction to products. Since the steps involved take time, and can sometimes be interfered with, some understanding of the steps involved is essential in any analysis of the incineration.

In general, reactions occur in a number of simultaneous steps involving radical or active species in addition to stable molecules. For example, carbon monoxide is reacted to form carbon dioxide by the following equation:

$$CO + OH = CO_2 + H$$

This shows that the stable component, carbon monoxide, reacts with the hydroxyl radical to form stable carbon dioxide and release a hydrogen atom. For this reaction to proceed with any speed, water vapor must be present to provide the hydroxyl radicals, as well as further chances for reaction of the hydrogen atom thus formed.

The number of steps in any given fuel reaction is significant. In general, for the hydrogen-oxygen reaction alone, a set of about ten equations is usually necessary. If the material to be burned is methane, quite typically anywhere from 15 to 35 equations are needed. With anything more complex than methane, the number of reactions increases dramatically. Moreover, many reactions become involved whose real existence is problematical, and whose kinetic constants can only be guessed at or are totally unknown. The problem of predicting the reaction of such complex components as volatile products from pyrolyzing solids is therefore extreme. A common way around this difficulty is to assume that anything much more complex than hydrogen or methane is decomposed or pyrolyzed to carbon monoxide and hydrogen in a very rapid first step, after which the carbon monoxide and hydrogen are assumed to react by what are now fairly well established reaction sequences: the first step is thus:

$$C_nH_m + \frac{n}{2} O_2 \rightarrow nCO + \frac{m}{2} H_2$$

Table 4.5 lists typical rate constants (velocity constants and activation energies) adopted for the elemental steps listed in the "quasi-global" initial hydrocarbon decomposition step. The rate equations take the following form for the rate of destruction of the fuel (waste or waste products):

$$d(\text{fuel})/dt = \sum_j (\alpha'_{ij} + \alpha''_{ij})\,(R_j - R_{-j}) \tag{4.16}$$

where α'_{ij} and α''_{ij} are the inherently positive and negative coefficients in the chemical equilibrium equation

$$\Sigma'\,(\alpha'_{ij} + \alpha''_{ij})\,I_i = 0 \tag{4.17}$$

TABLE 4.5 C-H-O Chemical Kinetic Reaction Mechanism

$k_f = AT^b \exp(-E/RT)$

REACTION	FORWARD		
	A	b	E/R
1. $C_nH_m + \frac{n}{2} O_2 \rightarrow \frac{m}{2} H_2 + nCO$	$\frac{5.52 \times 10^8}{p.825} \cdot C_{C_nH_m}^{\frac{1}{2}} CO_2$	1	12.2×10^3
2. $CO + OH = H + CO_2$	5.6×10^{11}	0	$.543 \times 10^3$
3. $OH + H_2 = H_2O + H$	2.19×10^{13}	0	2.59×10^3
4. $OH + OH = O + H_2O$	5.75×10^{12}	0	$.393 \times 10^3$
5. $O + H_2 = H + OH$	1.74×10^{13}	0	4.75×10^3
6. $H + O_2 = O + OH$	2.24×10^{14}	0	8.45×10^3
7. $M + O + H = OH + M$	$1. \times 10^{16}$	0	0
8. $M + O + O = O_2 + M$	9.38×10^{14}	0	0
9. $M + H + H = H_2 + M$	$5. \times 10^{15}$	0	0
10. $M + H + OH = H_2O + M$	1×10^{17}	0	0

Note: Reverse reaction rate, k_r, is obtained from k_f and the equilibrium constant, K_c.

units: $[A] = \frac{cc}{\text{mole-sec}}$ for bimolecular reactions

units: $[A] = (\frac{cc^2}{\text{mole}})/\text{sec}$ for termolecular reactions

Source: Reference 34

where I_i is the chemical formula of specie i (e.g., hydroxyl, or oxygen, or hydrogen, etc.); and R_j and R_{-j} are the respective forward and reverse reaction rates of the j th reaction:

$$R_j = k_j \pi_i (\rho\sigma_i) \alpha'_{ij} \tag{4.18a}$$

$$R_{-j} = k_{-j} \pi_i (\rho\sigma_i) \alpha''_{ij} \tag{4.18b}$$

where k_j and k_{-j} are the forward and reverse rate constants for the j th reaction; ρ is the local fluid density; and σ_i is the mole/g of mixture concentration of the i th specie. The velocity constants, of course, are related by the equilibrium constants for the reaction at the appropriate temperature:

$$K_{eq} = k_j/k_{-j} \tag{4.19}$$

These equations suggest the complexity of the problem. If the fuel is ill-defined, which is the case when wastes are burned, even the quasi-global approach may be impossible to use. One problem is knowing the component's concentration. In a kinetic study of the combustion of smoke [35], the smoke mass fraction was successfully used, but even this is difficult or frequently impossible to measure. Further difficulties arise if there is any suspicion that components in incinerated wastes (notably halide compounds) interfere with any part of the reaction, including the heat of combustion (see Figure 4.6). The main value of information on complex cases lies in alerting the user or the designer to possible reaction interferences.

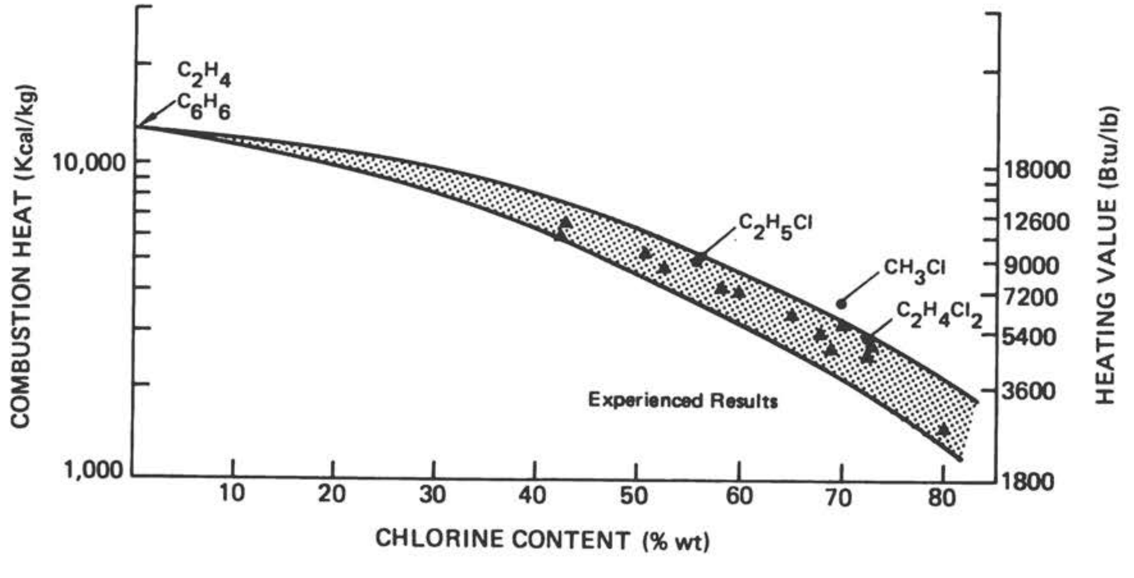


Figure 4.6 Heat of Combustion of Chlorinated Hydrocarbon [36]

One simplifying factor is that one particular sequence of reactions involving CO, CO_2, H_2, and H_2O goes so fast that the water gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

is usually close to equilibrium. Figure 4.7 plots the equilibrium constant for this reaction, together with some others of significance in hydrocarbon reactions.

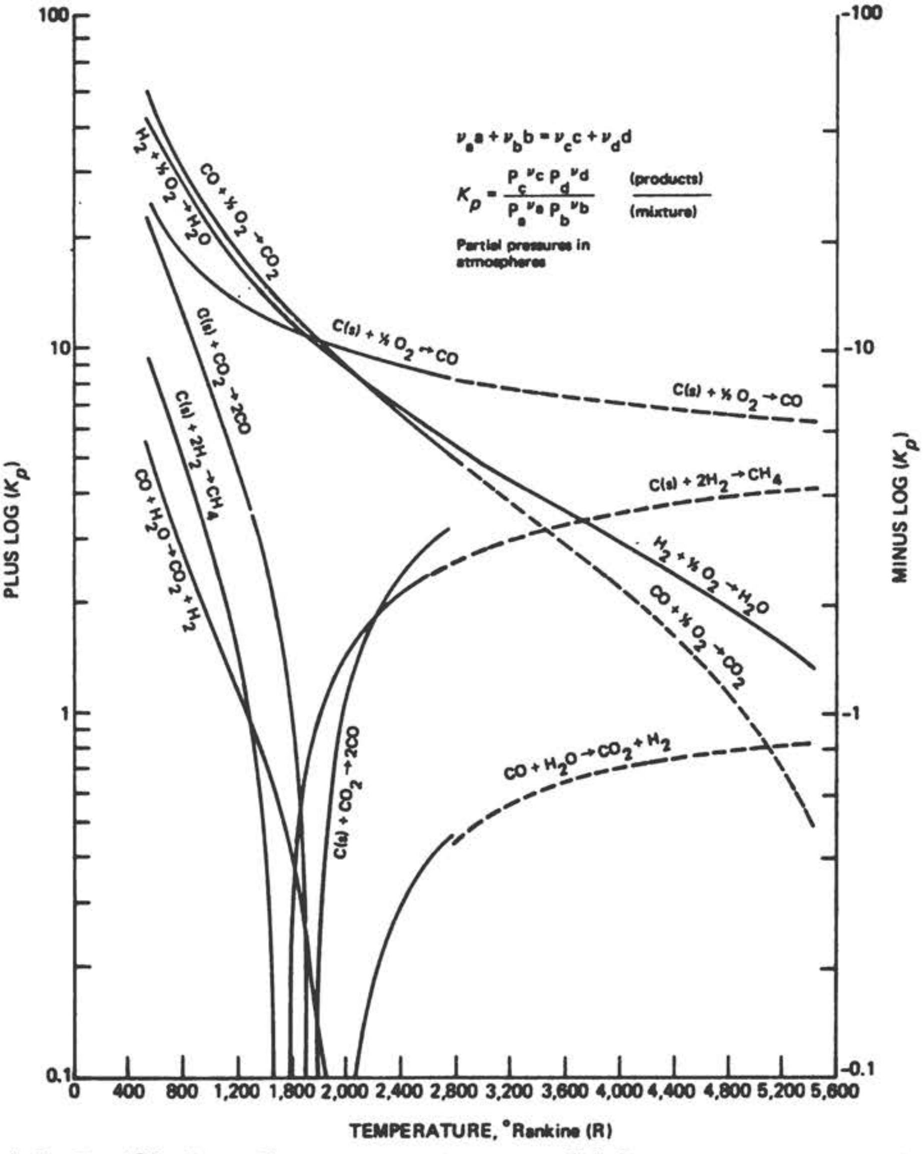


Figure 4.7 Equilibrium Constants. (Note: Solid lines: API Research Project 44, tables 1y, 0y, NBS, Wash., D. C., 8/31/44 & 8/31/46. Dashed lines: B. Lewis & G. von Elbe, "Combustion Flames and Explosions of Gases," Table II, Cambridge University Press, N. Y., 1938.). [37]

3. Liquid sprays present additional problems. In one way or another, the spray must vaporize, after which the vaporized components burn according to the sequence of events described in the paragraph above. The speed of the reaction, however, which determines the combustion space required, is more generally determined by the rate of vaporization. The processes can best be understood by considering the behavior of a single drop.

A drop of volatile material, such as water or oil, when injected into a hot gas, vaporizes. A thermal boundary layer is established between the drop surface and the surrounding atmosphere across which heat flows because of the temperature gradient thus established. Analysis shows that the rate of evaporation is approximately proportional to the diameter of the drop, and the time to evaporate is approximately proportional to the square of the initial diameter (d_o):

$$t_{evap} = K_{evap}\, d_o^{\;2} \tag{4.20}$$

The constant of proportionality (K_{evap}) lies roughly in the range 100 to 500, if the diameter is expressed in centimeters; the burning time or evaporation time is measured in seconds. Thus, a one millimeter particle or drop would burn or vaporize in something between one and five seconds. Therefore, where residence times in a combustion chamber are less than one second, and sometimes less than one tenth of a second, the need for reducing the drop size becomes clear.

If the drop is composed of combustible liquid, an additional phenomenon is generally recognized: the burning mechanism often depends on formation of a spherical flame around the drop, where the diameter of the flame is typically 5 to 50 drop diameters. Figure 4.8 illustrates the typical temperature and concentration curves on a radius out from the drop surface. Under such conditions, the rate of evaporation during burning may only be 10 or 20 percent faster than the rate of evaporation during evaporation in hot gas of a temperature equivalent to the flame temperature. This means in practice that the rate of evaporation is a good estimate for the rate of burning.

Investigations have also indicated that this burning mechanism (with the individual flames surrounding the drops) is evidently true for drops greater than 40 microns which are predispersed in air, with the overall flame then traveling through the preformed cloud. For drop sizes less than 10 microns, it appears that the drop always vaporizes before the local surrounding flame can be established [38]. The diameters between 10 and 40 microns evidently represent something of a transition region between total vaporization and the surrounding of all drops by individual flamelets.

This picture is further modified, however, if the drops are present in fairly high concentration. In that case, the vaporizing drops tend to generate sufficient vapor for a flame to form around the group of drops. When fuel is injected into a combustion chamber by an atomizer, the drop concentration can then be so high that no reaction occurs to any significant degree within the cone of the spray and, instead, the drops only vaporize within the spray cone. The vapor thus formed diffuses to the boundaries of the spray cone where the drops feed a surrounding sheath of flames which in turn feeds back heat to maintain evaporation.

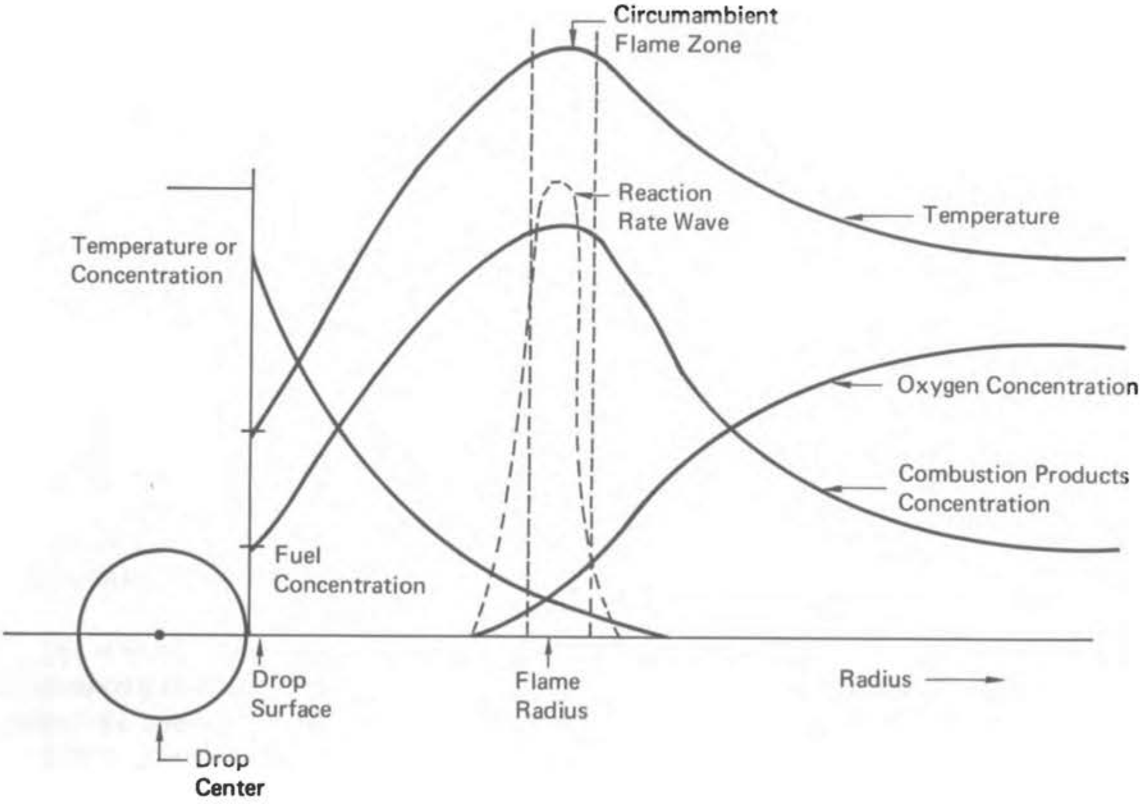


Figure 4. 8 Typical Gas Concentrations and Temperature Profile on Radius Out From Drop Surface

4. If the material being injected is finely divided solids, the processes of reaction can be something of a mixture of all three processes already described. If the particles are heated relatively slowly (less than about 1000°C per second), then the particle pyrolyzes, if it can, with oxygen diffusing, in due course, to the solid surface of the char thus formed and the volatile products migrating into a space between the particles to burn by the gas phase reactions indicated previously (see paragraph 2 of Section 4. 3. 2).

If the particles are heated fast (greater than 10, 000°C per second), then they will reach ignition temperature before they pyrolyze. Under these conditions, ignition occurs first, after which the particle may pyrolyze, followed by the sequence of solid reactions previously described.

For fairly large particles (greater than 100 microns) the time to burn out is again approximately proportional to the square of the initial diameter (as with the oil drops), but the constant of proportionality has a value of about 1000 cgs units. For particles smaller than this, the burning time is more likely to be proportional to the initial diameter to the first power but it can be estimated that char particles formed by pyrolysis of organic solids in the flame will take roughly 10 times as long to burn out as do oil drops. Temperature also must be considered, but for roughly comparable flame temperatures, the approximation works. When coal particles and oil sprays of comparable particle sizes and size distributions are compared within the range of 1 to 100 microns, burning times are roughly one second for the coal particles, and 0. 1 second for the oil drops.

5. A further set of reactions to be considered is that which results in production of smoke. Unfortunately, all too little is known about the mechanism of smoke production. The generation of smoke is believed to start with initial cracking of hydrocarbons (such as any volatiles produced from initial pyrolysis of solids, or pyrolysis of fuel oil vapor, etc.). A long process of condensation follows the cracking during which solid particles are built up. Initially, these contain substantial proportions of hydrogen, but finally most of the hydrogen is eliminated. The particles thus formed tend to be submicron, and tend to be both highly unreactive (and therefore difficult to burn out) and of respirable size. Table 4. 6 summarizes present views of the mehcanisms and products involved in smoke and soot formation.

This solid end product, carbon, is generally known as soot; however, between the initial pyrolysis of the fuel and the final production of soot, the intermediates generally form what can best be described as "smoke" which, if sampled and condensed, frequently turns out to be a liquid. Flames or fuels that are potentially smoke-producing burn yellow. At one time it was believed that the yellow radiation was emitted from carbon particles produced in the flame, and ultimately destroyed if the flame burned cleanly. However, the awareness that the soot particles, if formed, are highly unreactive, in addition to some spectroscopic investigations of the yellow emissions themselves [39] have indicated that the yellow radiation is banded, and is probably being emitted from some soot smoke precursor. What is of interest is that halogen compounds tend to promote the production of the smoke and soot, while water vapor and other diluents tend to reduce their formation [40].

4.3.3 Atomization and Vaporization of Liquid Sprays

Fuel oil or aqueous wastes must be vaporized to burn. This can be done in a special vaporizing unit, or through the intermediary of atomizing the liquid, i.e., breaking it up into a fine dispersion of small drops. Vaporizing burners that do not use atomization are commercially available, but most are small and the bulk of the oil is burned by atomization.

TABLE 4.6 Summary of Smoke and Soot Formation Mechanisms and Products

A. GENERAL MECHANISM

Smoke and soot are formed from fuels and organics in two principal stages

Stage I: Cracking (C% drops) Stage II: Condensation (C% rises)

$$\text{fuel} \longrightarrow \begin{array}{c}\text{low}\\ \text{MW}\\ \text{fractions}\end{array} \longrightarrow \text{soot}$$

B. PROCESSES AND PRODUCTS

Stage I: Cracking (C% drops)

- Process: Fuel molecule decomposition by pyrolysis/reaction. Number of C atoms lower than in parent fuel.
- Products: Low MW fractions: liquid/condensible particulates.

Stage II: Condensation (C% rises)

- Process: Nuclei creation and growth; particle agglomeration and curing.
- Products: Agglomerated, cured soot particles (>98% C)

C. SOOTING TENDENCY OF FUELS

1. Premixed Flames: Straight chain > branched; paraffins > olefins and acetylenes.
2. Diffusion Flames: Tendency decreases with increasing MW (except paraffins): paraffins < monolefins < diolefins < benzenes < naphthalenes.

D. STAGE II (CONDENSATION) DETAILS

II A: Nucleation

- Process: Alternative theories:
  - (1) no critical or initiating nucleus required; nuclei formed by ring closures and H_2 evolution and
  - (2) positive ions act as initiating nuclei.
- Product: Polyacetylenes (PA) and/or polynuclear aromatics (PNA) formed as 20 to 30 Å "crystallites."

II B: Growth

- Process: Addition reactions to nuclei by further gas/solid cracking reactions on nuclei surfaces (v. rapid).
- Product: 100 Å particles (high carbon).

II C: Agglomeration and Curing

- Process: Particulate collision and adhesion: curing (thermal removal of residual species).
- Product: Particle agglomerations up to 500 Å (some to 1000 Å) of 10^5 to 10^7 carbon atoms (~ 10^4 crystallites). Approximate molecular descriptions C_8H to $C_{12}H$.

To atomize, a liquid must be formed into a fine jet or thin sheet traveling at some considerable velocity. The result, as found experimentally, is that after traveling some certain distance, the jet or sheet becomes unstable and ultimately breaks up into an array of fine drops (Figure 4. 9). There are three essential methods of generating the sheet or fine jet as illustrated in Figure 4. 10: (a) the swirl spray or pressure jet atomizer; (b) some mehcanical device, notably a rotary cup; or (c) the two-fluid atomizer. The pressure jet will probably be the most common for clean, free-flowing fuel for shipboard incinerators. This is the device almost invariably found in oil burners for domestic use. The two-fluid atomizer may also be considered for waste fuel or other liquids.

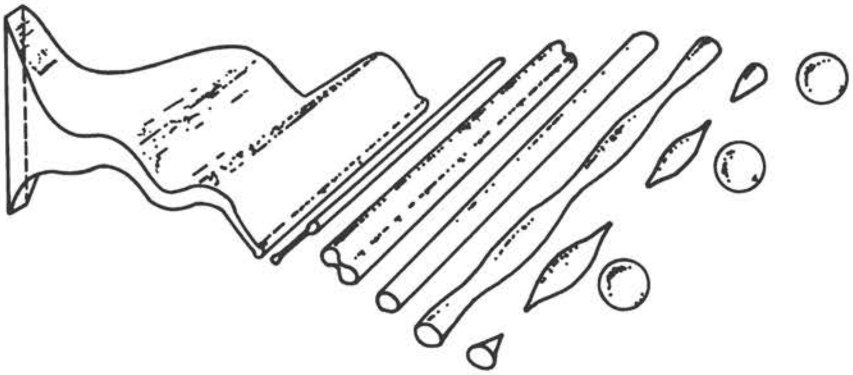
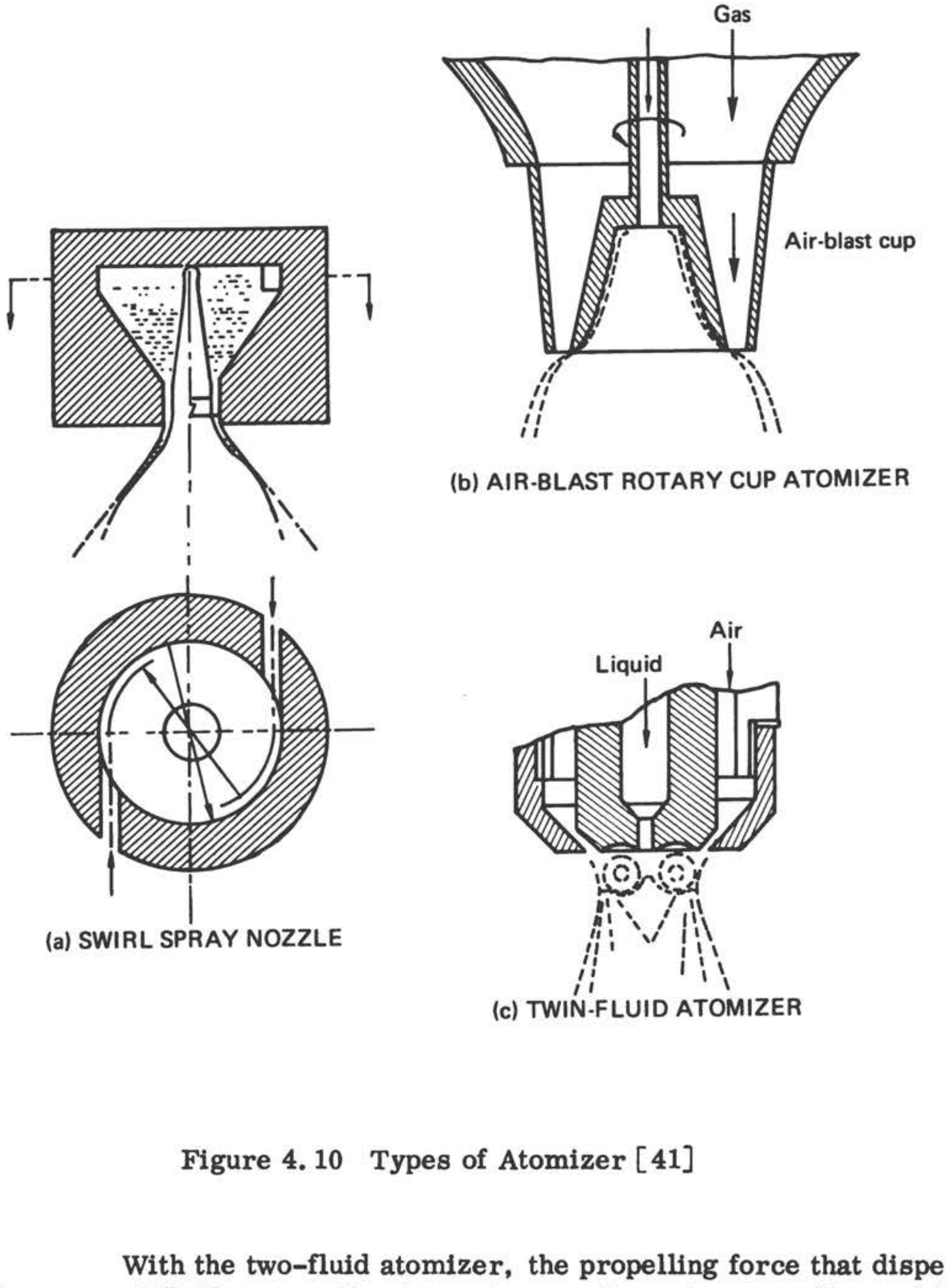


Figure 4. 9 Idealized Process of Drop Formation From a Liquid Sheet [41]

When the pressure jet is used for oil combustion, the oil is fed to the atomizer at a pressure of generally about 100 psi. The atomizer consists of a body containing a small hole of a few hundredths of an inch in diameter at the tip of the nozzle (see reference 33 for atomizer designs). Behind the hole of the nozzle is a small chamber (see Figure 4. 10a). The fuel oil is fed into this chamber through grooves so that the oil in the chamber rotates. As it emerges from the hole in the tip of the nozzle, the oil jet is spun by rotation into a conical sheet. As the oil sheet travels away from the nozzle, it breaks up quickly into a fine spray. Most commonly this produces what is known as a hollow cone; by appropriate design, however, the volume inside the cone can also be filled with oil drops, although research has established that this is often a less desirable configuration.



(a) SWIRL SPRAY NOZZLE

(b) AIR-BLAST ROTARY CUP ATOMIZER

(c) TWIN-FLUID ATOMIZER

Figure 4.10 Types of Atomizer [41]

With the two-fluid atomizer, the propelling force that disperses the oil is a second fluid, generally air or steam. Steam is generally used if the oil has high viscosity. As illustrated schematically in Figure 4.11, the atomizing can be arranged to take place either inside or outside the atomizer. With two-fluid atomizers, the clearance holes for supply of the fuel oil are larger. Such nozzles are better able to carry contaminated oil, particularly when it contains particles (see reference 42 for additional atomizer designs). The designs provide for the spray of oil driven by the air or steam to be dispersed in a cone, again usually hollow, but with these atomizers the space inside the cone is more likely to contain a certain number of droplets.

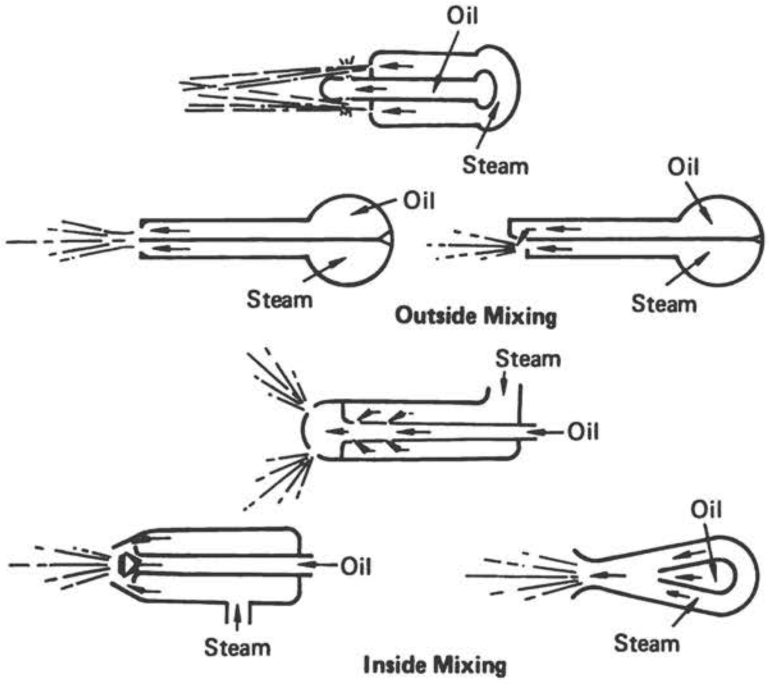
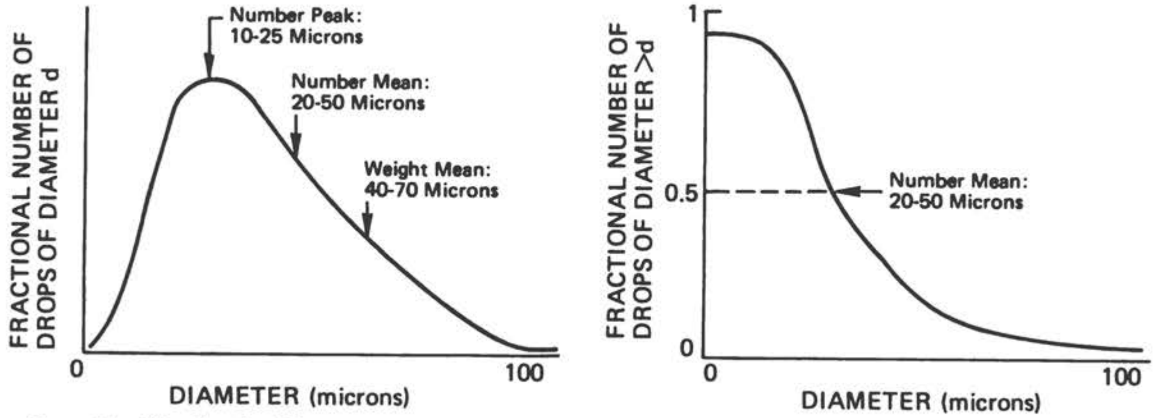


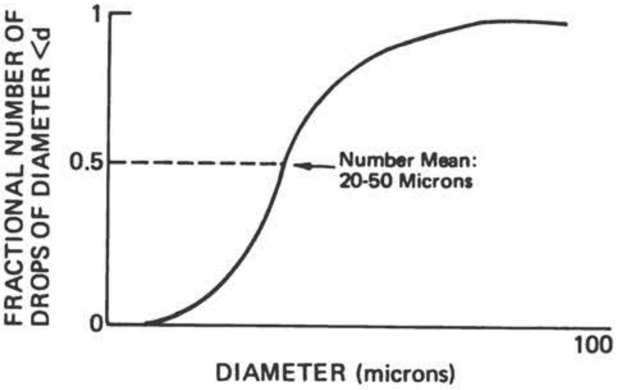
Figure 4.11 Principles of Atomization Employed in Steam and Air Atomizing Nozzles [13]

The drops from such atomizers vary in size depending on a variety of factors such as the velocity of the oil, the pressure of atomization, the pressure or relative volume flow rate of the atomizing fluid, the size of the orifices, the angles and directions of the channels used to create the rotation of the oil in the atomizer, the flow rate, the degree of preheat, the liquid density, surface tension, and viscosity. Nevertheless, as a general rule, the bulk of the drops lie between one micron and one-hundred microns. The drop size distribution curve tends to be a skew-shape or a log-normal distribution (see Figure 4.12). The number peak tends to occur at the smaller end of the scale, typically in the range from 10 to 25 microns, with the number mean in the range from 20 to 50 microns, and weight mean in the range from 40 to 70 microns. When oil is fired, one objective is for only one or two percent of the drops to exceed 100 microns, but when atomization is bad, it can be as high as 5 to 10 percent. Since the combustion chamber must accommodate the largest drops, or all but the very largest drops, the question of the upper size limit can be quite critical in determining the chamber size.



a. Drop Size Distribution Wave

b. Oversize Distribution Curve



c. Undersize Distribution Curve

Figure 4.12 Characteristics of Drop Size, Oversize and Undersize Curves from Oil Sprays

To describe the curves shown in Figure 4.12, many equations have been proposed. The Rosin-Rammler (Equation 4.21), though empirical, still seems to be the most successful. This in fact describes the oversize curve (Figure 4.12b) on a weight basis. If a characteristic size, $\bar{d}$ is defined, the residue weight, r, of all drops with diameter greater than d is described approximately by

$$r = \exp\left(-d/\bar{d}\right)^{n} \tag{4.21}$$

where n is an empirical constant to be determined by experiment. A small value of n (near unity) corresponds to a wide distribution of sizes. A large value of n corresponds to a narrow distribution about the characteristic diameter, $\bar{d}$. If $d = \bar{d}$, $r = 1/e = 0.37$.

The different atomizer types generate different mean diameters and size distributions for a given fluid. The rotary cup tends to produce the most uniform size, with diameters falling inversely with increase in rotation rate. An expression given by Fraser [43], quoted by Thring [14], is

$$d_m = (360,000/S)\ (\eta/D\rho_f)^{1/2} \tag{4.22}$$

where d_m is the mean drop size; S is the cup turns per minute (tpm), η is surface tension; D is the cup diameter; and ρ_f is the fluid density.

Both the pressure jet and the two-fluid atomizer generate a much wide range of drop sizes, with better atomization for the same fuel flow rate with two fluids. With the pressure jet, the mean drop diameter is approximately inversely proportional to the square root of the pressure, Consequently, if pressure is used to vary the flow rate, atomization suffers on turn-down. To avoid this, various spill-control burners have been designed so that pressure can be maintained but delivery is controlled by spill control to a return line.

With the two fluid atomizers, Nukiyama and Tanasawa [44] proposed an empirical equation that, for water atomized by air, was reduced by Strauss [45] to

$$\text{dia} - (16,050/u) + 1.41L^{1.5} \tag{4.23}$$

where u is the relative velocity between water and air, and L is the water flow rate.

The essential mechanism of vaporization, whether with water or a combustible fuel, has already been outlined in the paragraphs above, and nothing further needs to be added here.

If the atomized fluid (water or oil) contains particulates, these can influence both atomization and vaporization. The particulates affect atomization by providing a fluid of effectively increased viscosity. Atomization is generally less good if particles are present. The effect on vaporization is normally expected to be negligible if heat is transferred to the drop by conduction through a boundary layer. However, since there is a substantial radiation flux through any flame, especially through an oil flame, and most significantly through a flame containing solid particles, many oil drops or other droplets that are essentially transparent to radiation can become translucent or opaque if they contain solid particles. In such instances, if the radiation flux is sufficiently intense, the particles may heat up more or less independently of the surrounding drop, and, with their temperatures rising rapidly above the boiling point of the fluid, may locally superheat the fluid, which then will tend to boil locally with sufficient violence to disrupt or explode the drop. The presence of particles thus may accelerate the atomization, as well as produce finer atomization. Such results are generally advantageous.

4.3.4 Combustion Aerodynamics

Combustion aerodynamics [6,46] refers to the whole flow and mixing pattern inside the incinerator and is a particularly complex problem. It is important both for systems in which the waste and fuel are fired with atomization straight into the incinerator, and for incinerators where part or all of the waste is initially fed onto a grate. In the latter case, combustion aerodynamics refers primarily to the mixing behavior above the bed. Flow of air and combustion products up through a solid bed is still an important problem, however. Other important aspects of combustion aerodynamics include the effects of fluctuations that can be related to turbulence or to standing waves (organ pipe oscillations) and oscillatory combustion (which relates to noise).

In any combustion chamber, it can be said that two extreme flow patterns exist. All real systems have flow patterns which lie between the two extremes, but tend more to one extreme or the other. The first of the two extremes is generally known as piston or plug flow. In this flow pattern (see Figure 4.13), all fuel and air supplies enter at one end of the combustion chamber and travel to the other end in an essentially piston flow manner, so that all molecules entering at one time also leave simultaneously at a certain fixed time later. All molecules, therefore, have the same residence time in the chamber: the transit time required to travel from one end to the other. The other extreme mixing pattern is known as the perfectly mixed or perfectly stirred reactor pattern. In this system, any group of molecules entering the chamber, either fuel or air, premixed or not premixed, and entering at any point on the boundary of the combustion chamber, is assumed to disperse instantaneously and uniformly throughout the reactor. By assumption, therefore, some few molecules of those entering will, theoretically, be instantly transported to the exit of the combustion chamber. Some molecules will thus theoretically start to leave the combustion chamber immediately after they have entered in this theoretical limit of perfect stirring.

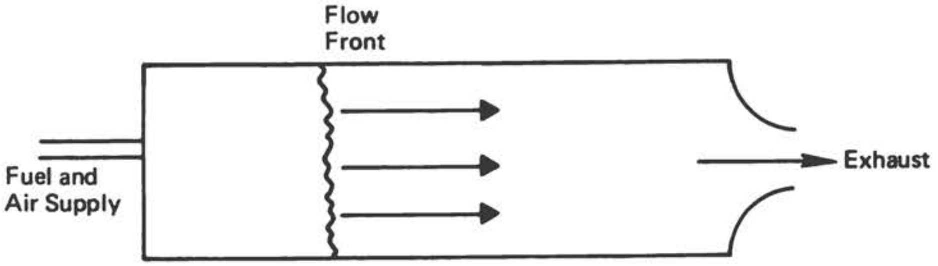


Figure 4.13 Schematic of Plug or Piston Flow in a Combustion Chamber. (All material entering at any time, t_0, will be found on a common plane downstream at some time—$t_0 + t$.)

It is obvious, of course, that such perfect mixing is a theoretical and not a practical limit, but some real systems have been built, nevertheless, that have approximated remarkably well to this theoretical limit. The molecules entering a perfectly stirred reactor, therefore, will never leave together as they do in the plug flow reactor, but will leave in succession with (theoretically) the concentration in the chamber of these molecules that entered together decaying exponentially. This process is described by a residence time distribution function [47].

Real systems have mixing characteristics that combine those of the stirred reactor and the plug flow reactor, with generally a bias towards one extreme or the other. In particular, many systems tend to show a physical division into two mixing regions. In the first region, the stirred reactor mixing model is the best approximation; and in the second downstream region, the plug flow reactor is the best model. A particular characteristic that tends to separate out a stirred region from a plug flow (or once through) region is the ability of a stirred region to transport material back upstream against the general direction of flow. The existence of such a mixing region can always be demonstrated experimentally by injecting a tracer such as helium at some downstream point and detecting the tracer in significant quantities at points upstream [48]. Such backmix behavior has both advantages and disadvantages for combustion. This will be clearer if we first consider some extended mixing patterns shown by standard burner types.

The simplest of all burners is a single pipe injecting premixed fuel and air into a combustion chamber as illustrated in Figure 4.14. Any jet emerging into surrounding, but stationary, fluid tends to accelerate the surrounding fluid while at the same time the margins of the jet itself are retarded by viscosity. The net result is that the jet spreads out, as indicated in Figure 4.14. This can be detected in various ways. In part, the result of the interaction of the jet on the surrounding fluid is that part of the surrounding fluid is incorporated into the jet. This enables the jet to expand as illustrated. The surrounding fluid which is entrained must be drawn from somewhere else; in an unconfined or free jet, the jet action is thus felt a considerable radial distance away from the jet. With the confined jet, as illustrated in Figure 4.13, the entrainment of fluid immediately adjacent to the jet tends to lower the pressure further out, as in the corners of the combustion chamber. The result of this tendency to create a pressure difference between the corners of the combustion and points further downstream but close to the wall is that the entrained fluid is ultimately drawn from downstream where combustion is substantially advanced and sometimes even completed. This back-flow (which is illustrated in the diagram by the arrows) is important in practice because it supplies hot combustion products to the root of the incoming (but cold) fresh fuel and air mixture. This heat supplies from 60 to 95 percent of the heat required for ignition. As the jet expands, its boundaries reach almost to the wall and tend to curve downstream and parallel to the wall. However, if there are sufficient particles in the jet, those particles will sometimes impact on the wall and, if sticky, can start to form deposits there. The region marked A in Figure 4.14 is, therefore, the backmix region; the region marked B is sometimes found to have a low level of backmix component, but generally speaking is well approximated as plug flow with no backmix.

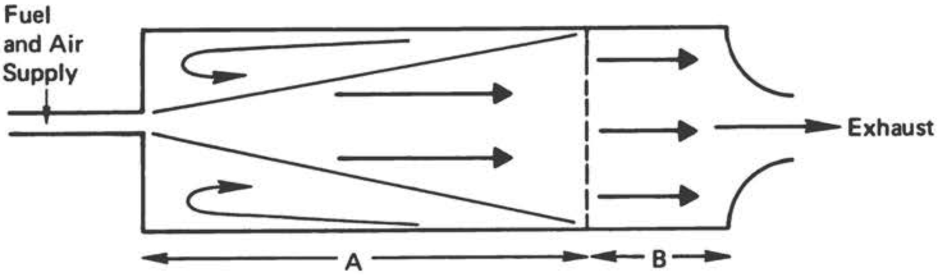


Figure 4.14 Schematic of a Single, Unswirled Jet. This diagram illustrates the creation of a backmix flow region (A) due to jet entrainment with a non-backmix flow region (B) generally approximating to plug flow downstream from region A.

If the incoming jet passes through vanes just before it enters the combustion chamber, so that the fluid in the pipe rotates, this produces what is known as a swirled jet. A swirled jet causes certain effects. The first is that the angle of the jet opens out from between 10 to 15 degrees for the unswirled jet to something that is determined by the degree of swirl—in practice, the angle is generally between 30 and 60 degrees. In extreme cases, the jet may be overswirled, with the result that the stream will attach itself to the wall and thus form a wall jet. A well-behaved swirled jet produces a small drop in pressure due to the rotation of the fluid inside the cone on the axis of the jet. This causes an upstream (backmix) flow along the axis in the opposite direction to the jet in addition to the smaller but still significant backmix flow outside the jet, in the corner of the combustion chamber, as in Figure 4.14. This additional inside backmix effect is illustrated in Figure 4.15. As before, downstream of the nominal point of impaction of the jet cone on the wall, the flow reverts to plug flow. The backmix region, again marked A, tends in this case to be somewhat shorter and more compact than with the unswirled jet. In general, this mixing volume tends to contract as swirl is increased, but with the intensity of mixing generally reaching a peak and then declining again as swirl is increased still further. The additional backmix flow inside the cone tends to produce even more uniform temperatures and concentrations than in the case of the single unswirled jet (Figure 4.14).

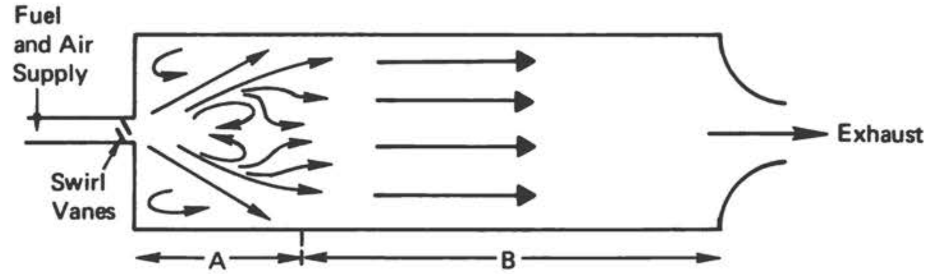


Figure 4.15 Schematic of a Single Swirled Jet. This figure illustrates the opening up of a jet angle and formation of internal backmix flow on geometric axis of jet. Reversion to non-backmix flow occurs in a shorter distance than with unswirled jet.

There are other means of producing a well-mixed or uniformly mixed region. One simple method is to insert a baffle inside a pipe, as illustrated in Figure 4.16. The arrows indicate the type of motion produced by such a baffle. Because of this mixing pattern, a baffle can be used to stabilize a flame in a fairly high velocity flow. The baffle need not be a single plate or disc; it can have a variety of shapes. One commonly used in the tail pipe of jet engines for additional boost under certain circumstances is a V-shape, known as a V gutter (Figure 4.17). Another means of achieving a locally mixed zone is a high velocity jet across the direction of the stream in a pipe. The jet tends to produce the same effect as a baffle on its downstream side. An appropriately designed set of jets can create an aerodynamic flame holder, due to this baffle effect of the jet streams across the direction of flow, in the middle of the pipe. Somewhat similar effects can also be obtained by a sudden enlargement of the cross section of a combustion chamber or sudden changes of direction. These can often produce unexpected mixing or lack of mixing behavior, and affect the locations for deposition of particles or formation of slag. Figure 4.17 illustrates several of these concepts. All these devices create what was referred to above as the "flame ball."

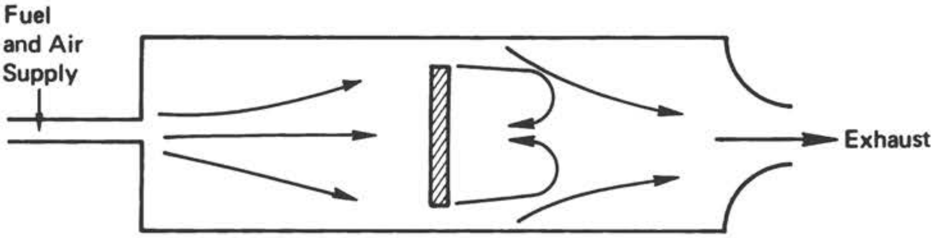
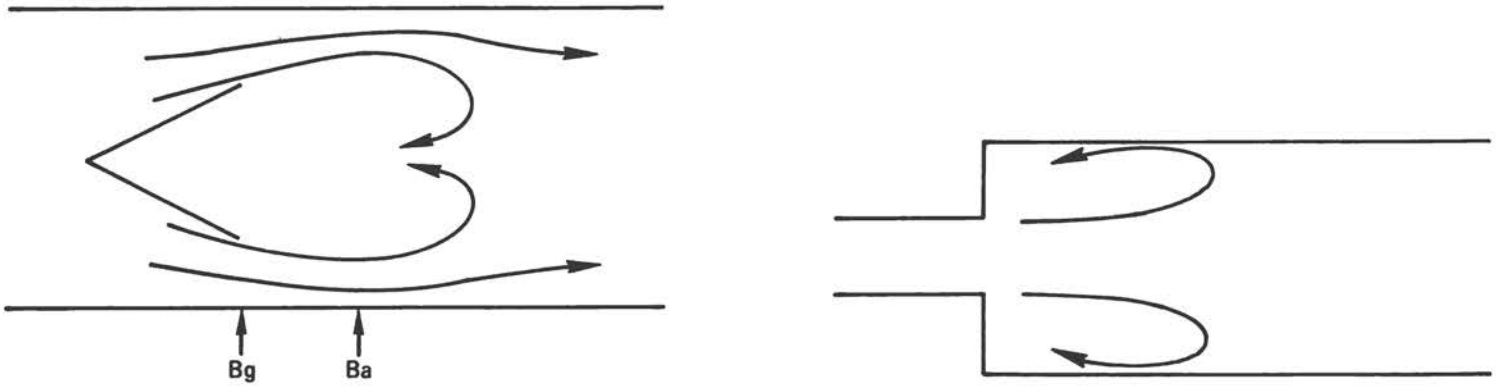


Figure 4.16 Use of a Baffle to Create a Downstream Backmix Flow. In flame stabilization this can perform the same function as with a swirled jet.



(a) Bluff Body Stabilizer (V-Gutter)

(b) Tunnel Burner

(c) Aerodynamic Bluff Body

(d) Vortex Stabilizer

Figure 4.17 Methods of Creating Backmix Flow for Flame Stabilization

The value of backmix flow centers on its actions in mixing diverse streams, particularly if they are fuel and air streams initially supplied separately, or if they are flame and waste streams also supplied separately, or fresh pre-mixed fuel and air that has to be mixed with hot combustion products already in the chamber. The mere creation of a backmix flow, however, does not necessarily solve all the problems. This can certainly produce substantial mixing but, on the micrscopic scale, may lead to formation of striations where the different streams flow adjacent to each other (like a moving pack of cards), with relatively little cross mixing between the adjacent streams.

Another aspect of striation is illustrated in Figure 4.18. This figure shows two streams of different fluids, A and B, initially in separate concentric pipes, joining each other downstream from the ends of the two pipes. An expanding mixing region exist between them. However, as the mixing region expands its boundaries, it may turn downstream when it gets close to the walls, leaving a narrow stream of unmixed A or B close to the walls. These represent striation streams. They are significant in being potential causes of bypass in which unburned fuel, or unincinerated waste, is able to pass through a combustion chamber and escape unburned. To reduce or eliminate these problems, the generation of turbulence is often advised. Such turbulence is generally advantageous, but only up to a point. If turbulence becomes too coarse, so that large vortices are formed, the vortices themselves may have lifetimes that are significant compared with the residence time of the total fluid in the combustion chamber. Such turbulent vortices may then behave almost independently of the rest of the fluid—very much like independent particles—and may be able to pass right through the combustion chamber on their own. If their residence time is fairly short (which is possible for some of them because of the distribution of residence times), then such short residence time vortices can carry unburned fuel or waste out of the combustion chamber. This argument has been used recently to explain the pattern of emissions from a double vortex burner with a high mixing intensity [49].

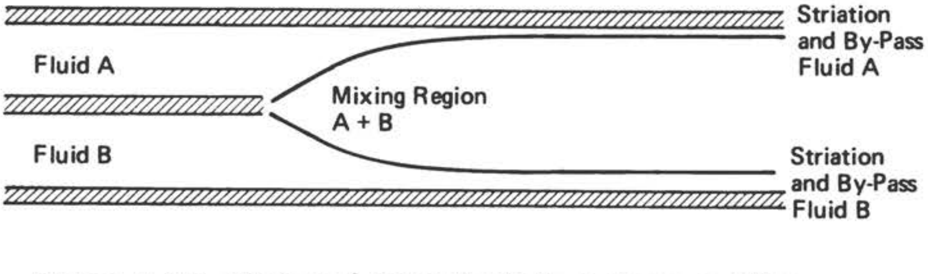


Figure 4.18 Mixing of Two Fluids in a Common Pipe. Incomplete mixing at the boundary due to striation can lead to bypass of partly burned products.

A final point to consider is the effect of particle loading on the flow streams. If sufficient concentrations of particles or drops are present in the streams, the behavior of the flow can sometimes be profoundly modified. High concentrations cause the gas stream carrying the particles to behave as a viscous stream in an inviscid medium. In such a case, the stream may travel without expansion, drilling through the surrounding medium as if it were not there. In particular, when such a stream approaches a wall, where a normal fluid stream would be diverted, a particle-laden stream may tend to precipitate the particles on the wall. This is a particularly important possibility in the incineration of waste streams carrying solid particles.

4.3.5 Heat Transfer

Heat in any system is transferred by one or more of only three possible mechanisms: conduction, convection, and radiation [7, 8, 9, 50, 51]. In combustion chambers, heat transfer is important in the following respects:

1. In the exchange of heat between different parts of the flame and combustion gases. This exchange is accomplished both by radiation and by the convective streams, particularly in the backflow or backmix regions.

2. In the heat-up of incoming cold materials—fuel, air, or injected wastes. This heat-up is partly by radiation but, as indicated in the previous section, also partly by the entrainment of hot combustion products by incoming jets which generally provide a signficant fraction of the heat required. Again, convection streams are involved.

3. In the heat-up of particles, particularly those in waste streams. These would be particles in streams that first entrain surrounding fluid. A surrounding fluid which consists of hot combustion products, in effect, suddenly surrounds the particles with hot gases. The mechanism of final heat-up of the particles is then conduction across a heat transfer boundary layer around the particle.

4. In the heat transfer from the flame gases to the walls. The transfer is jointly radiation and convection, with the final step of convection being provided by conduction across an aerodynamic boundary layer. In most industrial combustion chambers radiation generally supplies most heat transferred to the walls [7]. In small jet engines, on the other hand, the radiative contribution may be less significant, except where the combustion chamber is substantially pressurized, and the radiative contribution rises again. In wastes incineration, special cases can occur in which liquid streams that have not fully vaporized impact on the wall, generally contributing to thermal shock by local overcooling, rather than local overheating. Local overheating can, of course, occur if an independently stabilized flame is allowed to impact on the wall.

Overall, however, radiation is the most significant mode of heat transfer in such systems as incinerators. Radiation can be derived from particulates, vapors, or gases. These different sources tend to produce radiation of certain different characteristics. Solids tend to generate continuous radiation, that is to say, radiation with emissions continuously across the spectrum. Gases, on the other hand, tend to provide banded radiation, that is to say, radiation missing certain ranges of frequencies. The most significant sources of banded radiation will almost invariably be carbon dioxide and water vapor (and possibly soot precursors). These have certain intense bands in the infrared capable of transferring substantial amounts of heat. If smoke is formed, however, these components will also provide additional radiation. The best evidence indicates that the liquid particulate smokes generally radiate in bands while the smokes containing solid carbon particles fill out the missing frequencies with increasing continuum radiation across the spectrum.

The intensity of the radiation depends jointly on the temperature of the components, their concentration, and the path length of the line of sight through the flame. If the line of sight is fairly short, emissivities of the flame will be low; if long, emissivities can rise close to unity, whatever the intervening medium. In general, however, it is possible to say that gases provide nonluminous radiation, with emissivities in the range of 0.1 to 0.2 or 0.3. If smoke is formed, emissivities may rise to the 0.5 to 0.6 range. With particles, emissivities increase up to unity. Therefore, a slight change in waste composition that may start to generate smoke, or that introduces significant quantities of particulates, may also significantly change the radiation characteristics of the flame, and produce local overheating of the liner where previously the liner had been able to sustain the thermal stress. The effect of changes has been demonstrated in recent experiments with oil/water emulsions [52] in which the addition of water reduced the flame emissivity; but the addition of traces of coal, or operation in a smoky region, restored or even increased the emissivity.

4.3.6 Combined Reaction, Flow, and Heat Transfer

The combination of exothermic reaction, flow, and heat transfer constitutes the flame in any incinerator.

The first problem to be considered, as has been indicated, is that of flame stabilization. Briefly, a region must exist in which there is steady-state combustion and flow at sufficient temperature for the reaction to be maintained at the level required to balance heat losses. In general, the velocity of injection of fuel or fuel/air mixtures into combustion chambers substantially exceeds the flame speed. A flame cannot stabilize under such conditions. If an ignition source is initially provided, however, a flame can be stabilized because the added heat from the ignition source in effect increases the flame speed to the point where the flame will stabilize, if the flame is stabilized by velocity balancing (see Figure 4.14). Once the flame has stabilized, the ignition source can be removed. Stabilization generally requires walls sufficiently heated so that the backmix flows do not lose too much heat as they flow back, and are thus able to maintain the system in a self-stabilizing backmix flow. In a more uniformly mixed region, such as that illustrated in Figure 4.15, one can regard stabilization as being determined by slightly different requirements. This configuration can be described as having a flame ball. The requirements for stabilization are that the flame ball lie between certain extinction limits, and that the in-flowing and out-flowing streams provide a momentum balance on the flame ball so that it does not move away. This condition is illustrated with more detail in Figure 4.19.

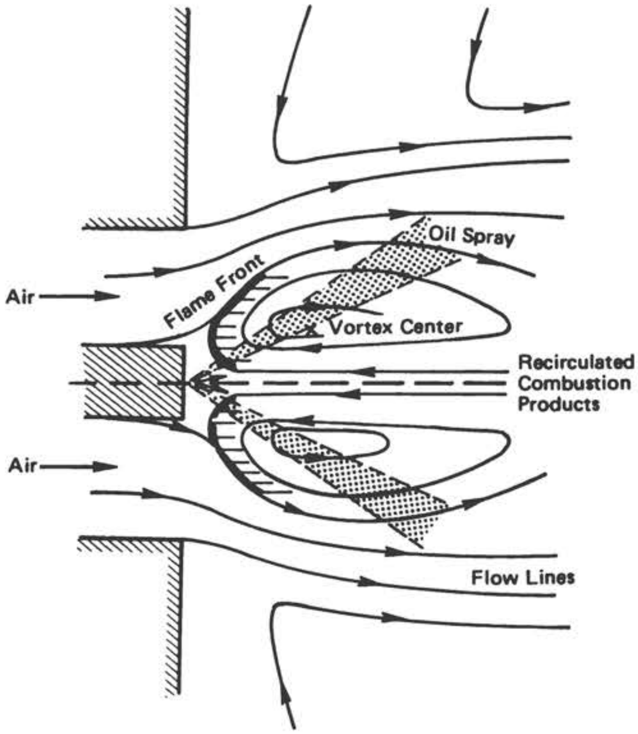


Figure 4.19 Stabilization of Pressure Jet Oil Flames by Internal Recirculation Zone in Swirling Annular Jet [6]

As discussed earlier, a second problem is that the temperatures inside the flame ball must lie between 1200°C and 1980°C. Consequently, there are significant temperature gradients between the flame ball and the shell of the combustion chamber.

A third problem is that of mixing inhomogeneity. This means that the mixing of fuel and air in the combustion chamber (if not already premixed), or mixing of the fuel and air with combustion products already in the chamber, is not uniform. As a result, some parts of the combustion chamber contain gases that are fuel rich, or air rich, or too cold, or contain components that can interfere with the reaction. If local regions are fuel rich, or waste rich, this can lead to pyrolysis of the fuel or wastes, cracking of the pyrolysis products, condensation, smoke formation, production of odorous hydrocarbons, and other unwanted effluents. Unless these varied components then move into oxygen-rich regions, and at sufficient temperature for sufficiently rapid reaction, they may enter bypass routes and escape. In particular, the production of odor tends to be a remarkably effective index of inadequate mixing. Indeed, the human nose can detect odor at concentrations far lower than can be detected by any analytical instruments.

The problem of emissions is further complicated by the point already raised in Section 4.3.4 regarding residence time distributions. If this time only refers to molecules, the problem is marginal or nonexistent. However, where there is any degree of turbulence—which is generally the case—then turbulence vortices with a range of lifetime distributions and a frequency distribution of residence times can cause a number of different problems. In the first place, vortices of long lifetime but short residence time can pass rapidly through the combustion chamber. They emerge either unburned, thus providing a source of unburned hydrocarbons, or only part-burned, thus providing a means of smoke escape. If large turbulence vortices have long lifetimes and also long residence times then, particularly if they are close to stoichiometric, they have time to ignite and burn. Since they are almost independent entities inside the combustion chamber, they may tend to burn to nearly adiabatic flame temperatures. This produces what are frequently referred to as local "hot spots" or exothermic centers in the combustion chamber. Such exothermic centers are suspected sources of high NO_x emissions. Rapid combustion of large vortices is also a suspected source of combustion noise. Finally, the large vortices after burning can provide locally increased heat transfer, thus causing local overheating where otherwise unexpected.

4.3.7 Afterburners

Of all devices bearing directly on waste incineration, afterburners are the most relevant to shipboard operation. These devices are designed to incinerate fume and similar waste streams. In fume incineration, much attention has been given, in particular, to the problem of mixing [21]. If the fume is gaseous and adequately dilute, it can be carried in the combustion air. This generally provides the best mixing opportunities. However, if the concentration is high enough to interfere with combustion, or corrosive enough to affect the burner, the waste has to be injected downstream of the flame. Allied to the mixing problem there is also the problem of flame stabilization.

Figures 4.20 and 4.21 illustrate the first approach, with fume in the combustion air. Mixing at, or just downstream of, the flame is not always very effective. Figure 4.22 illustrates the effect of an annular baffle downstream of a ring burner. If such distances cannot be accommodated in the design, then recourse must be had to additional mixing devices, generally baffles. A variety of procedures for altering the flow to produce improved incineration is described in reference 21. This reference also describes procedures for introducing the material to be incinerated at different points. Baffling is also described.

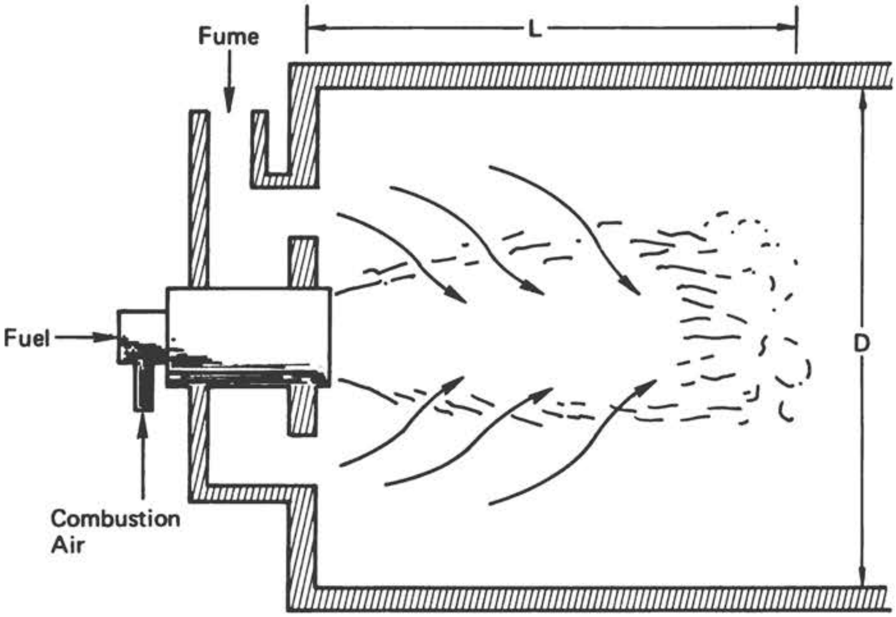


Figure 4.20 Discrete-Source Burner [21].

4.3.8 Special Problems

Two problems that require special recognition are:

1. Influence of sulfur on dew point. Combustion of sulfur forms SO_2. Part of this is converted to SO_3. This conversion elevates the dew point or the temperature at which condensation of the stack gas occurs.

Figure 4.23 illustrates the equilibrium concentration of SO_3 with SO_2 as a function of temperature at three oxygen levels. It shows, as might be expected, that the ratio drops with rising temperature and falling oxygen concentration.

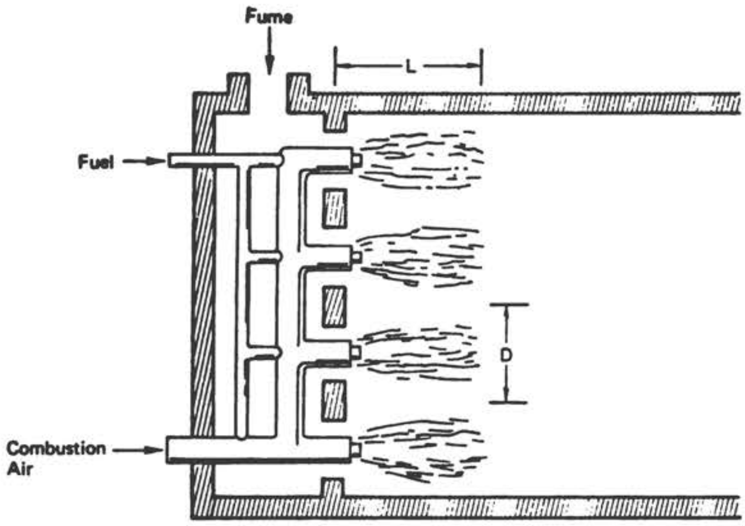


Figure 4.21 Distributed-Source Burner [21]

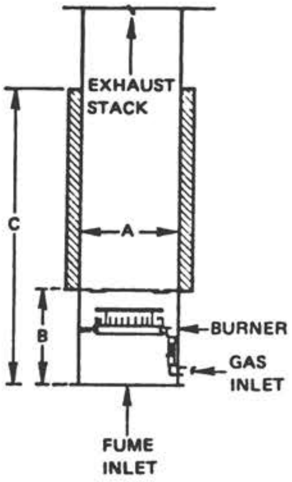
Figure 4.24 illustrates the dew point elevation with SO_3 concentration. Above about 35 ppm the elevation becomes effectively constant at about 150°C.

The significance of these figures relates to cooling of the stack gases and the potential for dew point condensation and corrosion if the stack gases are overcooled.

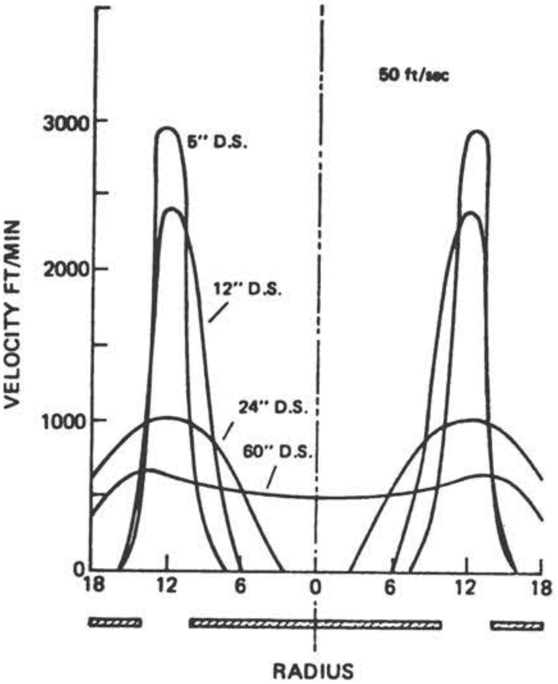
2. Odor burn-up requirements. Odor is generally attributed to complex hydrocarbons or other organics (hydrogen sulfide—H_2S—is an exception), possibly, but not invariably, with nitrogen or sulfur in the molecule. The compounds are stable but may be formed as intermediates in the combustion process. They may be destroyed by completing the interrupted oxidation process. The temperature and requirements vary from one compound to another, but a blanket assumption (lacking any better information) is that destruction requires a minimum of 0.5 second at about 800°C.

A problem of major significance is the allowable latitude on these limits. An assessment is possible if it is assumed that destruction occurs by chemical oxidation, and if oxygen is in large excess (as it generally is for this reaction), the oxidation can be treated as a pseudo-first order reaction with respect to the odor concentration. It can also be assumed that odor can only be detected above some limit concentration C_L. If some initial concentration C_o is reduced to C_L in a "standard" time t_o at a "standard" temperature T_o, then at any other temperature T, the time (t) required to reduce the concentration to the limit C_L is easily shown to be given by:

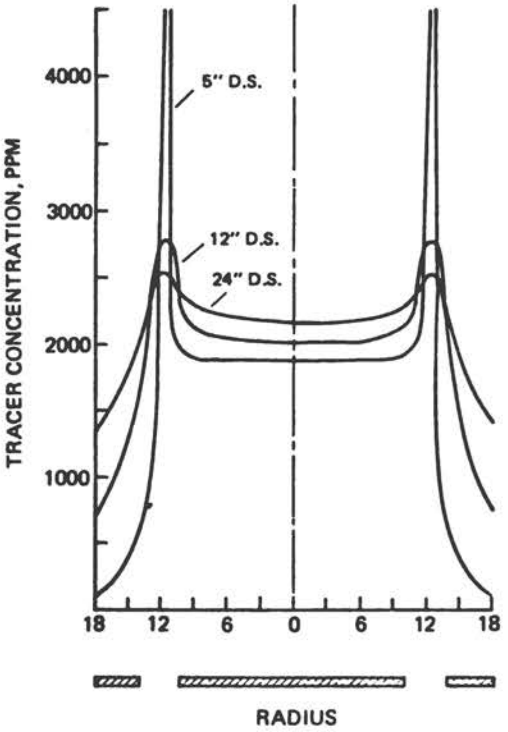
$$t = t_o \exp\{(E/R)([1/T_o] - [1/T])\} \tag{4.24}$$



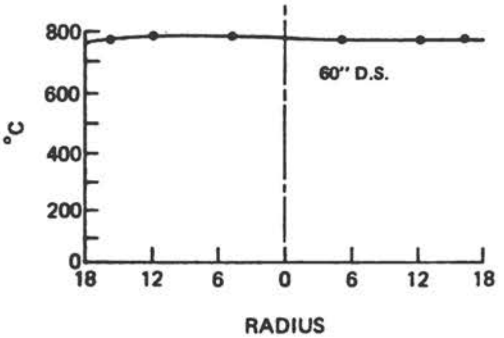
A. Burner Configuration



B. Velocity Development Downstream of Baffle



C. Tracer Concentrations Indicating Mixed Performance



D. Temperature Uniformity

Figure 4.22 Performance of Afterburner with Ring Burner and Annular Baffle [21].

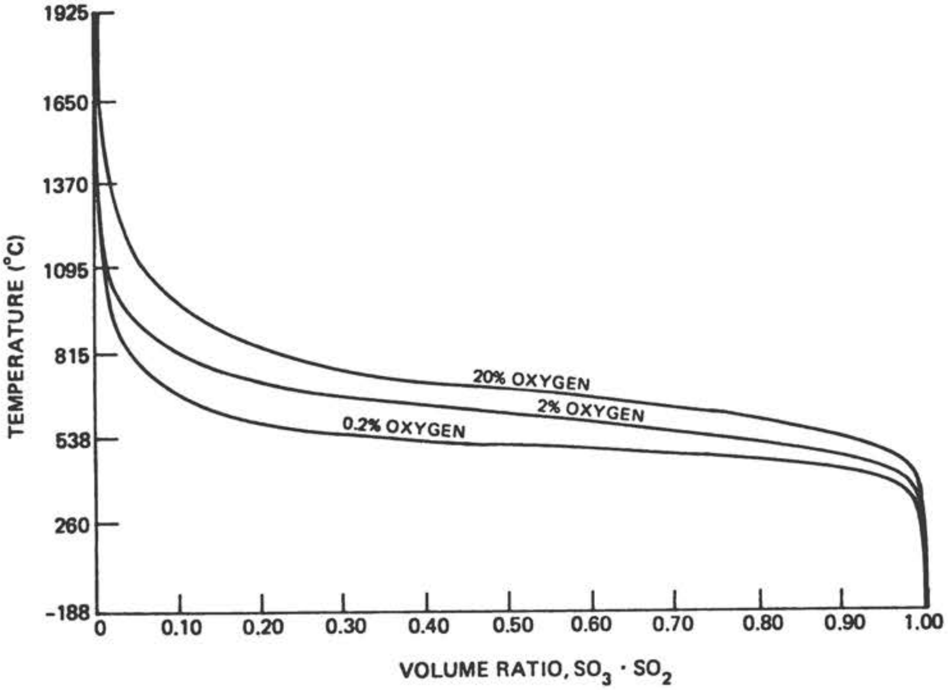


Figure 4. 23 Equilibrium Concentrations of SO_3 and SO_2 at Various Oxygen Concentrations. (Note: As per the reaction $SO_2(g) + 1/2\ O_2(g) = SO_3(g)$.) [16]

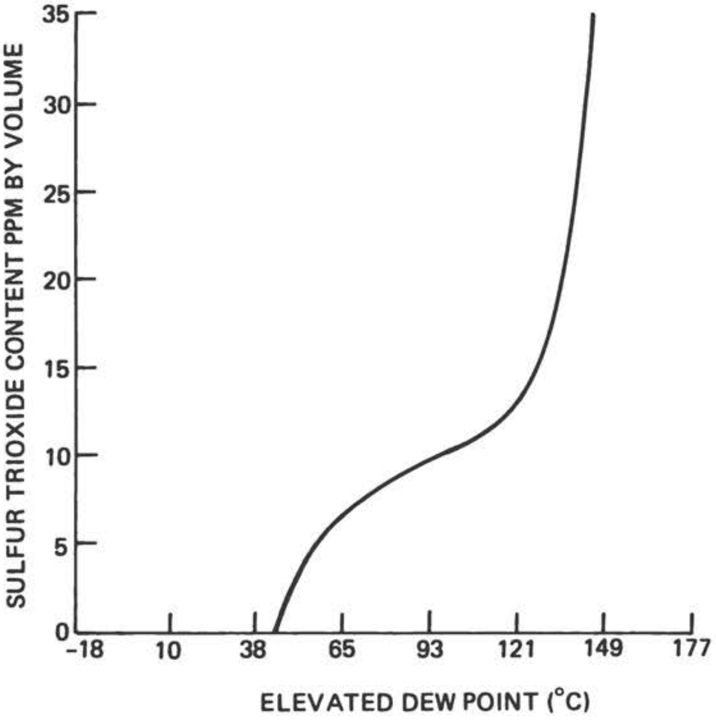


Figure 4. 24 Dew Point Elevation as a Function of Sulfur Trioxide Concentration [16].

Taking t_o = 0.5 second and T_o = 800°C, equation 4.24 has been evaluated for four different activation energies (5, 10, 25, and 50 kcal). The results are illustrated in Figure 4.25. This clearly shows the rapid drop in time requirements with rise in temperature for high activation energies, which is advantageous; but the rise in turn for falling temperatures is equally rapid, which is disadvantageous.

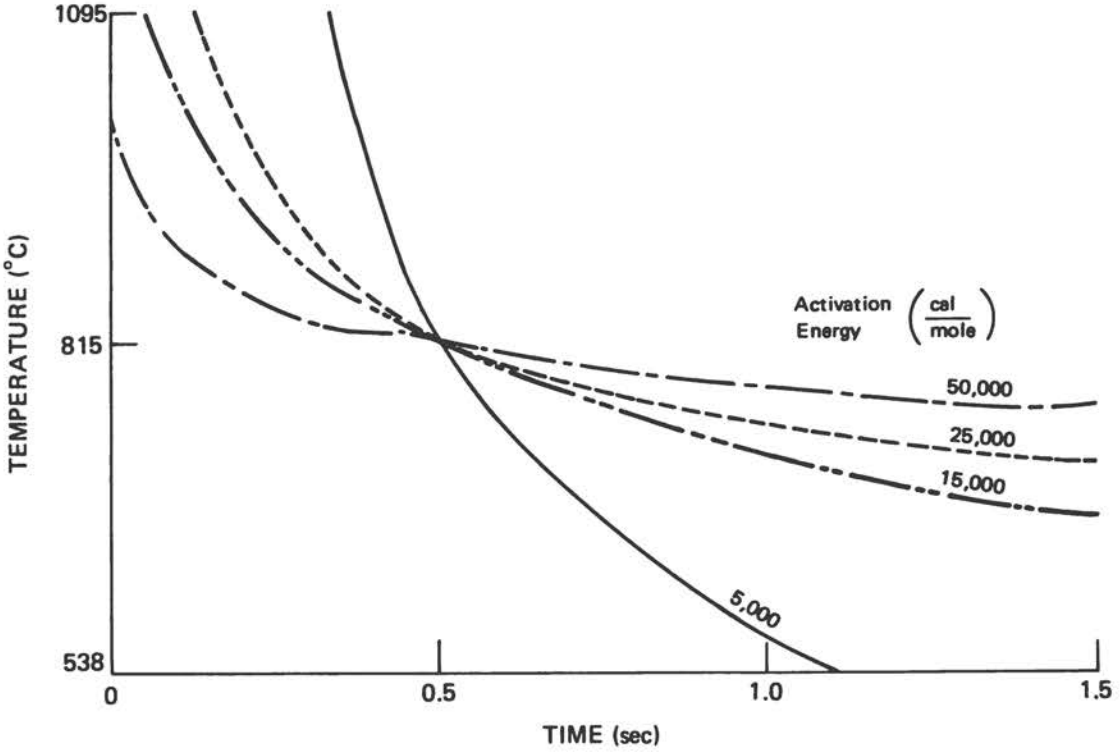


Figure 4.25 Estimated Variation of Odor Destruction Time With Temperature (°C) for Different Assumed Activation Energy of Reaction.

REFERENCES

1. Fristrom, R.M. & Westenberg, A.A., Flame Structure, McGraw-Hill, (1965).
2. Gaydon, A.G. & Wolfhard, H.G., Flames, Chapman and Hall, (1960).
3. Lewis, B. & von Elbe, G., Combustion, Flames and Explosions of Gases, Academic Press, (1961).
4. Strehlow, R.A., Fundamentals of Combustion, International Textbook Co., (1968).
5. Williams, F.A., Combustion Theory, Addison-Wesley Publishing Co., (1965).
6. Beer, J.M. & Chigier, N.A., Combustion Aerodynamics, Applied Sciences Publishers Ltd., (1972).
7. Hottel, H.C. & Sarofim, A.F., Radiative Transfer, McGraw-Hill, (1967).
8. Sparrow, E.M. & Cess, R.D., Radiation Heat Transfer, Books/Cole Publishing Co., (1966).
9. Love, T.J., Radiative Heat Transfer, Charles Merrill Publishing Co., (1968).
10. Brame, J.S.S. & King, J.G. Fuel, Edward Arnold, (1955).
11. Griswold, J., Fuels, Combustion and Furnaces, McGraw-Hill, (1946).
12. Trinks, W. and Mawhinney, M., Industrial Furnaces, (Vols. I & II), John Wiley, (1955, 1961, respectively).

13. Smith, M. L. & Stinson, K. W., Fuels and Combustion, McGraw-Hill, (1952).

14. Thring, M. W., The Science of Flames and Furnaces, John Wiley, (1962).

15. Hesketh, H. E., Understanding and Controlling Air Pollution, Ann Arbor Science Publishers, (1972).

16. Air Pollution Engineering Manual, (2nd Edition), Environmental Protection Agency Publication No. AP40, (1973).

17. Cheremisinoff, P. N. & Young, R. A., Pollution Engineering Practice Handbook, Ann Arbor Science Publishers, (1975).

18. Perkins, H. C., Air Pollution, McGraw-Hill, (1975).

19. Starkman, E. S., Combustion Generated Air Pollution, Plenum Press, (1971).

20. Air Pollution, Vol. 2, B. G. Liptak (Ed.), Environmental Engineers Handbook, Sec. 5.35, Chilton Book Co., Radnor, PA, (1974).

21. Rolke, R. W., Hawthorne, R. D., Garbett, C. R., Slater, E. R., Phillips, T. T., & Towell, G. D., Afterburner Systems Study, Shell Development Co. Report No. S-14121, Emeryville, CA, (1971).

22. Principles and Practices of Incineration, R. D. Corey (Ed.), Wiley, New York, (1969).

23. Niessen, W. R., Systems Study of Air Pollution from Municipal Incinerators, A. D. Little, Cambridge, Mass., (1970).

24. Combustion Fundamentals for Waste Incineration, A. S. M. E., New York, (1974).

25. A. S. M. E. Biennial National Incinerator Conferences Nos. 1 to 7, (1964, 1966, 1968, 1970, 1972, 1974, 1976), Am. Soc. Mech. Engrs., N. Y.

26. Rosin, P. O. & Friedlander, G., "Technical Data on Fuel, Proceedings of British World Power Conference, 6th Edition, H. M. Spiers Ed., pp. 98-104. British World Power Conference Committee, (1961).

27. Essenhigh, R. H., "An Introduction to Stirred Reactor Theory Applied to Design of Combustion Chambers", Combustion Technology, Palmer and Beer, Eds., Ch. XIV, Academic Press, (1974).

28. Pratt, D. T., "Theories of Mixing in Continuous Combustion", Proceedings of 15th Symposium (International) on Combustion, pp. 1339-1352, Combustion Institute, Pittsburgh, (1975).

29. Burgess, M.J. & Wheeler, R.V., J., Chem. Soc., Vol. 99, p. 2013, (1913).

30. Rosin, P.O., Braunkohle, 24, p. 241, (1925) & Proceedings of International Conference on Bituminous Coal, Vol. 1, p. 838, (1925).

31. Essenhigh, R. H., "Burning Rates in Incinerators", Proceedings (Third) National Incinerator Conference, pp. 87-100, Am. Soc. Mech. Engrs., N.Y., (1968).

32. Incinerator Standards Handbook, Incinerator Institute of America (IIA), New York, (May 1966).

33. North American Combustion Handbook, p. 56, North American Manufacturing Co., Cleveland, (1952).

34. Edelman, R.B., Fortune, O., and Weilersteim, G., Proceedings GM Symposium on Emission from Continuous Combustion Systems, Cornelius and Agnew, Eds., pp. 55-87, Plenum Press, N.Y. (1972).

35. Biswas, B.K. & Essenhigh, R.H., "Air Pollution and Its Control," Proceedings of American Institute of Chemical Engineers Symposium, Series No. 126, Vol. 68, pp. 207-215, American Institute of Chemical Engineers, New York, (1972).

36. Santoleri, J.J., Proceedings (Fifth) National Incinerator Conference, pp. 66-74, American Society of Mechanical Engineers, N.Y, (1972).

37. Obert, E.F. & Gaggioli, R.H., "Thermodynamics," McGraw-Hill.

38. Burgoyne, J.B. and Cohen
Proc. Roy. Soc. 225A, 375, (1954).

39. Echigo, R., Nishiwaki, N., and Hirata, M., Proceedings of 11th Symposium (International) on Combustion, pp. 381-389, Combustion Institute, Pittsburgh, (1967).

40. Palmer, H. B., "Equilibria and Chemical Kinetics in Flames," Combustion Technology Ch. I, Academic Press, (1974).

41 Dombrowski, N., "Biochemical and Biological" Engineering Science, Vol. 2, Ch. 16, Academic Press, N. Y., (1968).

42. Industrial Combustion Data Handbook, 3rd Ed., pp. 87 & 93, Hauck Manufacturing Co., Lebanon, PA, (1953).

43. Frazer, R. P., Transoceans of the Institute of Chemical Engineers, Vol. 35, p. 219, (1957).

44. Nukiyama, S., and Tanasawa, Y., Trans Soc Mech Engrs (Japan), Vol. No. 5, p. 68, (1939); Vol. 6, 11-7, 11-8, (1940).

45. Strauss, W., Industrial Gas Cleaning, p. 309, Pergamon Press, N. Y., (1966).

46. Beer, J. M., Combustion Aerodynamics in Combustion Technology, Ch. III, Academic Press, N. Y., (1974).

47. Levenspiel, O., Chemical Reaction Engineering, Ch. 9, John Wiley, N. Y., (1962).

48. Zeinalov, M. O., Kuwata, M., & Essenhigh, R. H., Proceedings 14th Symposium (International) on Combustion, pp. 575-583, Combustion Institute, Pittsburgh, PA, (1973).

49. Kuwata, M. & Essenhigh, R. H., "Correlation of Pollutant Emissions, Noise, and Heat Transfer with Mixing Parameters in a Natural Gas Combustor," AIAA Paper No. 75-1267, (1975).

50. Hottel, H. C., Sarofim, A. F. & Farag, I., "Heat Transfer From Non Luminous Flames in Furnaces", "Radiative Exchange in Combustion Chambers," Combustion Technology, Chs. VI & VII, Academic Press, N. Y., (1974).

51. Beer, J. M., "Radiation from Flames in Furnaces," Combustion Technology, Ch. VIII, Academic Press, N. Y., (1974).

52. Koval, A., Slupek, S., Kokkinos, A., Slaber, A., Miskovsky, N., Essenghigh, R. A., "Smoke Point and Heat Transfer Characteristics of oil/water/air Emulsions Without and with Coal Addition in a Hot Wall Furnace," Paper presented at 1976 (April) meeting of the Central States Section of the Combustion Institute, held in Columbus, Ohio.

CHAPTER 5.0

CONDITIONS INSIDE INCINERATORS WHICH AFFECT MATERIALS PERFORMANCE

5.1 Introduction

At a minimum, the materials of construction must perform reliably under the steady-state conditions of environmental temperature and chemistry. These steady-state circumstances are often referred to as "design conditions." In addition, there are variations in the thermal and chemical history which occur and which the materials of construction must resist; otherwise, premature failure will occur. These undesirable circumstances are often called accidental, transient, or adventitious conditions. Some, in fact, are considered and allowed for in the initial design; others are not, but if they can reasonably occur, they should be a part of the original design considerations.

This chapter describes as full a set of steady-state and transient circumstances as possible. Some of these considerations are based on previous experience with experimental incinerators; others are taken from industrial experience where there were similar thermal-environmental conditions.

Most of the available information is derived from experiences with metallic materials of construction; little information is available for ceramic materials.

The information in the chapter is useful for defining the actual circumstances in which materials must perform, the factors which should be included in testing to qualify materials, and optimum procedures for operation to avoid deleterious environmental conditions.

The solid surfaces that form the wall of the incineration chamber are subject to gases with various chemical compositions, temperatures, and solid deposits also of varying compositions. These conditions can produce an adverse environment for the most corrosion-resistant materials of construction. Most deterioration occurs during combustion of the waste. However, wet corrosive attack can also occur when the equipment is idle owing to condensation or rain finding its way down the stacks.

The following substances and conditions may harm incinerator walls:

- Chlorides
- Alkali sulfates
- Deposits of low-melting point residue mixtures
- Temperatures above 320°C, depending on the alloy
- Alternating reducing and oxidizing conditions at high temperatures
- Widely and rapidly fluctuating temperatures
- Moisture condensation
- Crevices or defects encouraging galvanic action
- Flame impingement
- High stresses from residual sources including welding, metal fabrication, and fit-up
- Changing metal properties with prolonged exposure at high temperature.

These are often synergistic; for example, fluctuating temperatures accelerate stress-corrosion cracking in the presence of chlorides, particularly at points of high stresses which may be inherent in a particular design or which may result from a particular fabrication method.

In most incinerators, particularly shipboard incinerators, wastes supplied for burning are highly varied in composition and are difficult to burn uniformly. Moisture is sometimes present, but not in uniform amounts. The resulting flame temperatures, combustion gas composition, and deposit chemistry vary unpredictably. Thus, the incinerator that is designed and built to withstand the worst conditions is the most likely to survive longest.

Incinerators that are limited to burning only liquid wastes or slurries are likely to be more uniformly operated than the multipurpose units which must handle both liquid and solid wastes. However, a sudden blockage of liquid waste flow to a chamber can cause a sudden temperature rise and overheat the wall materials even if controls are usually responsive and reliable. Similarly, a sudden surge of liquid can cool the wall very suddenly which may cause intense local stresses in ceramic or metallic walls. Thus, a design which performs well under carefully controlled stable conditions may deteriorate rapidly under less steady operating conditions.

Materials for incinerators are usually chosen to withstand these multiple attacks for the design lifetime. Incinerator design aims to limit such threats to the chosen materials. When design and materials selection achieve the desired design life, the system is a success. To date, there is no shipboard incinerator design that can be considered a success. This results from inherent limitations which are described throughout this volume.

5.2 Other Systems Having Similar Problems

High temperature attack by corrosive atmospheres has long been a problem in coal- and oil-fired boilers, garbage-fired boilers, gas turbines, and industrial waste incinerators. In each of these systems, the problems of materials deterioration have not been completely solved, but rather have been reduced to where the maintenance required is operationally and economically tolerable. Materials exposed to the hot-ash products of combustion from a fuel such as coal or waste may be destroyed by a variety of reactions if the temperature of the metal and the deposit exceeds 320°C in the case of dilute iron-base alloys. Above this temperature, some materials may withstand attack even above 950°C if the ash constituents are benign. For example, clay, alumina, and many other oxides are not a threat to metals or ceramics. However, under certain conditions, sulfates, chlorides, and certain alkalies can attack highly alloyed metals at relatively low temperatures.

Outlined below are types of industrial equipment which have environments and operating conditions similar to those expected in shipboard incinerators. Persons involved with the design of shipboard incinerators should familiarize themselves with the technology in these areas as it may provide useful suggestions for reliable operation.

5.2.1 Boilers

Attack by alkali pyrosulfates on superheater tubes has been alleviated primarily by sacrificing some thermal cycle efficiency through reduction of maximum steam temperature to 540°C instead of 595°C, which had been the design temperature for some advanced units. Another beneficial technique has been the modification of fuel-air flow patterns in the boiler furnace to eliminate the flow of very hot reducing gases against the oxide coating which normally protects metal surfaces. Also, in some cases replaceable alloy steel shields have been useful for comparatively short-term protection of limited areas of severely threatened superheater tubes. These techniques are summarized in reference 1.

5.2.2 Garbage-Fired Boilers

Problems and solutions similar to those in fossil fuel boilers apply also to refuse-burning boilers, except that the presence of chlorides from PVC plastics and from the salt in food wastes causes much more rapid attack on superheater tubes and on the tubes containing boiling water which form the walls of the combustion chamber [2].

Partial solutions to such attack come from reducing maximum steam temperature, greatly increasing excess combustion air at the expense of increased heat loss in the exhaust gases, using alloy shields for the most severely exposed superheater tubes, and using studded wall tubes to hold a silicon carbide protective layer in place over the most exposed areas.

Another important protection in actual boilers is the ash deposit covering the normal oxide layer, assuming the deposit is benign. Tube cleaning methods are devised to leave a thin but tightly adherent layer of this deposit.

5.2.3 Gas Turbines

Turbine blade or vane corrosion has been minimized by the use of cast, high-chromium, nickel- or cobalt-base alloys; by refinement of the liquid fuels to remove noxious impurities; and by introduction of internal cooling to reduce metal temperatures. The use of purer fuels inhibits the deposition of corrosion-inducing ash on turbine hardware. The use of cooling to minimize turbine blade or vane corrosion requires care since lower temperatures can cause larger amounts to be deposited. Hot corrosion attack can become more severe as the amount of the ash deposit is increased. The decrease in corrosion rate due to the lower temperature can, therefore, offset the larger amount of the ash that is deposited.

5.2.4 Industrial Incinerators

Where bulk and weight is not a problem, the use of thick refractories is reasonably successful in producing a wall surface that will withstand corrosive attack by combustion gases.

5.3 Temperature - Time Cycles

5.3.1 Temperature Extremes

Temperatures in combustions can vary over a range of as much as 1500°C as illustrated, for example, in Figure 5.1. This is a schematic design for a simple aqueous-waste incinerator in which principal cooling of the combustion products is by evaporation of the aqueous waste; and lowered wall temperatures are achieved by air cooling in a cooling cavity between the combustor lines and the outer jacket. For many materials, the wall temperatures shown in Figure 5.1 would be excessive and the material would not survive for an acceptable lifetime. The design problem is to find ways of reducing the temperatures by wall cooling or by improving the wall materials.

The maximum tolerable range of temperatures for low alloy materials under chloride attack is 260°C to 290°C as described in Chapter 6.0. Since theoretical stoichiometric flame temperatures attain about 2000°C, and practical flame temperatures mostly lie in the range 1350°C to 1960°C, the design problem is severe. Obviously, any design for metallic walls which fails to take maximum advantage of wall cooling by air, water, and/or radiation shielding is liable to rapid failure from chloride attack. As alloys containing higher concentrations of chromium, nickel, aluminum and other alloy elements are used, higher operating temperatures can be maintained. These limits are described in Chapter 6.0.

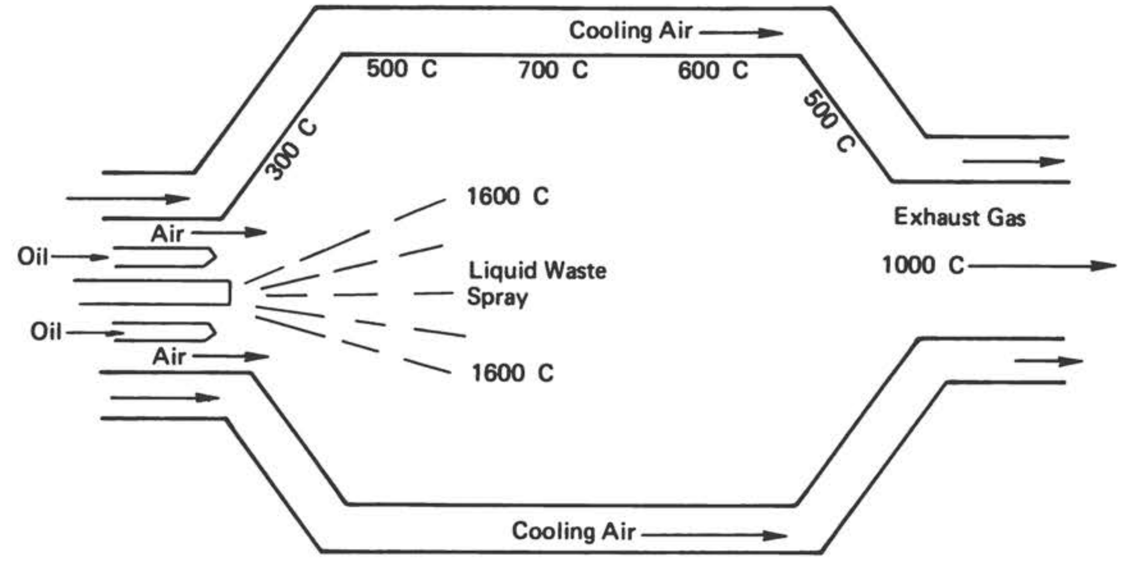


Figure 5.1 Estimated Maximum Temperatures Attained In a Simple Aqueous Waste, Oil-Fired Incinerator.

On the low temperature side, acid attack by "dew point corrosion" can occur if there is any sulfur in the fuel. Figure 4.23 illustrates the variation of SO_3 equilibrium with the ratio $[SO_3/(SO_2 + SO_3)]$ as a function of temperature and for those excess oxygen concentrations. The SO_3 is responsible for increasing the dew point temperature at which moisture will condense out, in which case the SO_3 also condenses out as sulfuric acid. Figure 4.24 illustrates the variation of dew point temperature with SO_3 concentrations. The dew point temperature can rise to about 160°C with 35 ppm of SO_3.

5.3.2 Typical Operating Temperatures

Direct experimental information which sets the matter of temperatures in perspective is given in Table 5.1 and Figure 5.2. These provide some recently measured temperatures in a prototype multifunctional and a vortex incinerator, respectively.

TABLE 5. 1 Multifunctional Incinerator Temperatures

	UNIT 1		UNIT 2			
	Waste Feed Rate 100 lbs/hr.		Waste Feed Rate 110-140 lbs/hr.		Waste Feed Rate 225 lbs/hr.	
Incinerator Section	Average	Peak	Average	Peak	Average	Peak
Primary Chamber	930°C	1100°C	810°C	1100°C	1000°C	1250°C
Sewage Chamber	705	790	370	540	370	540
Rotoclone/cyclone Inlet	540	595	260	345	290	370
Exhaust Stack	370	385	120	150	175	205

NOTE: Unit 1 is described as a "controlled" excess air incinerator and Unit 2 is described as an "excess" air incinerator.

Source: Reference 12

The vortex incinerator is essentially a cylinder with two end circular plates. Figure 5. 2 shows outside all temperatures measured by thermocouples on the end plates, and on the cyclindrical wall which is spread out in a plane for illustration. The temperatures vary from a low of 260°C to 665°C. Unexpectedly, the lowest and highest temperatures are relatively close to each other (within about 60 cm), probably representing vagaries due to the mixing pattern generated by the locations of the burner head, waste injection, and exhaust part.

Table 5. 1 lists temperatures from shielded thermocouples inserted through the walls of two different designs of multifuntional incinerators (see Chapters 4. 0 and 9. 0 for commentary on measurement of gas temperatures). Complete combustion, of course, always requires excess air for operation with minimal unburned. To achieve this good combustion practice always requires that the excess air be known and controllable. This is usually accomplished by gas analysis (O_2 and/or CO_2 and/or CO) to determine excess air and unburned, with proper damping to control air in-leakage, and with air gate control on the air fans to change the excess air to the desired point. Unit 1 of Table 5. 1 incorporates these features.

Unit 2 of Table 5. 1 is illustrated in Figure 2. 2 of Chapter 2. 0. It is described as an "excess" air unit. It has to be concluded from the designation that the necessary gas analysis and combustion controls required in good combustion engineering practice are absent.

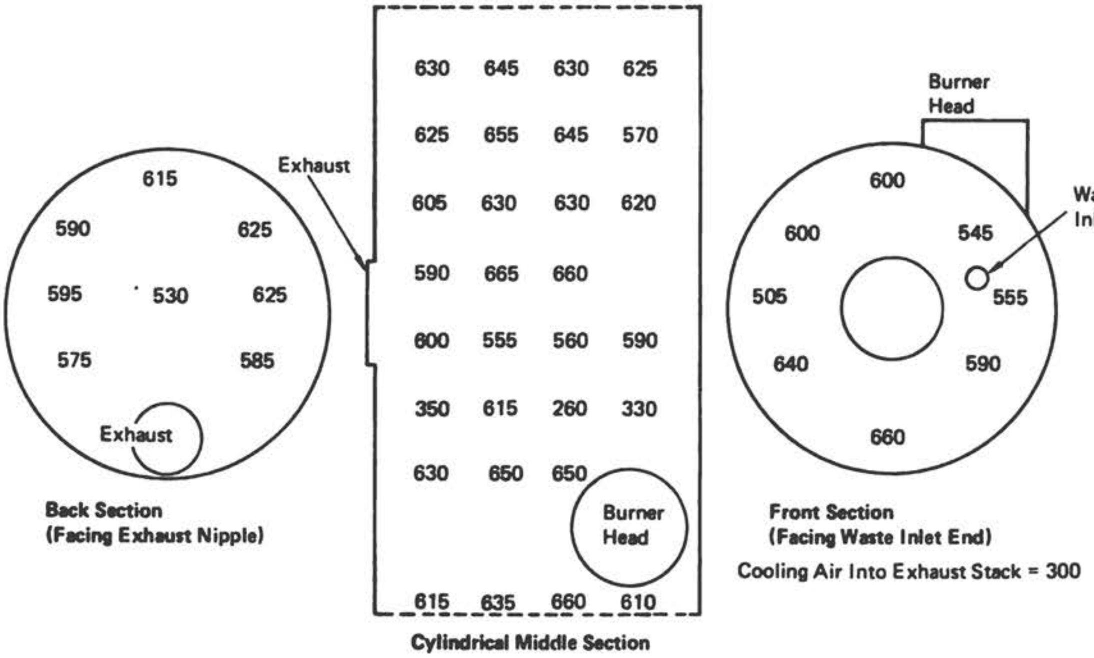


Figure 5. 2 Vortex Incinerator: Temperature in °C.

5. 3. 3 Variable Thermal History and Its Effect on the Life of Components

At the present state of development of high-temperature, corrosion-prone equipment, a component life of 10, 000 hours or slightly over one year (8760 hours) of continuous operation is considered acceptable and usually achievable for some industrial uses. A much longer life, perhaps up to 100, 000 hours or more, is a desirable goal and may be achieved by lowering the operating temperatures with the resulting lower efficiency. However, in general, high temperature combustion equipment, particularly incinerators, does not operate steadily but is subject to on-off cycles and to fluctuations in combustion rate. Such variations lead to more severe deterioration of wall materials than continuous operation; hence a life of 10, 000 hours under steady conditions may be substantially reduced by frequent cycling. Nevertheless, for comparison and evaluation, the resistance of various contruction materials to hostile environmental attack under conditions of steady operation can be useful.

Cyclic temperature conditions accelerate attack mainly through loss of the protective scale. When this scale is removed, the initially high corrosion rate obtains until the new scale is sufficiently protective. If the scale-breaking cycle is frequent, the overall rate of attack is greatly accelerated.

The basis for this behavior is illustrated by Figure 5.3 for the corrosion of a steel exposed to the products from the combustion of solid waste.

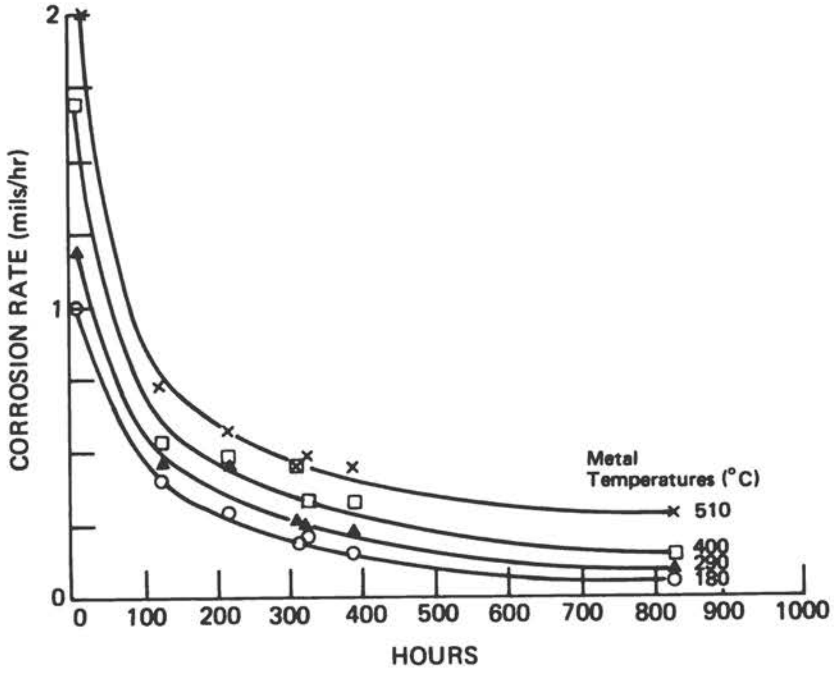


Figure 5.3 Isothermal Corrosion-Rate Data for A106 Steel Versus Time of Exposure to Solid-Waste Combustion Products [5].

Initially, the rate is higher. After 100 hours, the corrosion rate is greatly reduced, and a further reduction results at longer times. Thus, the most desirable circumstance is the continued maintenance of the protective scale formed after long times. If the metal were to corrode at the initially high rate, on a continuous basis, ready perforation would occur.

Conditions which can remove or destroy the protective layer are:

1. Rapid cooling of hot metal, causing spalling of the protective layer;

2. Erosion of the layer by abrasive particles carried at high velocity by the hot gases;

3. Impingement of liquid spray droplets on hot walls causing either spalling, dissolution or liquid erosion of the layer;

4. Careless cleaning of the chamber with sharp, heavy tools which cut or break the protective layer;

5. Vibration which dislodges the protective layer;

6. Overheating to the point where molten slag "washes" the protective layer away; and

7. Down-period condensation of water which penetrates and softens the protective layer.

In addition, the degree of protection produced by the oxide layer may diminish as its temperature rises. This is also influenced by gas temperature; as gas temperature rises at a nominally similar wall temperature, the gradient across the layer increases. Disruption of the layer then becomes more likely.

In recent municipal waste-to-energy experiments, chloride attack on boiler tubes was shown to be prevented by the tight adherence of a benign sulfate layer on the tube.

5.4 Environmental Chemistries

5.4.1 Lowered Melting Temperatures of Sulfates and Chlorides

Sulfates derive from the sulfur in waste as well as in fuels and chlorine derives from the seawater fluid or from chlorine-containing polymers. The lowered melting point of salts of chlorine and sulfur greatly accelerates corrosion; furthermore, this lowered melting point will lower the temperature for the onset of significant corrosion.

These salts melt at low temperatures: 800°C for NaCl and 884°C for Na_2SO_4. As these salts are mixed to produce binary or multicomponent systems, the melting temperatures are further lowered. Figures 5.4 and 5.5 show the binary systems of $NaCl-Na_2CO_3$ and $NaCl-Na_2SO_4$ where eutectic temperatures are 633°C and 623°C, respectively. Still further lowering is possible as other components are added.

In an oxygen atmosphere, only oxides are thermodynamically stable. This means that metals, carbides, nitrides, etc., are all unstable in the excess air combustion atmosphere of an incinerator. The reliable use of all materials of construction, other than oxides, depends on how fast the substrate reacts to form the more stable reaction products.

In the presence of molten $NaCl-Na_2SO_4$, even the oxides are unstable and may be taken into solution by reactions which form either simple ions (M^{++}) or complex ions (MO_x^{Y-}). Herein lies the basis for problems of incinerator lifetime. The oxides that protect metals at incinerator temperatures cannot be relied upon for protection if they are dissolved in salt melts. The rate of attack is then a problem of rate of dissolution, which is largely a function of salt composition and temperature.

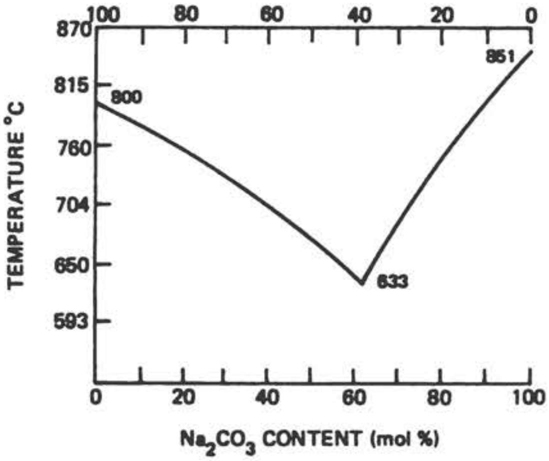


Figure 5.4 Melting Points of $NaCl-Na_2CO_3$ System [5]

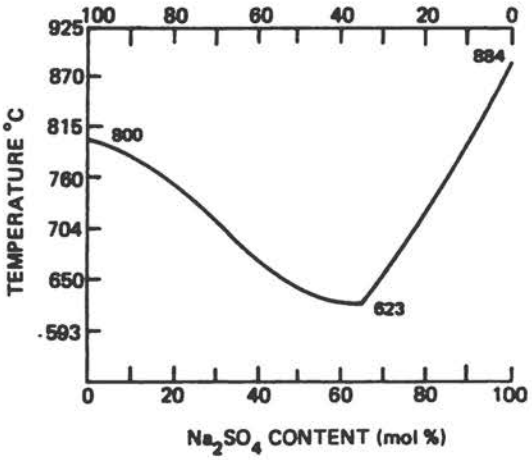


Figure 5.5 Melting Points of $NaCl-Na_2SO_4$ System [5]

The role of molten salts in accelerating corrosion is associated primarily with their being electrolytes which may dissolve protective oxides on structural materials and thereby accelerate deterioration. Specific features of this process are described in Chapter 6.0. Molten salts often accelerate attack at grain boundaries.

In addition to the lowered melting points shown in Figures 5.4 and 5.5, Table 5.2 shows other melting points of components which could exist in the deposits on incinerator surface.

5.4.2 Species Producing Deleterious Effects

Species such as sodium and potassium produce undesirable effects on materials used in incinerators. These metals occur in incinerators as sulfates or chlorides. Sodium-potassium sulfates increase the corrosion of alloys by fluxing protective oxide barriers on the surfaces of alloys or by fluxing protective oxide barriers on the surfaces of alloys or by promoting intergranular penetration by sulfur species. Chlorides of these metals also destroy oxide barriers on alloys. Figure 5.6 shows that the addition of chloride to sulfate produces more severe corrosion than that of sulfate alone.

TABLE 5.2 Possible Ash Constituents Formed During Combustion of Fuel and Their Melting Points

Compound		Melting Point °C
Aluminum oxide	Al_2O_3	2050
Aluminum sulfate	$Al_2(SO_4)_3$	Decomposes at 767 to Al_2O_3
Calcium oxide*	CaO	2570
Calcium sulfate	$CaSO_4$	1450
Ferric oxide	Fe_2O_3	1565 1565
Ferric sulfate	$Fe_2(SO_4)_3$	Decomposes at 480 to Fe_2O_3
Magnesium oxide*	MgO	2500
Magnesium sulfate	$MgSO_4$	Decomposes at 1125 to MgO
Nickel oxide	NiO	2090
Nickel sulfate	$NiSO_4$	Decomposes at 930 to NiO
Silicon dioxide	SiO_2	1720
Sodium sulfate*	Na_2SO_4	880
Sodium bisulfate	$NaHSO_4$	250
Sodium pyrosulfate*	$Na_2S_2O_7$	400
Vanadium trioxide*	V_2O_3	1965
Vanadium tetroxide*	V_2O_4	1965
Vanadium pentoxide*	V_2O_5	675
Zinc oxide	ZnO	> 1800
Zinc sulfate	$ZnSO_4$	Decomposes at 740 to ZnO
Sodium metavanadate*	$Na_2O \cdot V_2O_5$	630
Sodium pyrovanadate*	$2Na_3O \cdot V_2O_5$	640
Sodium orthovanadate*	$3Na_3O \cdot V_2O_5$	850
Nickel pyrovanadate	$2NiO \cdot V_2O_5$	> 900
Nickel orthovanadate	$3NiO \cdot V_2O_5$	> 900
Ferric metavanadate	$Fe_2O_3 \cdot V_2O_5$	860
Ferric vanadate	$Fe_2O_3 \cdot 2V_2O_5$	857
Sodium vanadic vanadates*	$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	625
	$5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$	535

* Most important constituents

NOTE: Sodium bisulfate decomposes at about 249°C to $Na_2S_2O_7 + H_2O$.

Sodium pyrosulfate decomposes at about 460°C to $Na_2SO_4 + SO_2$.

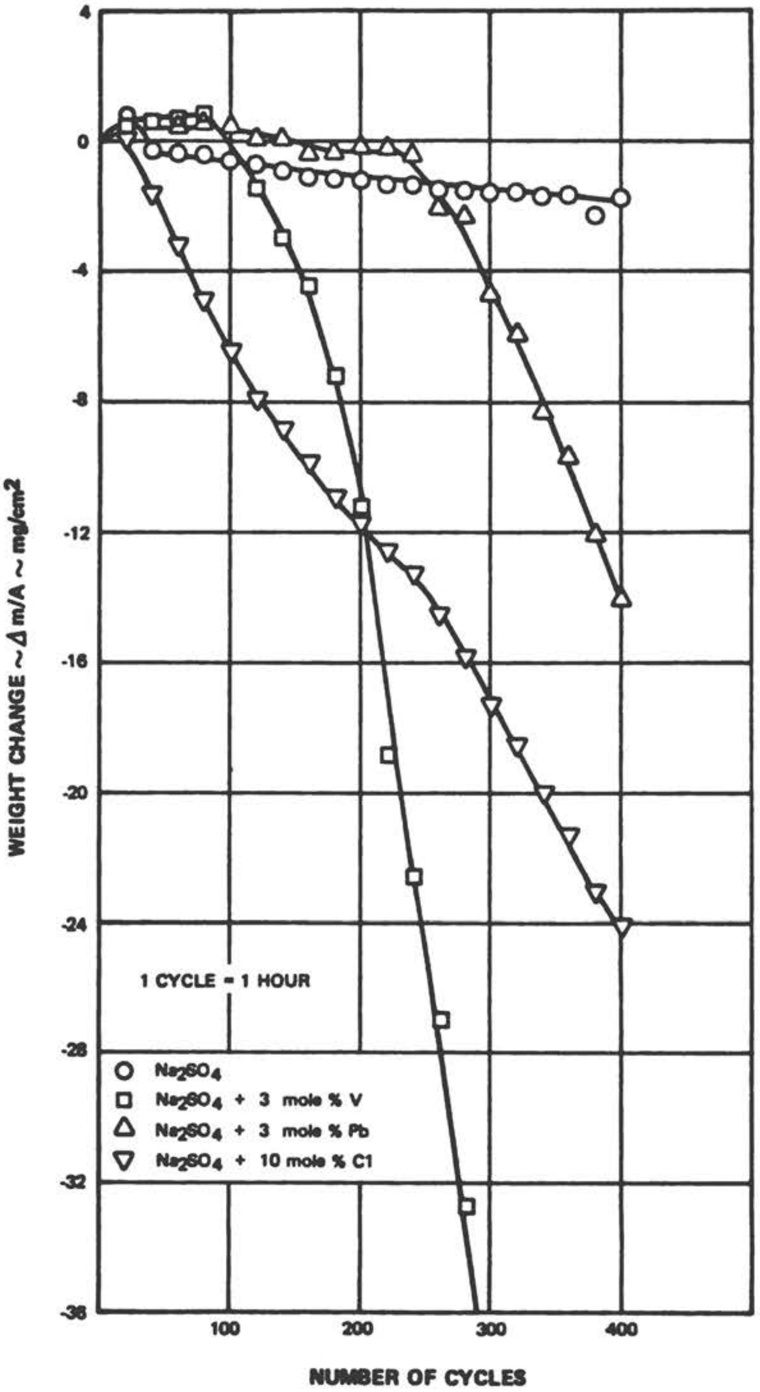


Figure 5. 6 Weight Change Versus Time Data for the Cyclic Hot Corrosion of X-40 Alloy at 900°C. Specimens cooled to room temperature once every hour; 1.0 mg/cm^2 Na_2SO_4 applied every 20 hours. Addition of chloride, lead or vanadium caused more severe degradation [7].

Vanadium, molybdenum, tungsten, and lead also accelerate corrosion of incinerator materials. The oxides of these metals react with the oxide barriers on alloys to yield liquid products at temperatures as low as 560°C to cause severe corrosion. The addition of these metals or their oxides to Na_2SO_4 also results in more severe degradation than that caused by Na_2SO_4 (see Figure 5. 6).

Alloys resist corrosion when oxide barriers are developed on the surfaces; and for this reason, oxygen is a desirable component of the incinerator environment. Carbon deposition on materials reduces the local oxygen pressure and causes deposited salts to be much more effective in destroying protective oxide barriers on the surfaces of alloys.

5. 4. 3 Inhibitors for High Temperature Systems

Sections 5. 4. 1 and 5. 4. 2 described the deleterious actions of environmental species which may be carried into the incinerators by fuels, fluid water, or the incinerated materials. Such detrimental effects may be counteracted by adding species which inhibit these accelerated corrosion processes.

These inhibitors may be injected into the incinerator by various means including their dissolution in the fuel. They seem to act either by raising the melting point of deposits formed on surfaces or by thermodynamically stabilizing the protective oxide films, i. e., this means that the local equilibrium on the surface is shifted from a fluxing regime to a regime where the protective oxide such as Cr_2O_3 or Al_2O_3 is stable.

The approach of raising the melting point of deposits has been considered by Wall, et al. [6]. When clay is used as an aluminum silicate of large surface area and high reactivity, the melting point of the salts is raised. Clay readily reacts to form sodium aluminum silicates to expel HCl and/or SO_3.

The ingestion of MgO significantly reduces the corrosion caused by V_2O_5; magnesia inhibits degradation induced by V_2O_5 by reacting with the liquid V_2O_5 to form a solid magnesium vanadate. As shown in Chapter 6. 0, the liquid nature of ash deposits is a sufficient condition for severe degradation of materials. The melting point of the resulting $3MgO \cdot V_2O_5$ is 1100°C. The magnesium can be added as fine dispersions of oxide or carbonate, as the oil-soluble napthenate and acetate, or as an aqueous solution. The amount added depends on the amount of vanadium; a magnesium to vanadium mole ratio in excess of 3:2 is required.

The ingestion of Cr_2O_3 into gas turbines by using a fuel soluble chromium additive [9] inhibits degradation caused by Na_2SO_4. It appears that chromia decreases the concentration of oxide ions in Na_2SO_4 and displaces sulfur in the ash deposit. Approximately 20 ppm by weight chromium in the fuel is used. The exact amount depends upon the amount of Na_2SO_4 deposited.

5.4.4 Analysis of Deposits from Refuse Incineration

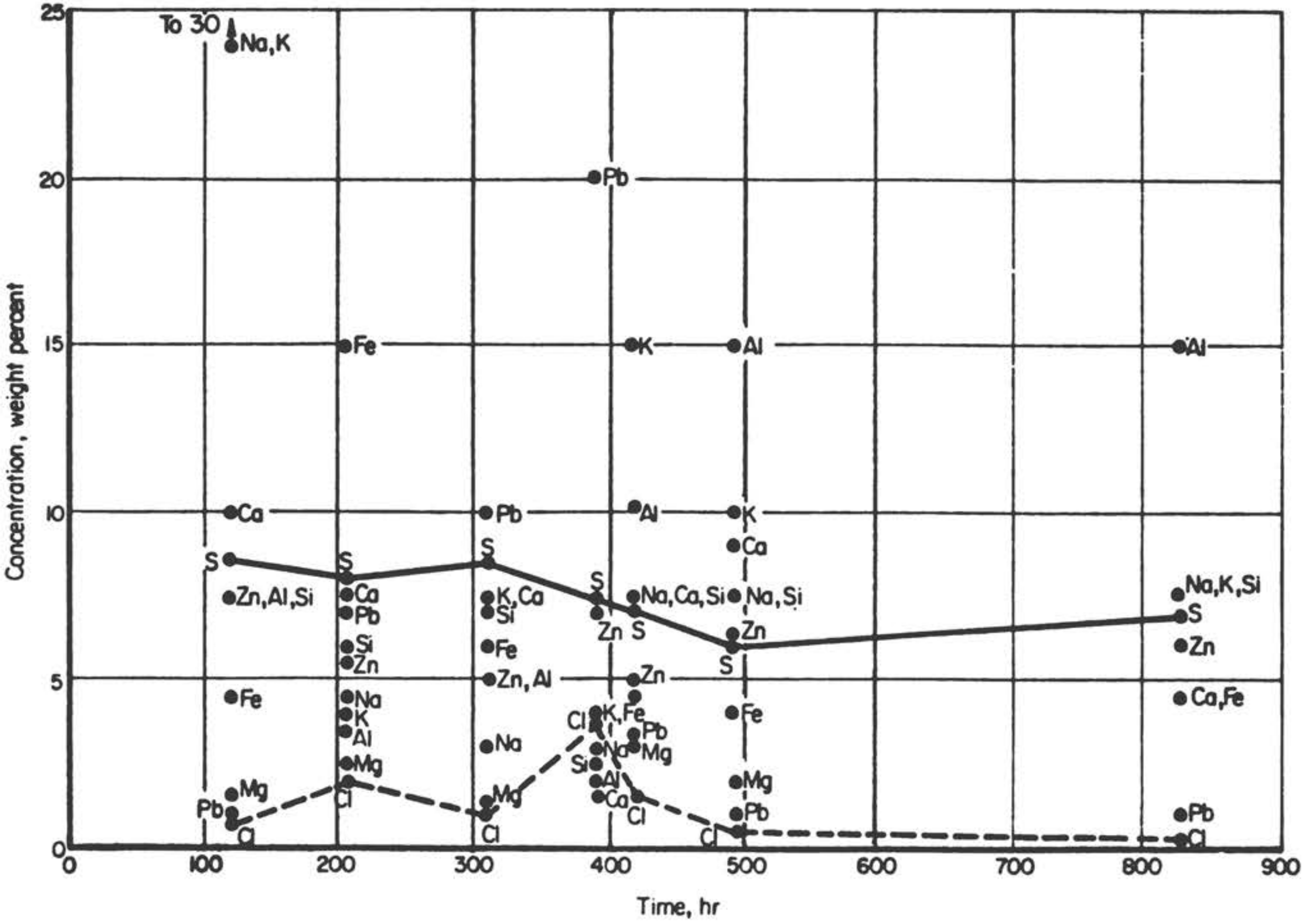
Deposits formed on boiler tubes as a result of incinerating refuse differ from those normally found with oil or coal firing. In addition to the alkali and alkaline earth sulfates and complex aluminum silicates of these metals commonly encountered with fossil fuel firing, there are often compounds of chlorine, lead, and zinc in the incinerator deposits. On the other hand, the vanadium often found with oil firing is encountered only in trace amounts.

Analysis of deposits formed on corrosion probes exposed for increasing periods of time in the incinerator flue gases gives insight into the deposition process and the chemical reactions. A typical distribution of chemical elements found in significant amounts in such probe deposits from a municipal incinerator is shown in Figure 5.7. The data include seven exposures in a municipal incinerator for times between approximately 100 to 800 hours. The results shown are for the low temperature zone (metal surface) of the probe deposits 130°C to 290°C. The sulfur and chlorine concentrations have been emphasized by connecting the points in the figure, since these elements are most significant in the corrosion process. Sulfur accumulated rapidly in the deposits and after 100 hours it seemed to saturate. As the metal temperature increased along the probe, the concentration of sulfur in the deposits decreased slightly, probably because of the volatility of the compounds. The percentage of sulfur also decreased slightly with time as other elements accumulated in the deposits.

The amount of chlorine in the deposits decreased both with temperature and time. Extremely high concentrations of chlorine (14-27 weight percent) have been measured in the first 8 hours of deposition. However, the chlorine compounds (NaCl, KCl) are rapidly converted to sulfates by reaction with sulfur dioxide and oxygen. This reaction releases HCl, or, after oxidation, elemental chlorine. As the metal temperature is increased, chlorine compounds are volatilized more readily, so the deposits contain less chlorine. However, as long as there is more than 0.1 weight percent chlorine in the deposits, serious corrosion can occur. The high chlorine content in the 400-hour exposure shown in the figure resulted from large amounts of polyvinyl chloride in the refuse.

Relatively high percentages of sodium and potassium are found in the early stages of deposition. It appears that these elements are deposited initially as oxides or chlorides and then are converted to sulfates by reaction with sulfur dioxide and oxygen. This conversion to compounds of higher mole molecular weight results in lower percentages of sodium and potassium in the deposits as time increases. The reason for these changes is not clear. Either sodium and potassium are lost from the deposit by vaporization or further additions to the deposit are lower in sodium and potassium.

The lead concentration builds up with time in the early stages of the deposition process and then decreases as reactions occur. That the compounds PbO, $4PbO \cdot PbSO_4$, and $PbSO_4$ have been identified in the deposits by X-ray diffraction shows there is stepwise conversion of lead oxide to lead sulfate via the intermediate oxy-sulfates. Lead concentrations also are highest in the lower temperature zones of the deposits (260°C).



Temperature Zone from 130-290°C

Figure 5. 7 Probe Deposit Composition as a Function of Exposure Time in the Miami County, Ohio Incinerator [10]

The zinc concentration in the deposits varies less with time or temperature than does the lead, indicating less volatility and slower reactivity. Although the scale next to the metal contained a higher concentration of lead and zinc than did the bulk deposit, the role of these two elements in the corrosion process remains unclear. If they were present as chlorides in the early stages of deposition, they could form low-melting eutectics and exert a fluxing action on the oxide scale at the metal surface.

As exposure time lengthened, aluminum became the predominant element; sodium, potassium, calcium, and silicon were present in large amounts This indicates that clay-like materials such as silicates containing these metals can be formed on long-term exposure. Materials of this type, forming a hard deposit, can build up a protective layer that is chemically inert and that serves as a barrier to diffusion on sulfur oxides, oxygen, and HCl. The decrease in corrosion rates with time indicates such protective action.

X-ray diffraction studies of incinerator deposits and corrosion scale layers reveal the presence of some 20 compounds. Figure 5.8 presents the results of such analyses for various metal temperature zones, along with a photomicrograph illustrating the general location and appearance of the scale and deposit as seen by reflected light [10]. The scale in contact with the metal contained $FeCl_2$ throughout the probe temperature range of 150°C - 395°C. At the high temperature end of the probe, the $FeCl_2$ layer melted and collected in small pools. A layer of FeS also was detected at the high-temperature end, indicating that sulfur participated in the corrosion reaction in this zone. The electron microprobe showed that some zinc compound was present in the area near the metal. This element apparently is not in a form readily detected by X-ray, but may be incorporated as $(FeZn)Cl_2$ or (FeZn)S in the iron chloride and sulfide structures.

Between the interface scale and the bulk deposit a multilayered scale of Fe_2O_3 and Fe_3O_4 was found. Microscopic examination showed that some melting had taken place near the oxide scale, and recrystallized phases of $(Na, K)_2SO_4$ and $PbO \cdot PbSO_4$ were noted on the external surface of the mixed iron oxide scale. The $(Ha, K)_2SO_4$ phase was also dispersed throughout the iron oxide scale that adhered to the bulk deposit. It appeared that the separation in the iron oxide scale occurred at the depth to which the salt phase permeated in sufficient quantity to destroy the integrity of the iron oxides. Possibly in the various stages of deposition, these salt phases and such compounds as $ZnCl_2$ and $PbCl_2$ permeate the oxide scale and destroy its protective characteristics.

The deposits that can be anticipated for shipboard incinerators are high in chloride content because of the seawater in the wastes. Even though a large source of chlorine in land-based incinerators, polyvinyl chloride may be low in shipboard wastes, the difference should be more than made up by the NaCl from seawater, which even pervades the combustion air supplied to the incinerator. If there is sulfur in the waste in relatively small amounts (<1 percent by weight), the deposits formed in the incinerator will be especially corrosive as a result of the release of chlorine-containing gases beneath the deposits. In addition, the sulfur can participate in corrosion reactions through the formation of sodium bisulfate or pyrosulfate, which readily attack steels.

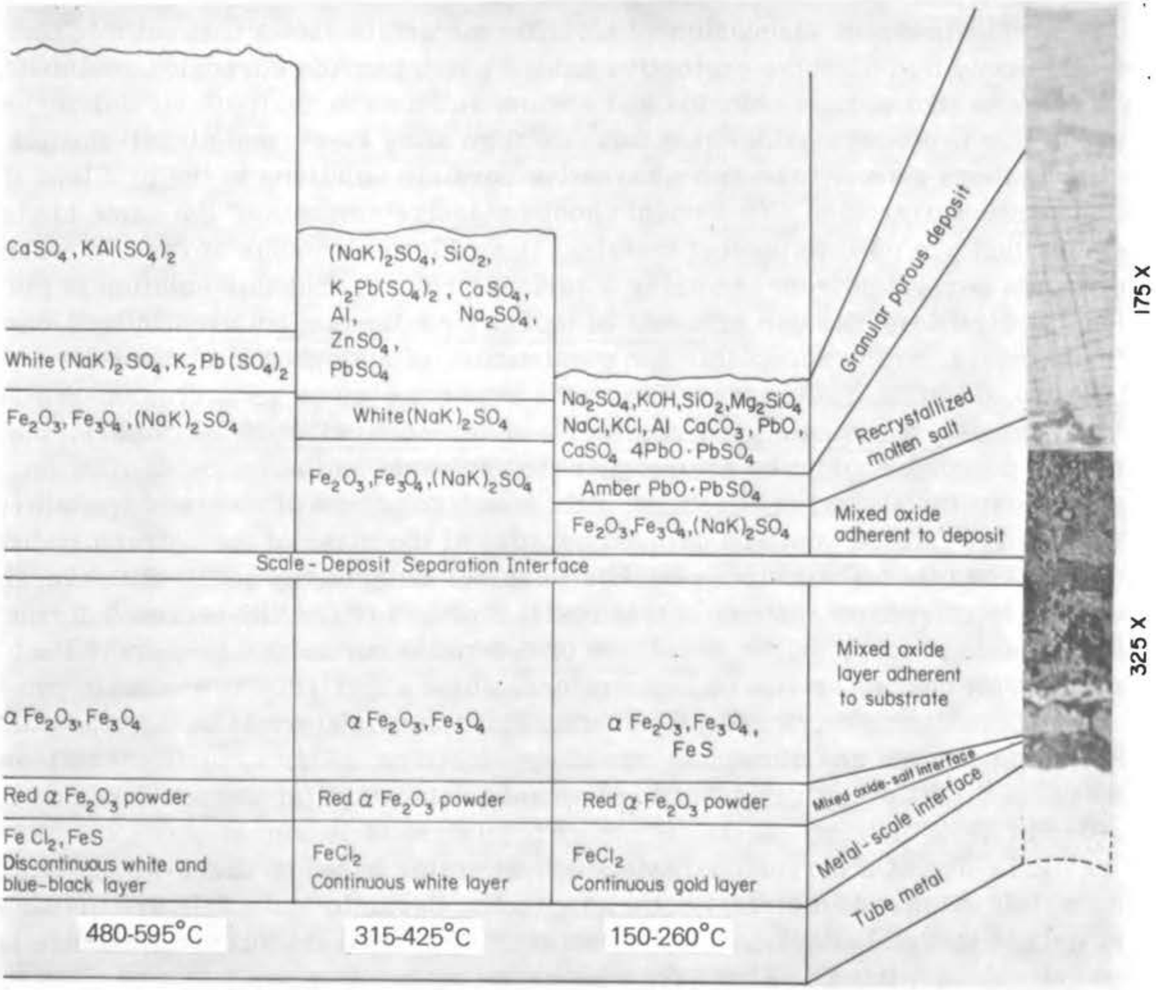


Figure 5.8 Schematic Location of Phases Identified by X-Ray Diffraction [10].

5.5 Problems with Ceramic Alternatives

While circumstances and implications of environments have been considered for metallic materials of construction, substantially less is known about the behavior of ceramic materials. Owing to the wide use of ceramic materials in high-temperature, heat-treating furnaces, metallurgical processing, space application, etc., there is an aura of indefatigability which is partially deserved but not without question.

Owing to the numerous means by which metals may be debilitated, ceramic materials are attractive, especially for higher temperature application where the expectation of satisfactory performance is proportional to the high melting points.

The previous discussion of metallic materials shows that salts in their molten condition dissolve protective oxides which provide corrosion resistance. Since salts like sodium chloride and sodium sulfate are particularly deleterious to the thin protective oxides that form on high alloy steels and nickel-chrome alloys, there appear to be two alternative ceramic solutions to the problem of incineration corrosion. One could choose massive amounts of the same kinds of oxides that are used to protect metals. Use of large amounts of these materials prevents corrosion from becoming a serious problem, but this solution is the least desirable. Massive amounts of oxides or silicates, as used in land-based incinerators, are unacceptable for construction of a shipboard incinerator because of weight limitations. Ceramics may not even be as corrosion-resistant. For example, by using a good clay-derived aluminum silicate refractory, the rate of corrosion might be even higher than it would be for the oxide film on nickel-chrome alloy; yet, because of the massive nature of an aluminum silicate refractory, failure would be delayed because of the mass of the refractory brick.

The other alternative would be to select and develop one of the several non-oxide refractory materials that resist molten salts. Although no information is available concerning the resistance of non-oxide ceramic materials to the molten salt characteristic of incinerators, some experience is available concerning the corrosion of special ceramic refractory materials in molten salts in the magnesium and aluminum smelting industries. This experience indicates that several different nitrides are resistant to corrosion at temperatures on the order of 1000°C.

Design of a corrosion-resistant incinerator based on light-weight ceramic materials requires an entirely new approach. Ceramic materials are brittle and subject to thermal shock. For this reason, a thin wall monolithic structure is inadvisable. A thin tile structure with back-up fiber insulation comes closest to current industrial experience.

REFERENCES

1. Reid, W. T., External Corrosion and Deposits, American Elsevier, New York, NY, (1971).

2. Miller, P. D., Corrosion Studies in Municipal Incinerators, Report SW-72-3-3 to Solid Waste Research Laboratory, EPA, National Environmental Research Center, Cincinnati, OH, (1972).

3. Wyatt, S. V. and Hagedorn, G. D., "Shipboard Malfunctional Waste Incinerators," ASME Paper 75-ENAS-32, American Society for Mechanical Engineers, (July 1975).

4. Vaughan, D. A., Krause, H. H., and Boyd, W. K., "Fireside Corrosion in Municipal Incinerators Versus Refuse Composition," Paper No. 169, The International Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials, Toronto, Ontario, Canada, (April 14-18, 1975).

5. Wall, C. J., Groves, J. T., and Roberts, E. J., "How to Burn Salty Sludges," Chemical Engineering, pp. 77-82, (April 14, 1975).

6. Bowden, J. Inst. of Mech. Engrs., Vol. 167, p. 291, (1953).

7. Unpublished data from Pratt and Whitney Materials Engineering and Research Laboratory, (February 1975).

8. Edwards, C. J. A., Fireside Deposits and Corrosion in Oil-Fired Naval Steam Raising Installations, Literature Survey, compiled for Panel A of the Admiralty Fuels and Lubricants Advisory Committee, B. P. Publication, (September 1964).

9. Farmer, R. C., "R_x for Sodium Sulfidation," Gas Turbine International, page 32, (September-October 1974).

10. "Corrosion Studies in Municipal Incinerators," Report No. S.W. 72-3-3, U.S. Environmental Protection Agency, (1972).

11. Unpublished data from David W. Taylor Naval Ship Research and Development Laboratory, Annapolis, MD, (1975).

CHAPTER 6.0

MATERIALS OF CONSTRUCTION

6.1 Introduction

Choosing materials of construction depends upon operating procedures and the chemistry of materials which enter the incinerator. These conditions are described in Chapter 5.0. The anticipated conditions for shipboard incinerators are sufficiently harsh that only a few commercial metallic materials can be expected to perform economically for desired lifetimes. Achieving a satisfactory lifetime depends both upon modifications in design and improvements in alloys or ceramic materials.

This chapter discusses results from studies of materials which are pertinent to the performance of shipboard incinerators; considerations of ameliorative practices through design are discussed in Chapter 8.0. Included in this chapter is a brief discussion of fundamental aspects of corrosion which pertain to the materials-environmental circumstances of incinerators. This discussion of fundamentals both rationalizes the results from engineering tests as well as providing a basis for interpolating and extrapolating information.

Testing materials for corrosion and performance in engineering conditions is far from mature. The principles outlined herein will be valuable in choosing prospective materials and in designing corrosion tests. This is followed by a specific discussion of performance of both metallic and ceramic materials. Possible failures due to more complex systems problems are described in Chapter 7.0.

6.2 Performance of Shipboard Incinerator Materials to Date

The Navy and Coast Guard have begun both field and laboratory studies of candidate materials of construction for several incinerator designs. Some of the early shipboard studies used an Inconel 601 liner in a vortex type incinerator. Figures 6.1 and 6.2 show the corrosive failure of an Inconel 601 liner from a vortex sludge incinerator on board the USCGC Mackinaw (WAGB 83) [1]. The failure, discovered after 408 burn hours, is located in the lower right-hand quadrant of the liner, directly under the oil burner. Extensive deterioration of the liner's exhaust nipple also occurred. This incinerator burns the comminuted sewage from a reduced volume, fresh water, flush-vacuum collection system. Other alloy liners including Inconel 671, Haynes-188 (which has performed without problems for 800 hours), and Type-309 stainless steel are currently undergoing shipboard evaluation. Alloys of potential interest to shipboard incinerators are listed together with their compositions in Table 6.1.*

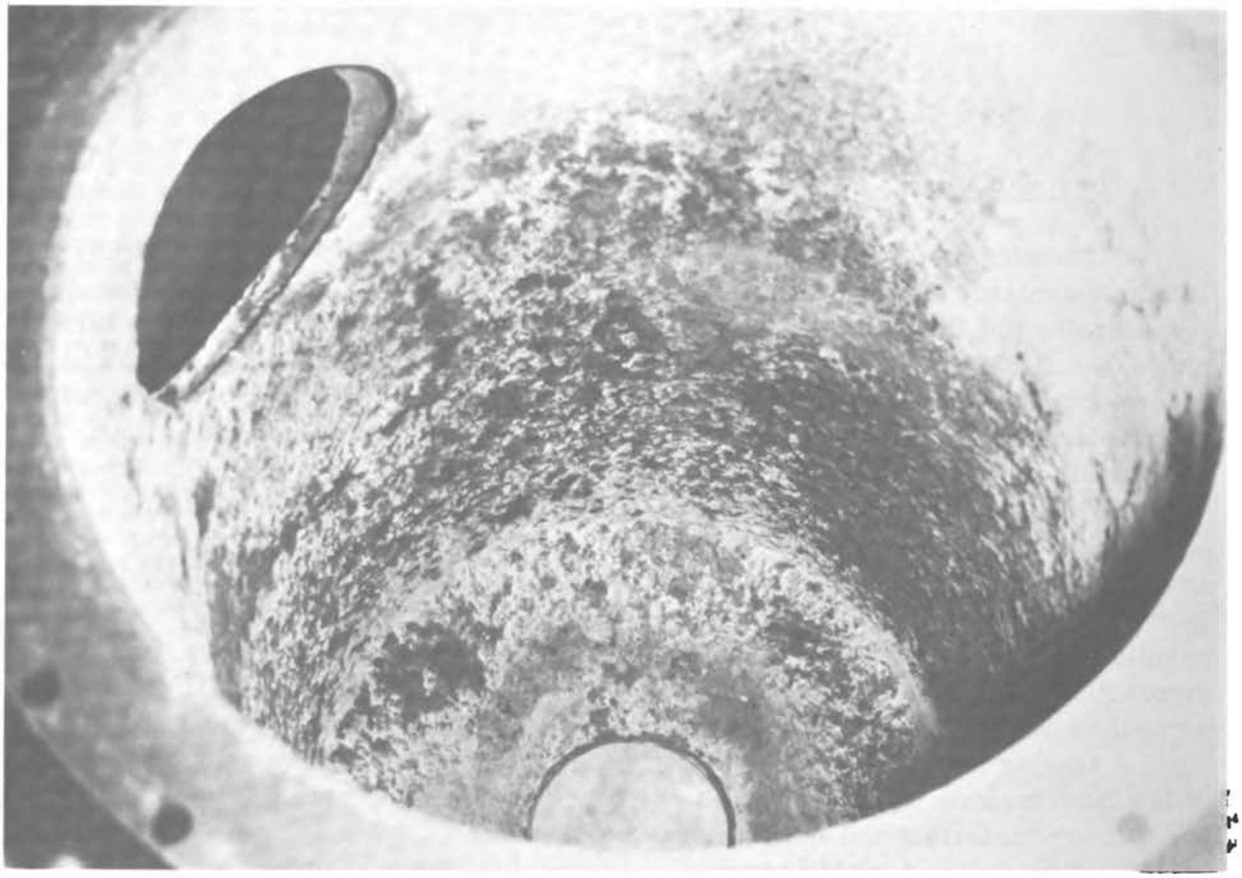


Figure 6.1 Deterioration of First Inconel 601 Liner After 408 Burn Hours. Note that exhaust nipple in cone section has completely corroded away.

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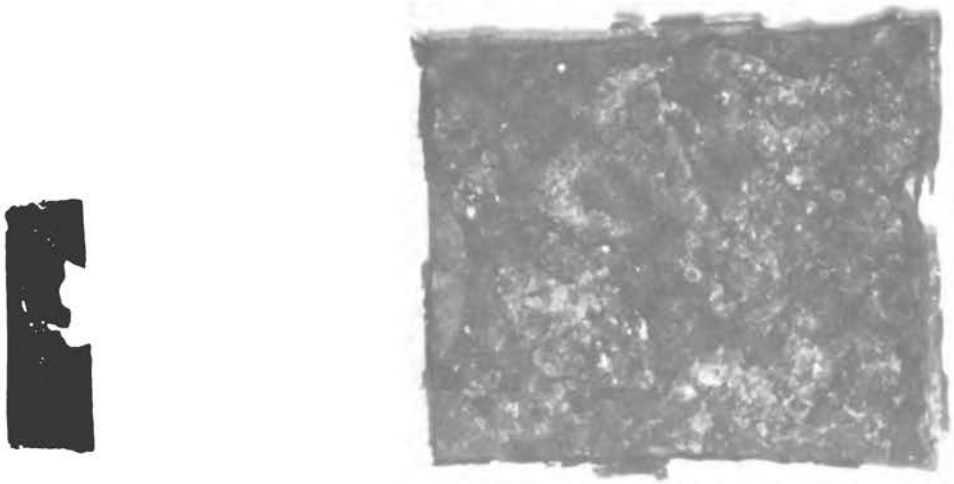
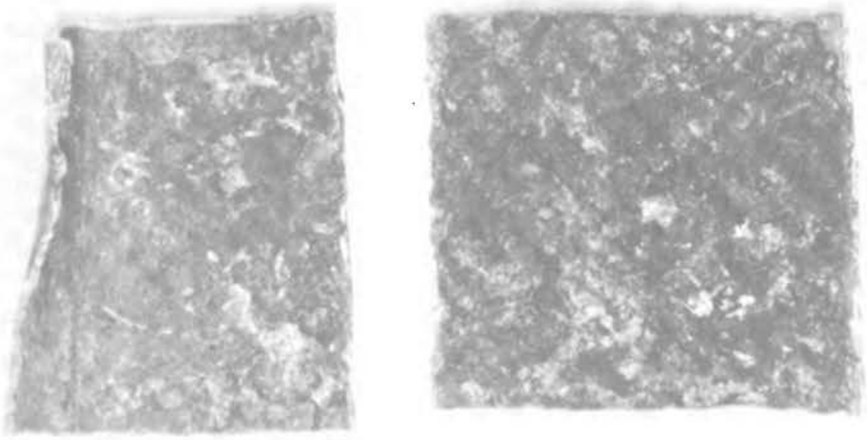
* Following completion of the Committee's work, an important paper on the performance of incinerator materials was prepared by the Navy Laboratories:

G. Wacker and W. L. Wheatfall, "Corrosion Problems Associated with Shipboard Waste Incineration Systems," Submitted for the 1976 Tri-Service Corrosion Conference, Philadelphia, Pennsylvania, 26-28 October 1976.



a. From Conical Section (Perforated)

b. From Conical Section



c. From Cylindrical Section

Figure 6.2 Corroded Samples Cut from First Inconel 601 Liner After 408 Burn Hours. Note that sample "a" is from 0.30 cm-thick conical section. This piece was perforated.

TABLE 6.1 Composition of Alloy Types Considered for Incinerator Service and Related High-Temperature Service

Alloy	C	Si	Mn	Ni	Cr	Co	Mo	Fe	Other
Carbon and Low-Alloy Steels									
A106 Grade B	0.3	0.1	0.8	---	---	---	---	Bal	
A213 Grade T11	0.15	0.75	0.4	1.25	0.5	---	---	Bal	
Chromium Steels									
Type 416	0.08	1.0	0.5	---	13.0	---	---	Bal	
Type 446	0.20	0.75	1.5	0.5 (max)	26.5	---	---	Bal	
Fe-Cr-Ni Alloys									
Type 304	0.06	0.75	2.0	9.5	19.0	---	---	Bal	
Type 216L	0.03	0.75	2.0	12.5	17.0	---	2.3	Bal	
Type 321	0.08	0.78	2.0	11.0	19.0	---	---	Bal	To 5 x c
USS-18-18-2	0.08	2.0	---	18.0	18.0	---	---	Bal	
Chromo 15-13-8	0.06	1.0	5.0	13.0	22.0	---	2.0	Bal	
Type 309	0.20	1.0	2.0	12/15	22/15	---	---	Bal	
Type 310	0.08	1.0	2.0	19/22	25.0	---	---	Bal	
Carpenter 20	0.08	1.0	2.0	29.0	20.0	---	2.0	Bal	3.0 Cu
RA 330	0.05	1.0	1.5	35.0	19.0	---	---	Bal	
Cr-Ni Alloys									
Incoloy 800	0.05	0.5	0.75	32.5	21.0	---	---	46.0	0.4 Cu, 0.4 Al
Incoloy 825	0.03	0.25	0.5	42.0	21.5	---	3.0	30.0	2.25 Cu, 0.1 Al
Hastelloy F	0.05	1.0	1.5	45.0	22.0	2.5	6.0	21.0	1.0 Cu
Hastelloy G	0.05	1.0	1.5	45.0	22.0	---	6.5	20.0	2.0 Cu
Hastelloy S	0.02(max)	0.4	0.5	68.0	15.5	---	45.0	1.0	0.009 B
Hastelloy X	0.10	1.0	1.0	47.0	22.0	1.5	9.0	18.5	0.6 W
Inconel 600	0.08	0.25	0.5	76.0	15.5	---	---	8.0	0.26 Cu
Inconel 601	0.45	0.25	0.5	60.5	23.0	---	---	14.0	1.35 Al, 0.25 Cu
Inconel 625	0.05	0.25	0.25	61.0	21.5	---	9.0	2.5	0.2 Al
Inconel 617	0.07	---	---	54.0	22.0	12.5	9.0	---	1.0 Al
Hastelloy C-276	0.02	1.0	1.0	56.5	15.0	2.0	16.0	5.5	4.5 W
Inconel 671	0.05	---	---	Bal	48.0	---	---	---	0.35 Ti
Inconel 690	---	---	---	60.0	30.0	---	---	10.0	
RA 333	0.05	1.25	1.5	45.0	25.0	3.0	3.0	18.0	3.0 W
Cobalt-Base Alloys									
Haynes 25	0.15	---	---	10.0	20.0	Bal	---	3.0	15 W
Haynes 188	0.15	---	---	22.0	22.0	Bal	---	---	14.5 W, La 0.15
N-155	0.15	0.5	1.5	21.0	20.0	20.0	3.0	Bal	2.5 W, 1.0 Cb
H-150	0.08	0.75	0.6	---	28.0	51.0	---	20.0	
Titanium-Base Alloys									
RMI-0.2 Pd	---	---	---	---	---	---	---	---	99.8 Ti, 0.2 Pd
RMI-5 Al-2 Zn-2 Mo-0.25 Si	---	0.25	---	---	---	---	2.0	---	85.75 Ti, 5.0 Al, 2.0 Zn

In addition to the field studies, the Navy is conducting laboratory studies of both ceramic and metallic materials in a hot corrosion test facility [2]. In these studies undiluted urine is injected into the air/fuel stream to simulate incinerator environments. The facility is operated cyclically to simulate expected operating procedures. Results of these studies are presented in Tables 6.2 and 6.3. The data show that Inconel 690, Inconel 671, and Haynes-150 are among the most resistant materials studied. Coatings are also being evaluated. Data for ceramic materials are discussed in Section 6.5.

TABLE 6.2 Maximum Penetration of Candidate Liner Materials (Based on Microscopic Measurements at 200 X).

	Initial Dimensions (Mils)		Maximum Penetration (Mils)	
Alloy	Width	Thickness	Width	Thickness
Nickel-Base				
Inconel 601	291	119	291	119
Inconel 617	236	123	143	123
Inconel 671	292	127	5	nil
Inconel 690	295	151	8	nil
Hastelloy S	277	225	277	225
Hastelloy X	261	150	123	150
RA-333	290	130	24	41
Iron-Base				
Haynes 309	282	117	7	35
Haynes 310	292	115	4	35
Haynes 446	279	117	44	15
RA-330	281	115	281	115
Titanium-Base				
RMI-0.2 Pd	235	132	235	132
RMI-5 Al-5 Sn-2 Zr-2 Mo-0.25 Zi	273	139	273	139
Cobalt-Base				
Haynes 25	338	129	7	5
Haynes 150	237	73	15	10
Haynes 188	292	158	7	9

Test Conditions: Length of test: 500 hours
Temperature: 760°C
Number of Thermal Cycles: 11
Fuel: Diesel with 1.0% sulfur
Air/Fuel Ratio: 30/1 (by weight)
Corrodent: Undiluted Urine (Natural)

TABLE 6.3 Hot Corrosion Rates of Candidate Incinerator Liner Materials Based on Weight Losses

Alloy	Density		Average[a] Exposed Area, in^2	Average[a] Weight Loss, mg	Average Corrosion Rate		Remarks
	lb/in^3	g/cm^3			mdd[b]	ipy[c]	
<u>Nickel-Base</u>							
Inconel 601	0.291	8.04	1.364	3773.5	2134	0.3815	Heavy Scaling (Fell Apart)
Inconel 617	0.302	8.36	1.264	2312.2	1359	0.2342	Heavy Scaling
Inconel 671	0.284	7.86	1.350	34.95	19	0.0035	Very Light Scaling
Inconel 690	0.294	8.14	1.439	30.9	16	0.0028	Very Light Scaling
Hastelloy S	0.316	8.75	1.460	12460.6	6347	1.0449	Completely Corroded (No Metal Left)
Hastelloy X	0.297	8.22	1.294	2472.9	1421	0.2488	Heavy Scaling
RA-333	0.298	8.25	1.380	444.2	239	0.0418	Moderate Scaling
<u>Iron-Base</u>							
Haynes 309	0.287	7.94	1.299	243.5	139	0.0253	Light Scaling
Haynes 310	0.287	7.94	1.286	123.8	72	0.0130	Light Scaling
Haynes 446	0.270	7.47	1.299	220.4	126	0.0243	Moderate Scaling
RA-330	0.289	7.99	1.282	6556.8	3800	0.6841	Completely Corroded (No Metal Left)
<u>Titanium-Base</u>							
RMI-0.2 Pd	0.163	4.51	1.187	2460.6	1541	0.4918	Heavy Scaling (Fell Apart)
RMI-5Al-5Sn-2Zr-2Mo-0.25Si	0.163	4.51	1.316	3626.8	2049	0.6541	Heavy Scaling (Fell Apart)
<u>Cobalt-Base</u>							
Haynes 25	0.330	9.13	1.473	683.4	345	0.0544	Moderate Scaling
Haynes 150	0.291	8.05	0.954	54.1	42	0.0075	Very Light Scaling
Haynes 188	0.330	9.13	1.469	584.7	296	0.0466	Moderate Scaling

<u>NOTES:</u>
[a] Average value for two (2) specimens in the same test.
[b] mdd = milligrams per square dm per day = 372W/AT; where W = weight loss (mg), A = exposed area (in^2), T = length of test (hours).
[c] ipy = inches penetration per year = mdd x 0.00144/density of metal

<u>TEST CONDITIONS:</u>
Length of Test = 500 hours
Temperature = 760°C
Number of Thermal Cycles = 11
Fuel = Diesel (with 1.0% sulfur)
Air/Fuel Ratio = 30/1 (by weight)
Corrodent = Undiluted Urine (Natural)

6.3 Principles of Materials Stability

6.3.1 Thermodynamics

Before considering specific materials of construction, the principles which determine the stability of alloys and ceramics in incinerator environments are discussed. Equilibrium thermodynamics is used to develop reasonable assumptions to predict the general direction of corrosion reactions. The fact that corroding systems are not at equilibrium does not necessarily vitiate this approach.

The thermodynamic criterion for stability of materials in two adjacent mdeia (i.e., gas and oxide) is that the chemical potentials of components in the two systems be equal. When a metal, alloy, or ceramic is exposed to a liquid or a gas, corrosive reactions will occur until equilibrium is achieved. In practice, equilibrium between materials of construction and the media usually does not exist, and the materials are instable. Examples of typical instabilities are the solution of metals and alloys in liquid media, the growth of scales (e.g., oxides, sulfides, etc.) on metals exposed to gases, and vaporization processes.

When materials instabilities exist, kinetic processes control the rates at which equilibrium is approached. Such reaction processes usually can be visualized as a sequence of steps or partial reactions. These partial reactions may be in series or in parallel, with the slowest step in series controlling the rate of reaction. The partial steps in the total reaction do not proceed independently. In fact, the rates of the different partial reactions are coupled so that the rates of all the processes in the total series sequence are equal to that of a rate-controlling process.

Even though materials instabilities arise because of the lack of thermodynamic equilibrium, equilibrium thermodynamics can be used to help describe the nature of these instabilities. For example, the stability diagram presented in Figure 6.3, which was constructed by using equilibrium thermodynamics, can help to describe the corrosion of nickel in SO_2-O_2 gas mixtures by identifying the phases that can be stable on the surface of nickel in such environments [4]. The partial pressures of oxygen and sulfur established by SO_2 at 1000°C are indicated by the dot in Figure 6.3. NiO is the stable reaction product. When nickel is heated in flowing SO_2 at 1000°C, however, a reaction product is formed as shown in Figure 6.4. The stability diagram can help to account for the observed results. Formation of the NiO as a continuous barrier reduces the oxygen pressure at the NiO/Ni interface. The sulfide phase can therefore be formed beneath the oxide layer providing sulfur can diffuse through the oxide barrier.

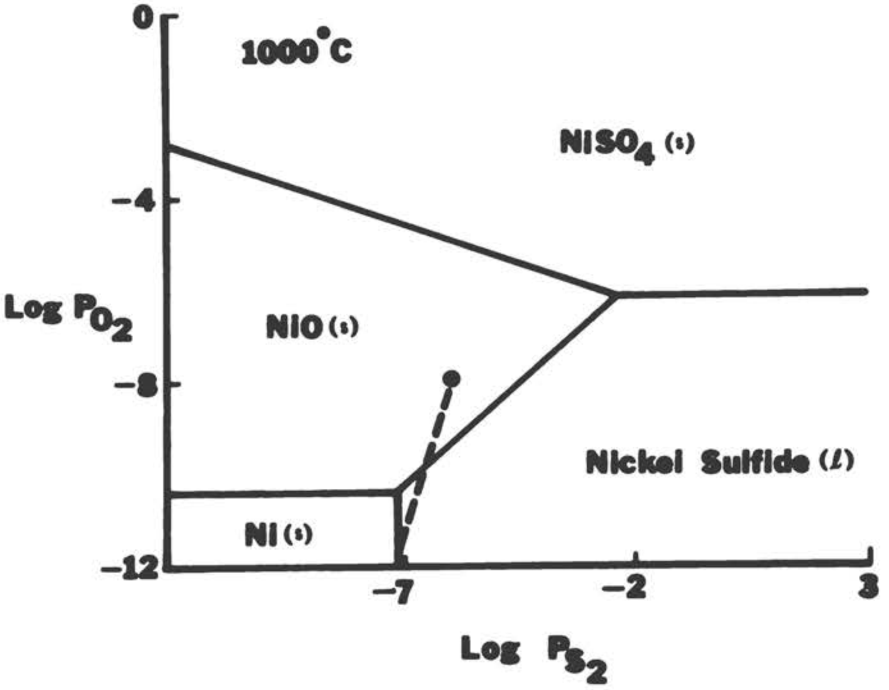


Figure 6.3 Isothermal Section of the Ni-S-O Phase Diagram Showing the Oxide and Sulfide Phases That May Be Stable on Nickel. The dashed line indicates a compositional gradient across the reaction product barrier for which a sulfide phase will be stable beneath a layer of oxide [4].

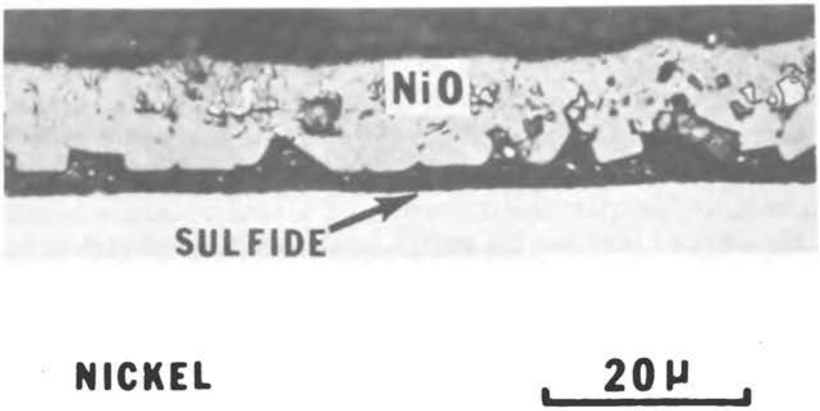


Figure 6.4 Photomicrograph Showing Microstructure of Nickel Specimen After Eight (8) Hours of Oxidation in Flowing SO_2 at 1000°C [5]

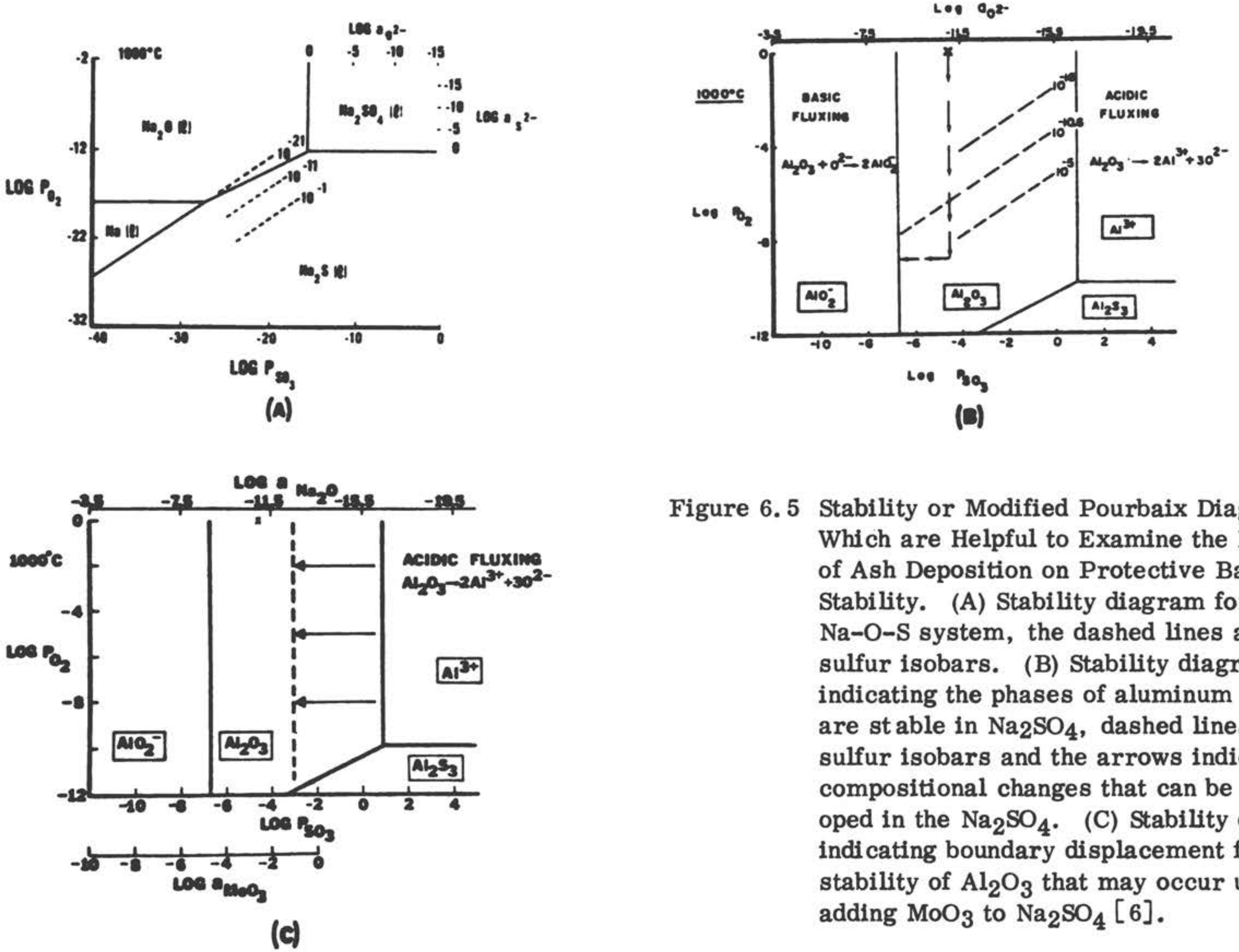
The sequence of reaction products observed in Figure 6.4 is indicated in the stability diagram by the dashed line in Figure 6.3. In instances where the NiO layer is not continuous and protective, the composition of the gas adjacent to the nickel can be modified so that both the oxide and sulfide are stable; this situation corresponds to compositions along the boundary between the NiO and sulfide regions of Figure 6.3. For such a case, a duplex scale composed of NiO interspersed with nickel sulfide may be formed.

Stability diagrams can also be used to compare the stability of reaction product barriers in various salt or ash deposits. If the stability of Al_2O_3 barriers in Na_2SO_4 is taken as an example, it is first necessary to describe the compositional limits of Na_2SO_4 by using the diagram presented in Figure 6.5a [6]. After the composition of the Na_2SO_4 is defined using oxygen and SO_3 pressures, or any other appropriate variables (e.g., P_{O_2}, P_{SO_2}; P_{O_2}, P_{S_2}), the phases of aluminum that are stable in Na_2SO_4 can be identified by constructing the stability diagram presented in Figure 6.5b. Examination of this stability diagram shows that Al_2O_3 is stable in Na_2SO_4 for a range of compositions. However, for low SO_3 pressures (or high oxide ion concentrations) aluminate (i.e., AlO_2^-) rather than Al_2O_3 is stable. At high SO_3 pressures (low oxide ion concentration) Al^{3+} ions are stable instead of Al_2O_3. Al_2O_3 barriers will protect alloys from Na_2SO_4-induced corrosion for only those compositions of Na_2SO_4 where the Al_2O_3 is stable.

In many instances, the deposited ash is not only Na_2SO_4, but contains other oxides such as V_2O_5 or MoO_3. The influence of such oxides on the stability of Al_2O_3 in the oxide-Na_2SO_4 mixture can also be described by using stability diagrams. The stability diagram presented in Figure 6.5c shows that upon adding MoO_3 to Na_2SO_4, the region in which Al_2O_3 is stable is decreased by the Al_2O_3-Al^{3+} boundary being displaced to lower SO_3 pressures.

As in the case of the corrosion of nickel in SO_2, the development of continuity of the Al_2O_3 barriers on the surfaces of alloys is cruicial in determining whether the Al_2O_3 will protect the alloy. This is especially true for ash or salt deposit-induced corrosion because the composition of the deposit can change during the course of the corrosion process. For example, if a specimen develops an Al_2O_3 barrier upon immersion in Na_2SO_4, the amount of oxygen which must diffuse through the Na_2SO_4 deposit to let the oxide grow is small, and the composition of the Na_2SO_4 remains close to that of the gas from which it condensed. On the other hand, if the Al_2O_3 is not continuous upon immersion in the Na_2SO_4, an oxygen gradient can be developed across the Na_2SO_4 deposit, which in turn can cause the composition of the Na_2SO_4 to be changed to a composition where Al_2O_3 is not stable (see Figure 6.5b).

In summary, equilibrium thermodynamics is useful for examining materials instabilities. The effective application of equilibrium thermodynamics to material instabilities, however, requires a complete characterization (e.g., microstructure, phase identification, composition) of the reaction products which are formed as a result of the materials instabilities.



(A)

(B)

(C)

Figure 6.5 Stability or Modified Pourbaix Diagrams Which are Helpful to Examine the Effects of Ash Deposition on Protective Barrier Stability. (A) Stability diagram for the Na-O-S system, the dashed lines are sulfur isobars. (B) Stability diagrams indicating the phases of aluminum that are stable in Na_2SO_4, dashed lines are sulfur isobars and the arrows indicate compositional changes that can be developed in the Na_2SO_4. (C) Stability diagram indicating boundary displacement for the stability of Al_2O_3 that may occur upon adding MoO_3 to Na_2SO_4 [6].

6.3.2 Development of Reaction Product Barriers

Gases and/or liquid ash or salt deposits cause instabilities in materials of construction used for shipboard incinerators. To develop materials resistant to such media, the reaction products, formed as a result of the instabilities, must inhibit the reaction. Such inhibition occurs when a reaction product barrier is formed on the surface of the material to separate the reactants and to control the rate and the nature of the reaction. For example, the corrosion of nickel in SO_2 at 1000°C appears to be controlled by transport of nickel and sulfur through the continuous layer of NiO which separates the gas from the metal. Since transport through Al_2O_3 is much slower than transport through NiO, a more corrosion-resistant system may be obtained by alloying nickel with Al_2O_3, providing the Al_2O_3 is formed as a continuous, dense barrier over the surface of the alloy.

Theoretical analyses of the factors which influence the development of continuous reaction product barriers on the surfaces of materials have been pioneered by C. Wagner and others [7-23]. Continuity in reaction product barriers develops during a transient period at the beginning of the corrosion process (see Figure 6.6) for the formation of NiO, Cr_2O_3 and Al_2O_3 barriers on NiCrAl alloys [24]. The development of oxide barriers on alloys exposed to oxygen is reasonably well understood. The development of sulfide and chloride reaction product barriers on metals and alloys exposed to sulfur [6] and chlorine [25], respectively, has been described, but less extensively than the oxide barriers. The development of reaction product barriers in multicomponent gas environments or in the presence of ash deposits has not been studied extensively. Such conditions frequently produce adverse effects on the formation of the continuous barriers which are most effective in developing corrosion resistance in materials.

Oxide reaction product barriers are usually more effective in protecting alloys than the other type of barriers that can be formed on alloys (e.g., sulfide, chloride, nitride). For example, in Table 6.4, the parabolic rate constants for growth of oxides on different alloys can be seen to be substantially less than that for the growth of sulfides [26]. In addition, oxides are usually more thermodynamically stable than other types of reaction product barriers. In view of these conditions, and since most environments encountered in practice contain some oxygen, oxide barriers are usually the most effective barriers used to develop corrosion resistance in materials.

Some oxide barriers are more effective in protecting alloys than others. For example, parabolic rate constants for the growth of some different oxides are compared in Figure 6.7 [4]. Al_2O_3, Cr_2O_3, and SiO_2 barriers produce slower oxidation rates than either NiO or CoO. Most of the commercially available alloys used at elevated temperatures (i.e., 800°C and above) rely upon the formation of either Al_2O_3 (e.g., B-1900, aluminide coatings, MCrAlY overlay coatings) or Cr_2O_3 (e.g., Hastelloy X, Haynes-188, X-40, Inconel 601, Inconel 671, Types 304, 309 and 310 stainless steels) to develop oxidation resistance [27]. The upper use temperature of the alloys with Cr_2O_3 barriers, however, is about 1000°C; above this temperature, the reaction of Cr_2O_3 with oxygen to form gaseous Cr_2O_3 becomes significant and the metal degrades by volatilization.

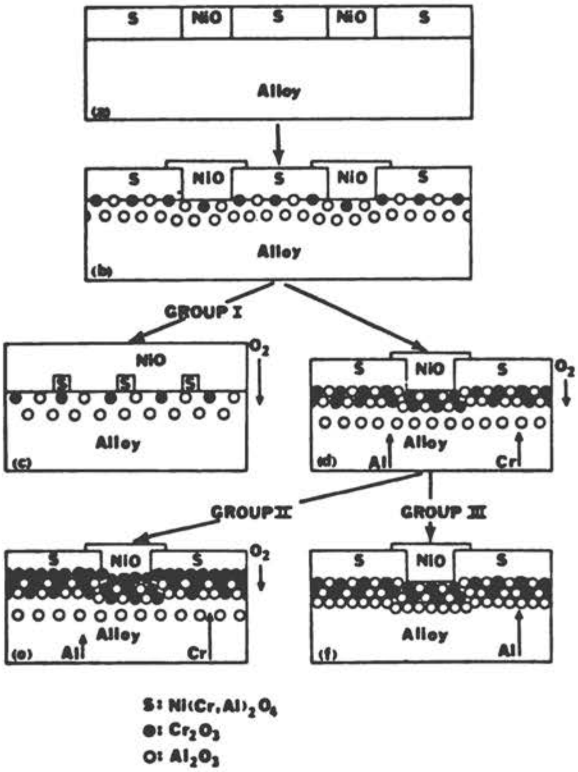


Figure 6.6 Schematic Diagram Illustrating the Transient Processes That Take Place During the Formation of NiO, Cr_2O_3, or Al_2O_3 Barriers on NiCrAl Alloys [24].

TABLE 6.4 Parabolic Rate Constants of Sulfidation and Oxidation of Some Binary and Ternary Alloys

Alloy	Temperature °C	k_p (g^2 cm^{-4} min^{-1})	
		Sulfidation	Oxidation
Fe-20Cr	1000	$5.9 \cdot 10^{-4}$	$1.2 \cdot 10^{-9}$
Fe-20Cr	900	$1.1 \cdot 10^{-4}$	$1.0 \cdot 10^{-10}$
Ni-20Cr	1000	$5.3 \cdot 10^{-4}$	$3.0 \cdot 10^{-9}$
Co-20Cr	800	$1.6 \cdot 10^{-5}$	$5.0 \cdot 10^{-11}$
Fe-25Cr-5Al	1000	$6.5 \cdot 10^{-5}$	$1.6 \cdot 10^{-11}$
Ni-20Cr	800	$6.0 \cdot 10^{-5}$	$1.2 \cdot 10^{-10}$

Source: Reference 26

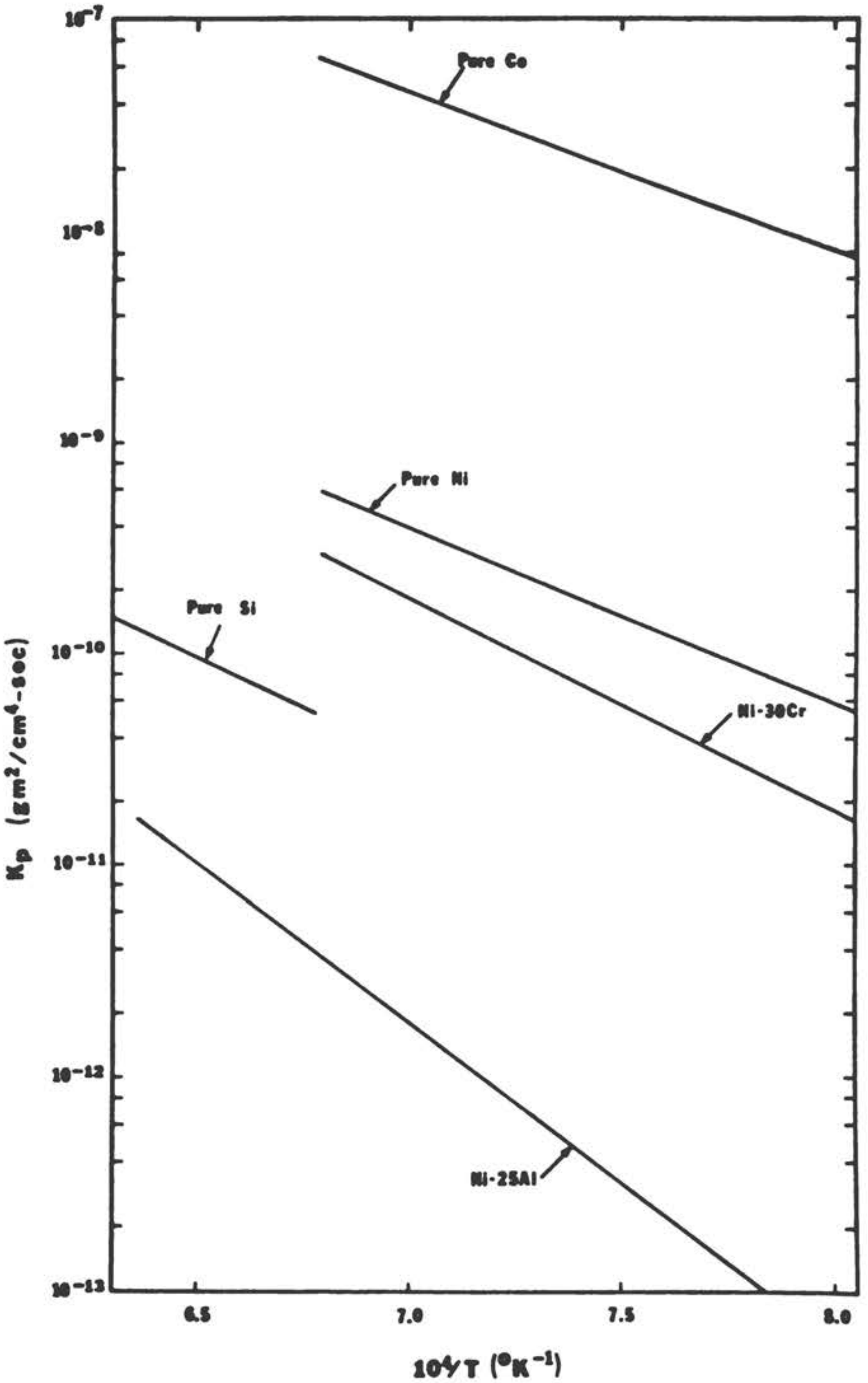


Figure 6.7 Temperature Dependence of the Parabolic Rate Constants Obtained for the Growth of Various Oxide Barriers on Pure Metals (CoO on Co, NiO on Ni, SiO_2 on Si) and Alloys (Cr_2O_3 on Ni-30Cr, Al_2O_3 on Ni-25Al). The oxidizing environments for the data presented were 0.1 atmosphere oxygen for Ni, Ni-30Cr and Ni-25Al; 0.125 atmosphere oxygen for Co; and 1 atmosphere oxygen for Si [4].

6.3.3 Destruction of Protective Reaction Product Barriers

Numerous alloys are available which are protected by barriers of Al_2O_3 or Cr_2O_3 which form in very severe environments, including the environments developed in shipboard incinerators. However, for many of the alloys, the oxide barriers are rendered nonprotective after relatively small exposure times. Protective oxide barriers can be rendered ineffective during use by three principal means, (1) cracking and spalling of the barriers as a result of the generation of stresses in the barriers, (2) chemical reaction of the barriers with the environment, and (3) erosion of the barriers. These are described in the following sections.

6.3.3.1 Stress-Induced Barrier Damage. There are three sources of stress in oxide barriers: growth stresses, externally applied stresses, and thermal stresses. The growth of oxide scales on alloys is almost always accompanied by stresses in the oxide scales [28]. Depending on the type of oxide barrier, these growth stresses may be either tensile or compressive. With Al_2O_3, Cr_2O_3, or SiO_2 barriers, the growth stresses are compressive. Growth stresses do not appear to be a major source of damage to the oxide barriers normally used to protect alloys.

Stresses can be developed in barriers on alloys as a result of externally applied loads. The nature of such stresses depends upon the particular application. Generally, the amount of strain for engineering purposes that can be tolerated in the alloy is small, and the effect of such stresses on the oxide barrier may therefore be negligible. This should certainly be true at temperatures above 1100°C since stress relief through deformation of the oxide scale is to be expected; the features of the Al_2O_3 scale in Figure 6.8 attest to high temperature plasticity of protective films [29]. The influence of cyclically applied loads on protective oxide barriers has not been studied in detail. It appears that cyclically applied loads may be the most deleterious external loads in damaging oxide barriers, but this has not been demonstrated.

Oxide barriers can be rendered nonprotective by thermally-induced stresses which cause cracking and spalling of the barriers. Usually, thermally-induced stresses are cyclic. Large amplitude, low-frequency thermal stresses are capable of producing substantial cracking and spalling of oxides from alloys (see Figure 6.9) [2]. Recently, Dils [30] proposed that thermal stresses with small amplitude and high frequency, as developed in materials during operation of gas turbines, may also substantially damage oxide barriers. Since cracking and spalling of oxide barriers is one of the principal modes by which alloys are degraded in corrosive environments, the adhesion of barriers to alloys is critical. The use of oxygen-active elements in alloys [31] improves the adhesion of oxide barriers (see Figure 6.10) [32]. Improved adherence of Al_2O_3 barriers on MCrAlY coatings, because of the oxygen-active element yttrium, is the basis for the improved performance of these coatings [33]. Inert oxide particles [34] of platinum [35] also can be used in some alloys to improve the adhesion of Al_2O_3 and Cr_2O_3 barriers.

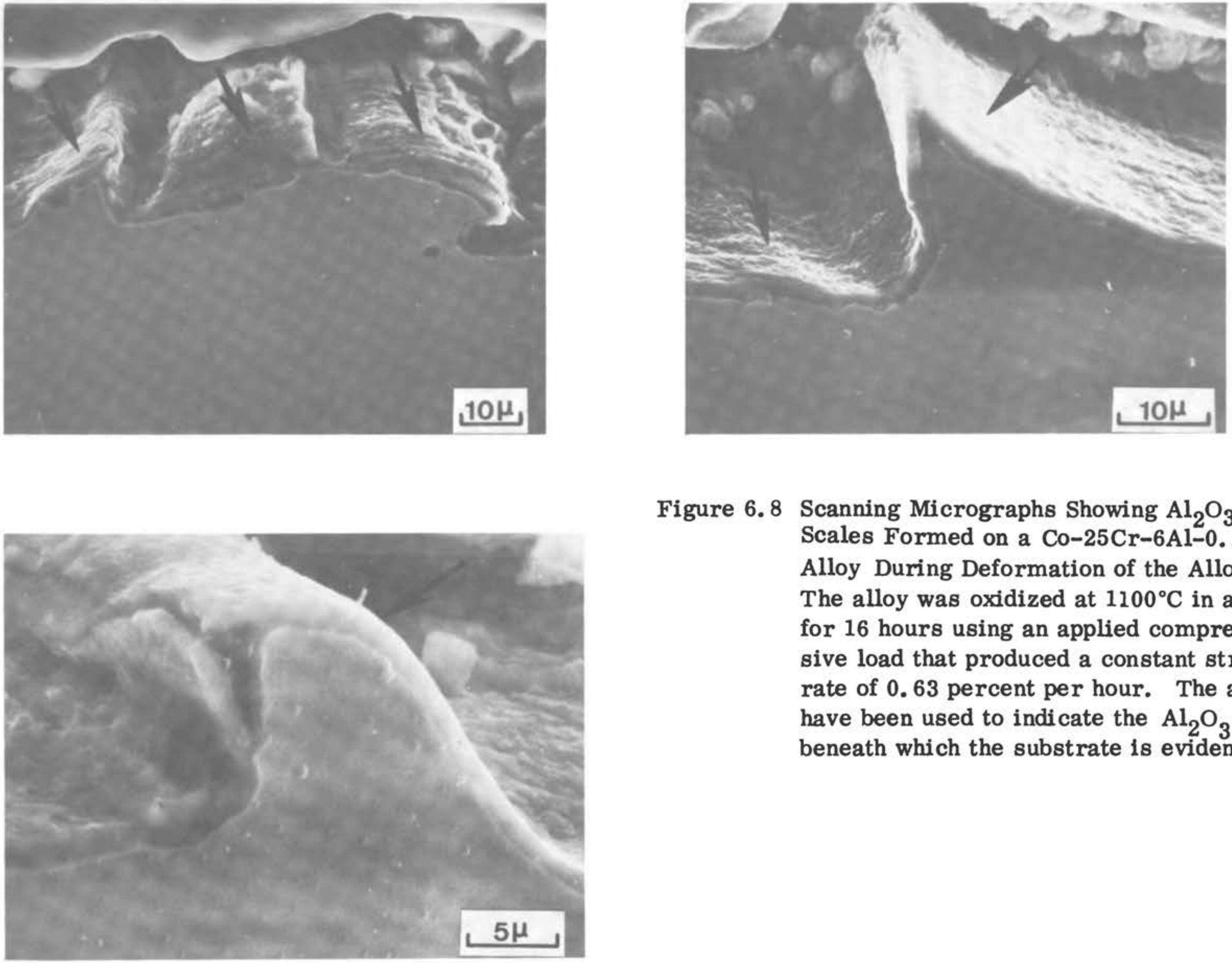


Figure 6.8 Scanning Micrographs Showing Al_2O_3 Scales Formed on a Co-25Cr-6Al-0.2Y Alloy During Deformation of the Alloy. The alloy was oxidized at 1100°C in air for 16 hours using an applied compressive load that produced a constant strain rate of 0.63 percent per hour. The arrows have been used to indicate the Al_2O_3 scale beneath which the substrate is evident [29].

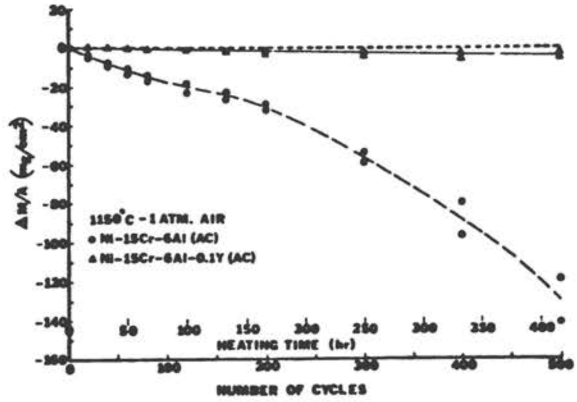
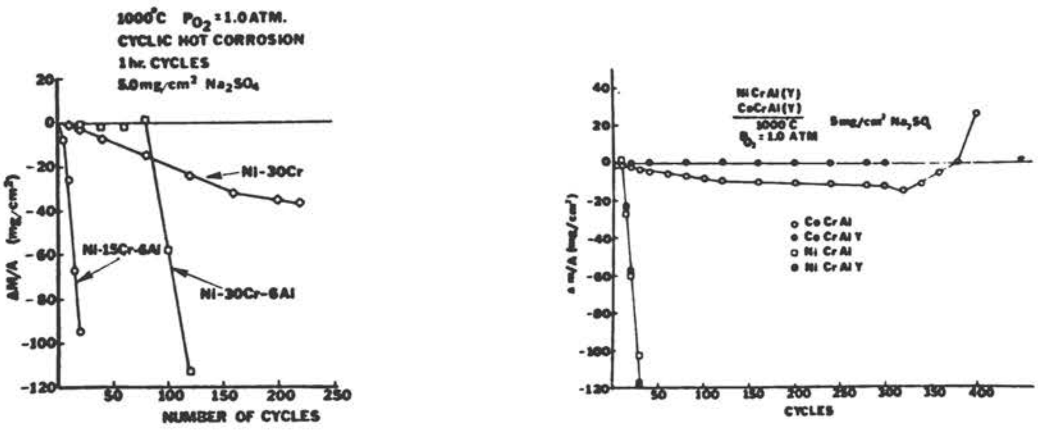
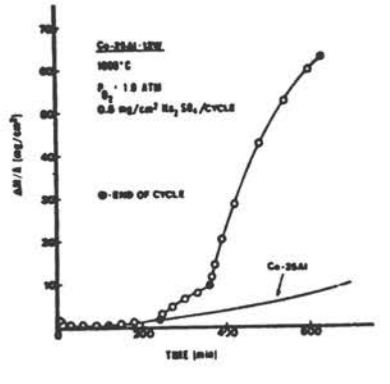


Figure 6.9 Comparison of Weight-Change Data Obtained with Ni-15Cr-6Al and Ni-15Cr-6Al-0.1Y Specimens. Yttrium improves the adhesion of Al_2O_3 scales and less degradation of the NiCrAlY alloy has occurred. (Each cycle consists of 50 minutes at the test temperature and 10 minutes at room temperature.) [4]



(A)

(B)



(C)

Figure 6.10 Data Obtained from the Cyclic Oxidation of Na_2SO_4-coated Specimens. (A) The time to initiate severe hot corrosion attack, as indicated by the specimen weight losses, is dependent on the chromium and aluminum concentration of the NiCrAl alloys. (B) CoCrAl(Y) alloys are much more resistant to the initiation of hot corrosion attack than NiCrAl(Y) alloys with the same concentrations of chromium and aluminum. (C) The hot corrosion attack of Co-25Al is much more severe when tungsten is added to this alloy [32].

6.3.3.2 Barrier Damage Induced by Chemical Reactions. In discussing barrier damage induced by chemical reactions, it is useful to divide the corrosion process into an initiation stage and a propagation stage. In the initiation stage, the protective oxide barrier is stable, or is being reformed on the alloy surface, but processes also occur that will produce eventual instability of this barrier. In the propagation stage, the most protective barrier is no longer stable on the alloy surface, and the corrosion rate is controlled by some other process than transport through the most protective oxide barrier.

All alloys, when used at elevated temperatures, eventually reach the propagation stage of the corrosion process. Certain environmental conditions, however, can greatly accelerate this process. Conditions that lead to cracking and spalling of the oxide barriers significantly reduce the initiation stage. Ash deposition on the surfaces of alloys or exposure of alloys to environments containing other oxidants in addition to oxygen can also shorten the initiation stage since the oxide barriers are destroyed or prevented from being reformed by the presence of the ash or certain components in the environment.

The mechanisms by which ash deposits or certain oxidants in the environment induce oxide barrier damage depend upon the ash composition and the nature of the various oxidants. Generally, such chemical reaction-induced effects are of two types [36]. The first involves the presence of a liquid phase on the surfaces of the alloys which dissolves the protective oxide barrier. The liquid phase is formed usually as result of ash deposition, but in some instances reaction of the ash with the alloy is necessary before a liquid phase is developed or before dissolution of the oxide barrier in the liquid is possible (see Figure 6.5c). The second type of chemical reaction barrier damage occurs because elements from the ash or the gas enter the alloy and develop conditions that prevent the oxide barrier from reforming after it has been damaged by some other means (e.g., thermally-induced stresses).

Sodium-potassium sulfate is a common component of the ash deposited in marine gas turbines and incinerators. As indicated in Figure 6.10, Na_2SO_4 deposits can cause severe degradation of alloys upon which protective layers of Al_2O_3 are usually formed during oxidation in air. The data presented in Figure 6.10 show the effect of different alloying elements on the Na_2SO_4-induced corrosion of alloys. Increasing the chromium content extends the initiation stage of the corrosion process, whereas aluminum appears to shorten it (see Figure 6.10 A). Aluminum produces deleterious effects, usually at low concetrations (e.g., 2 to 6 percent) and is effective in extending the initiation stage for aluminum contents of 10 percent and above. In Figure 6.10 B, the use of cobalt in place of nickel in alloys containing chromium and aluminum is an effective means to extend the initiation stage. Yttrium in a CoCrAl alloy prolongs the initiation stage by making the Al_2O_3 more resistant to spalling. Finally, the data presented in Figure 6.10 C show that alloys with tungsten are susceptible to severe corrosion induced by Na_2SO_4 deposits. Alloys containing tungsten, molybdenum, or vanadium are susceptible to Na_2SO_4-induced corrosion because oxides of these metals cause Na_2SO_4 to become an acidic flux for oxide barriers such as Al_2O_3 or Cr_2O_3.

Sulfate deposits at times contain a substantial amount of chloride. Sulfate-chloride deposits are usually more effective than sulfates in decreasing the initiation stage for rapid oxidation. The mechanism by which chloride contributes to damaging the oxide barriers has not been clearly described. When chloride is present in the deposit [37], cracking and spalling of the oxide barriers is more prevalent.

6.3.3.3 Erosion-Induced Barrier Damage. In incinerators, materials may be subjected to erosive as well as corrosive environments. Adler [38] and Finnie [39] have analyzed the effects produced by particulate erosion on bulk materials, but the erosion of thin reaction product barriers on alloys has not been investigated. There is no doubt that sufficiently severe erosive conditions shorten the initiation stage of the corrosion process for almost any alloy since oxide barriers are worn away or extensively and repeatedly cracked. The important, but still poorly understood, condition is combined erosion-corrosion that results in degradation more severe than in either of these processes by themselves. At present, in view of the inadequate understanding of combined erosion-corrosion effects, it appears reasonable to use in erosive environments those oxide barriers which are highly adherent to metallic substrates.

In some instances, the erosive conditions may be so severe that the corrosion processes are unimportant. When the erosion rates are not acceptable, it is necessary to lessen the severity of the erosion conditions or use materials more resistant to erosion. The modifications of alloys necessary to achieve erosion resistance (e.g., higher hardness) usually are not compatible with corrosion resistance. Consequently, as erosion resistance is improved, corrosion resistance decreases, and combined erosion-corrosion is approached.

6.3.4 Localized Attack Phenomenon

In dicussing the localized attack of materials, it is useful to consider, first, high temperature processes (about 600°C and above) and then the processes which take place at lower temperatures. This diversion according to temperatures follows different processes for corrosive attack.

6.3.4.1 High Temperature Localized Attack. High temperature localized attack of materials occurs for a number of reasons. Complex alloys are composed of numerous phases, and the reaction product barriers may not be equally protective for all phases, as shown in Figure 6.11. In some alloys, elements may be segregated to grain boundaries. Such segragation can result in localized corrosion because the phases which are formed at grain boundaries are not as resistant to attack as the alloy matrix, or this segregation causes the alloy matrix to be depleted of elements necessary for corrosion resistance. Preferential oxidation of carbides at the grain boundaries of Haynes-188 is shown in Figure 6.12.

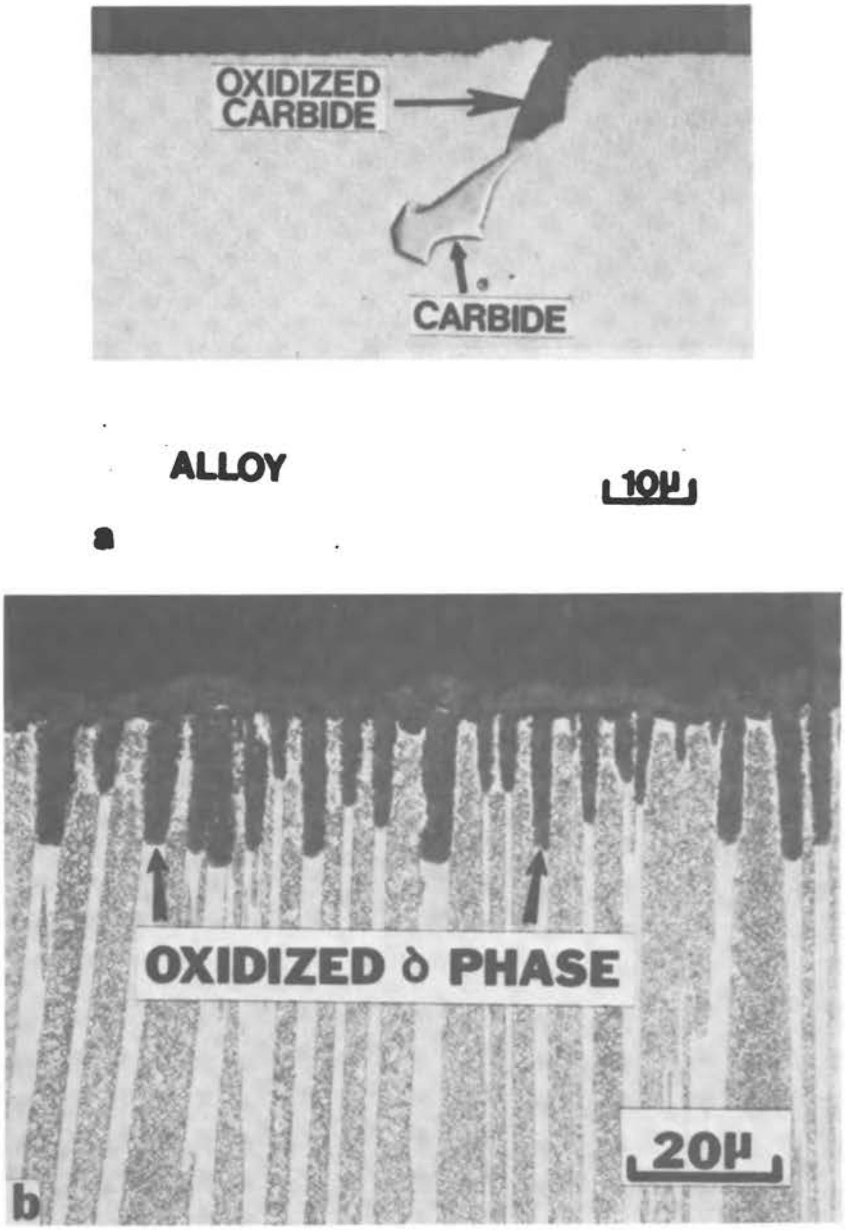


Figure 6.11 Photomicrographs Showing the Preferential Oxidation of Different Phases in Alloys. (a) A nickel-base superalloy (B-1900) after oxidation at 1100°C. (b) Directionally-solidified Ni-Cb-Cr-Al alloy after oxidation at 700°C. [4].

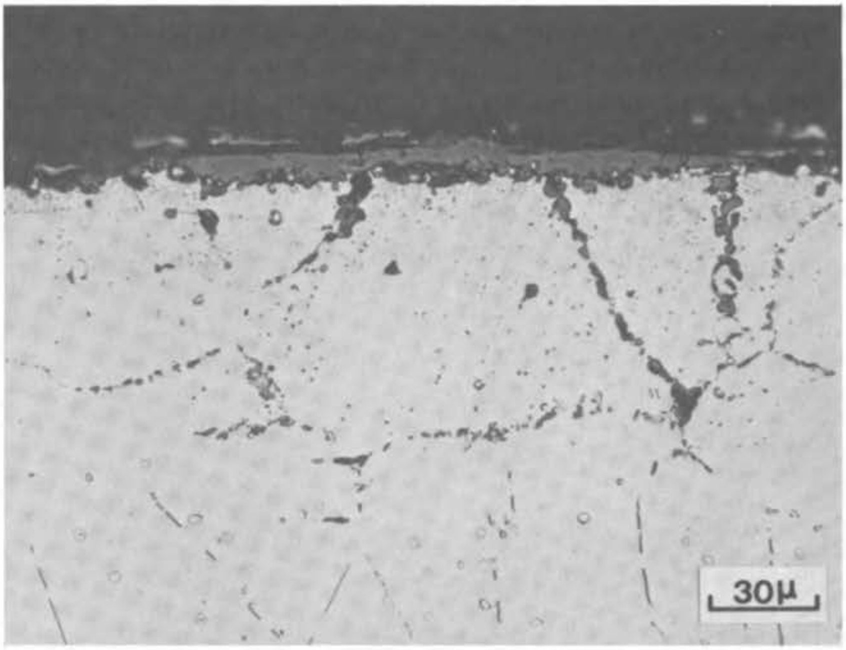


Figure 6.12 Microstructural Characteristics of Haynes-188 Alloy After Cyclic Oxidation at 1000°C in One Atmosphere of Air for 1000 Hours [40].

Crevices in alloys can produce undesirable corrosion phenomena. Compositional changes of liquids or gases in crevices can result in localized environmental conditions which are more severe than the unmodified environment, and attack is therefore initiated at these crevices.

In shipboard incinerators, materials will be subjected to ash deposition, thermally induced stresses, and perhaps particulate erosion. Such conditions accelerate localized attack of materials because ash deposition and oxide barrier cracking occur in localized regions rather than uniformly over the surfaces of materials.

6.3.4.2 Low Temperature Localized Attack. Metals are readily perforated by chemical attack at room temperature in the absence of stress. Many of the more corrosion-resistant metals are particularly susceptible to localized attack in the presence of halide ions, although they are not the exclusive environmental cause.

Localized attack of metals has been extensively considered in two special volumes [41,42] and is well treated in texts on corrosion [43,44].

Localized attack of metals follows several well known modes. Pitting produces more or less cylindrical penetrations which may progress as rapidly as 0.1 to 1.0 cm/hour in solutions when there are high chloride and oxidizing conditions. Preferential attack along the grain boundaries also progresses rapidly depending upon heat treatment of the alloy and environmental conditions. Such attack is formed by conditions which increase the corrodability of grain boundaries. This enhanced susceptibility of grain boundaries usually results from thermal treatments which cause local changes in the distribution of impurity or alloy species at grain boundaries. For example, the depletion of chromium at the grain boundaries of stainless steels by heating in the range of 500°C to 900°C makes the alloys sensitive to accelerated attack in many oxidizing solutions. The expected temperature range for operating incinerator liners may produce changes in grain boundaries. These boundaries are then susceptible to preferential attack either at operating conditions or at room temperature where precipitated water solubilizes aggressive chemicals from deposits or soot.

Two other modes of localized attack may operate. These are called crevice corrosion and galvanic corrosion. Under the worst of circumstances attack according to these modes may be equally as rapid as pitting. Crevices may be formed at mechanical joints between adjacent parts of the structure; or crevices leading to equally severe attack may exist under deposits. The principal environmental criteria for accelerated crevice attack include the presence of both oxidizing conditions which accelerate the cathodic reaction and a solubilizing medium in the crevice. These conditions could be readily available in incinerators during conditions of idleness, especially when moisture is present.

Finally, galvanic corrosion can occur if two metals of different electrochemical responses are adjacent and electrically connected.

In summary, localized attack at relatively low temperatures compared to operating temperature may occur rapidly. Such attack will be exacerbated if water is precipitated or if aggressive chemicals such as halides can be leached from deposits or soots.

6.3.5 Long Term Aging Effects

Most corrosion reactions are viewed as producing undesirable effects on alloys through the conversion of alloy to oxide, sulfide, or some other type of reaction product. During the exposure of alloys at elevated temperatures, elements from the environment can also dissolve in the alloy and affect its mechanical properties. Even in the absence of effects produced as a result of interaction between alloys and environments, long-term exposures can cause metallurgical changes in alloys that have adverse effects on mechanical properties. In the following sections, environmentally-induced aging effects are considered.

6.3.5.1 Environmentally-Induced Aging Effects. Cook and Skelton [45] conclude that premature failure of engineering components can be produced by the combined influences of corrosion and residual or applied stresses to produce effects found in corrosion fatigue and stress corrosion cracking. The choice of alloys for operation in the creep range has usually been based on the assumption that their strength and corrosion resistance are separately acceptable. There is now a growing awareness that chemical and mechanical effects interact at elevated temperatures.

Corrosion fatigue, the combined action of repeated or fluctuating stress and a corrosive environment to produce cracking, is another type of mechanical property deterioration related to the environment. Usually, an aggressive environment reduces fatigue life, producing failure in fewer stress cycles than would be required in a more inert environment. In certain instances, however, such as exposure of nickel-base superalloys to high-temperature oxidizing environments, an aggressive environment can slow the fatigue-fracture process, increasing the number of stress cycles to failure.

Hydrogen damage [46,47] is an example of a mechanical-environmental failure process that results from the initial presence or absorption of excessive amounts of hydrogen in metals, usually in combination with residual or applied tensile stresses. It occurs most frequently in high-strength steels and certain other high-strength alloys. Cracking caused by this process is often referred to as hydrogen-stress cracking and hydrogen-induced cracking.

Hydrogen damage occurs in many types of alloys, and in some instances severely restricts the use of certain materials. Because of the ready supply of hydrogen in such environments as water, moist air, hydrocarbons, acids and hydrogen sulfide, and in chemicals during processing, pumping, or storage, hydrogen damage can develop in a wide variety of circumstances.

Embrittlement by hydrogen damage manifests itself as a decrease in tensile ductility (reduction in area in laboratory testing), a decrease in notched tensile strength, and delayed failure by fracture under static loading. Yield strength is not significantly altered. In the absence of a sharp initial crack, hydrogen-induced fracture caused by the diffusion of hydrogen into the metal often begins at subsurface sites where triaxial stress is highest. When the critical stress is exceeded, a crack initiates and propagates through the region of high hydrogen concentration. Two recent volumes summarize important literature on the subject of hydrogen effects [48,49].

6.3.5.2 Non-Environmental-Induced Aging Effects. Undesirable metallurgical changes can occur in alloys as a result of long-term exposures at elevated temperatures. For example, nickel-base superalloys can be embrittled by sulfur segregation to alloy grain boundaries [50]. The data presented in Figure 6.13 show that less than 20 ppm sulfur can embrittle a nickel-base superalloy. Less embrittlement is evident with the same alloy containing hafnium due to the formation of hafnium-sulfide which inhibits sulfur segregation to the grain boundaries.

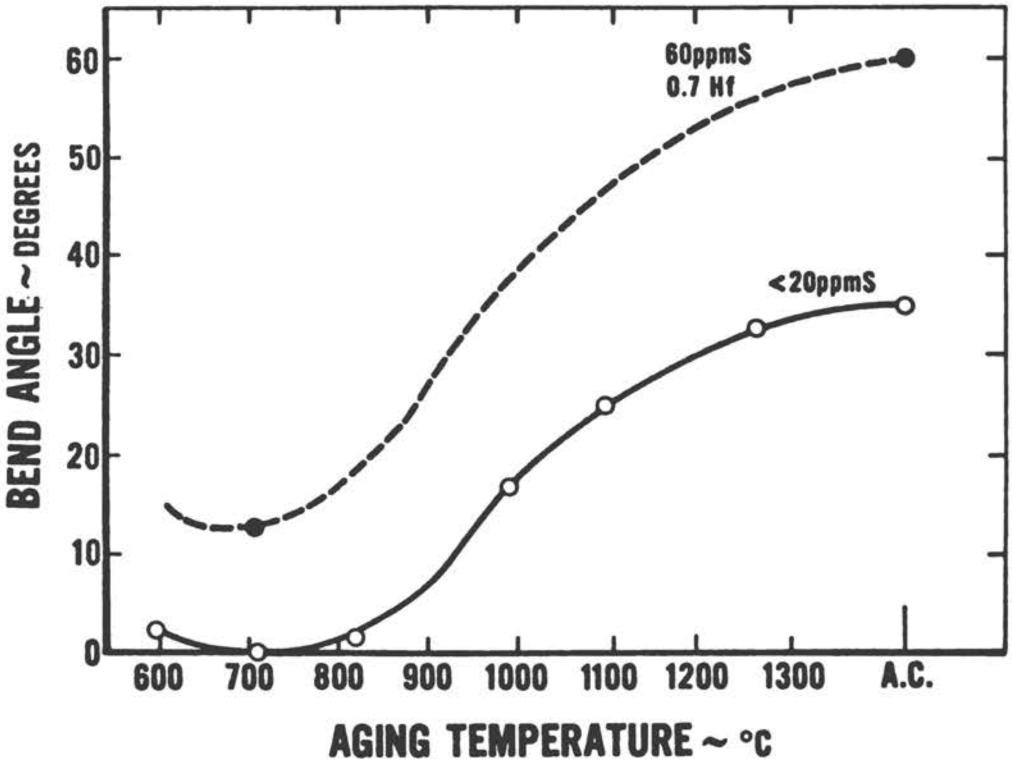


Figure 6.13 The Variation of the Bend Ductility of a Hafnium-Doped High Sulfur Alloy and An Undoped Low Sulfur Alloy with Aging Temperature. Aging time was 24 hours [50].

An aging effect of special concern is the formation of a sigma phase [28]. The formation of sigma phase in ferritic and austenitic stainless steels during long periods of exposure to temperatures between approximately 560°C and 980°C causes considerable embrittlement after cooling to room temperature. Sigma phase can be formed by either (1) slow cooling from temperatures of 1090°C to 1150°C; or (2) water quenching from 1090°C to 1150°C followed by heating at 560°C to 980°C. Heating at 850°C produces the greatest deterioration. The embrittlement is most detrimental after the steel has cooled to temperatures below 260°C. At higher temperatures, stainless steels containing sigma phase can usually withstand normal design stresses.

However, cooling to 260°C or below results in complete loss of toughness. Hence, high-temperature components containing sigma phase must be maintained with great care to prevent damage. After extended service life, boiler tubes made from high-chromium ferritic stainless steels, such as Type-466, have been known to shatter when dropped.

The presence of sigma phase greatly increases notch sensitivity. The hardness and tensile strengths are usually not significantly affected by the presence of sigma phase, but the impact strength is greatly affected. Sigma phase exerts a strengthening effect at high temperatures; however, the impact strength at high temperatures of an alloy containing sigma phase is lower than the impact strength at room temperature of an alloy without sigma phase. If resistance to impact loads at high temperatures is not required, the presence of sigma phase in high-temperature applications may be helpful. Because the high hardness of sigma phase improves wear resistance, some alloys have been designed to make use of this property.

6.3.6 Stress-Corrosion Cracking

Stress-corrosion cracking is a brittle fracture in an otherwise ductile material occurring under the combined action of corrosion and static tensile stress. The direction of the cracks is perpendicular to the direction of the applied or residual stresses. Depending upon the environment and the alloy, cracks may be either intergranular or transgranular. (See Figures 6.12, 6.13, 6.14, and 6.15.)

Stress-corrosion cracking is a particularly insidious corrosion phenomon that may be difficult to detect due to no visible indications of corrosion, and may occur in innocuous environments such as distilled water at room temperature and the earth's atmosphere. While techniques for rating the stress-corrosion cracking behavior of alloys are being developed it is not possible to predict the service life of a given alloy in a specific environment.

The important factors affecting stress-corrosion cracking are:

1. Alloy composition and heat treatment

2. The nature of the corrosive environment:

   a. Solution concentration
   b. Temperature
   c. Exposure time

3. Tensile stress, residual or applied.

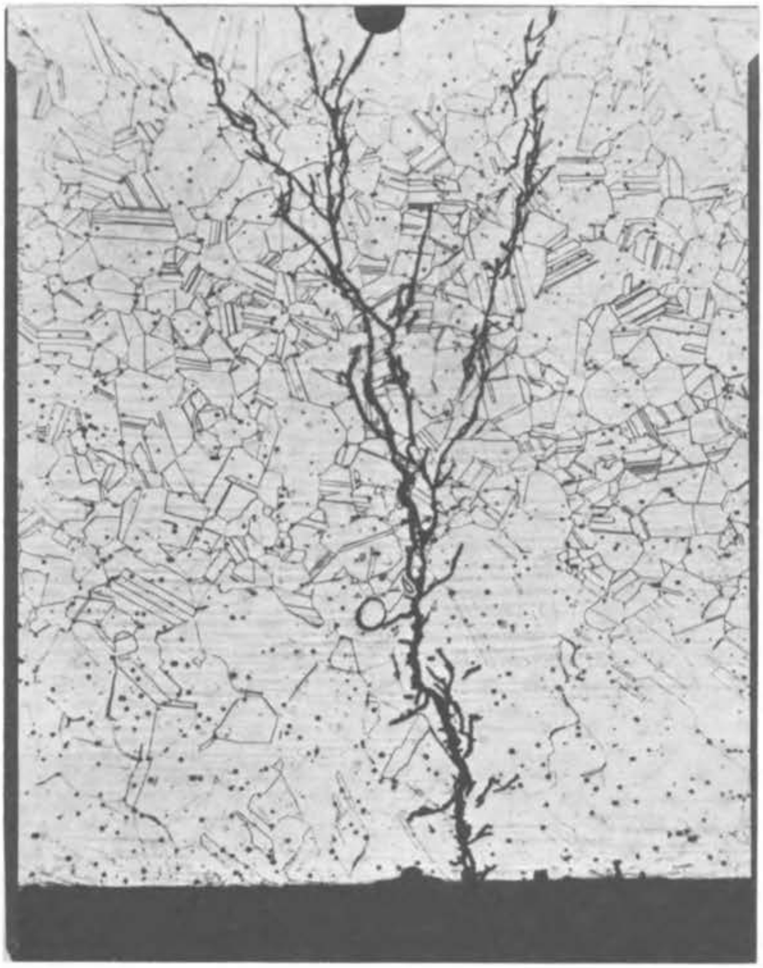
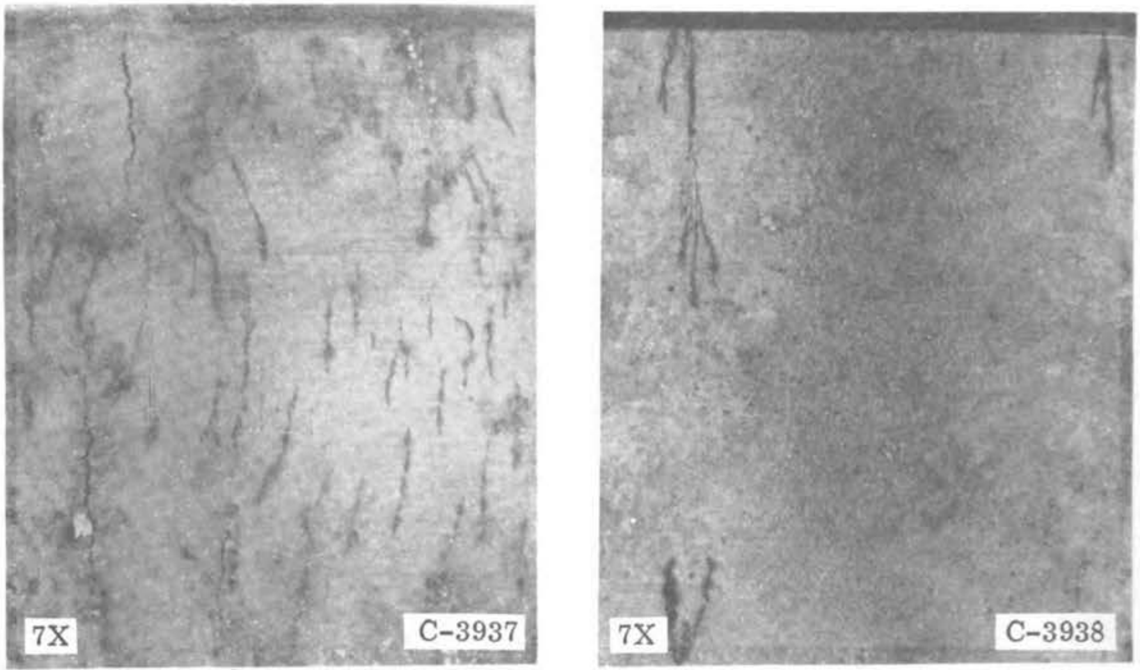


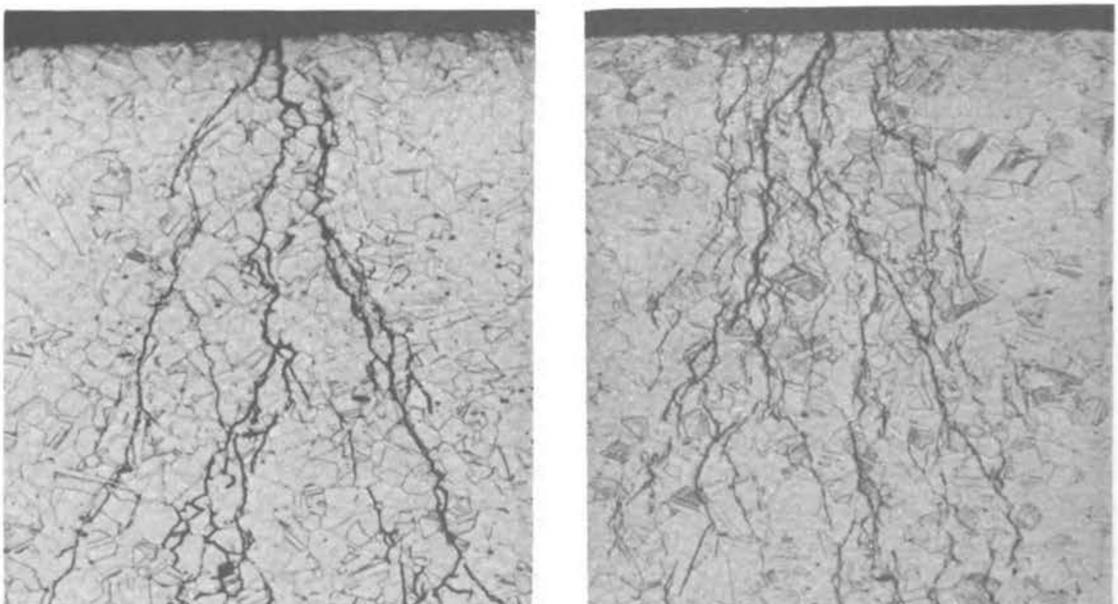
Figure 6. 14 Transgranular Stress-Corrosion Crack in C-Ring of Type 310 Stainless Steel Exposed to Incinerator Deposit Under Humid Conditions [51]

Although no environment has been identified that will universally cause cracking in all alloy systems, those containing halide ions, particularly chlorides, promote cracking in many alloy systems. Chlorides are of concern in incinerator application since they promote cracking of Fe-Cr-Ni alloys which are candidate materials of construction. Table 6. 5 shows environments in which stress-corrosion of structural alloys has been observed. Curves illustrating the action of the variables affecting stress-corrosion cracking are shown in Figure 6. 16.



a. Sensitized 2 ½ hours at 650°C.

b. Unsensitized



c. Photomicrograph of Sensitized Specimen.

d. Photomicrograph of Unsensitized Specimen.

Figure 6.15 Stress-Corrosion Cracks Resulting from Exposure of Stressed Type 304 Stainless Steel To Moist Incinerator Deposit at 75°C [51].

TABLE 6.5 Environments in Which Stress-Corrosion Cracking has Been Observed

Material	Environment
Plain carbon and low alloy steels	Caustic solutions; calcium, ammonium, and sodium-nitrate solutions; solutions containing H_2S or HCN; moist CO-CO_2; carbonate and bicarbonate solutions; seawater; marine and industrial atmospheres (high-strength, low-alloy steels); molten zinc, lithium, or Na-Pb alloys; anhydrous ammonia; $FeCl_3$ solutions (elevated temperatures); mixed acids (H_2SO_4-HNO_3).
Aluminum alloys	Moist air, marine and industrial atmospheres; seawater; NaCl, $CaCl_2$, and NH_4Cl solutions; mercury.
Stainless steels	Acid and neutral chloride solutions; seawater; molten chlorides; industrial and marine atmosphere (sensitized materials); high-purity water + O_2 at 314°C; high-temperature water + fluorides; polythionic acids.
Nickel-base alloys	Fused caustics; hot concentrated caustic solutions; hydrofluoric acid; hydrofluorosilicic acid; steam and high-temperature water containing O_2 or traces of Pb; molten lead.
Magnesium alloys	Sodium chloride-potassium chromate solutions; fluorides; tropical, industrial, and marine atmospheres; distilled water.
Titanium alloys	Red fuming nitric acid; N_2O_4 + O_2; seawater; chlorinated hydrocarbons; hot dry sodium chloride and other chloride salts at temperatures above 290°C; HCL; methanol; molten and solid cadmium; mercury; moisture.

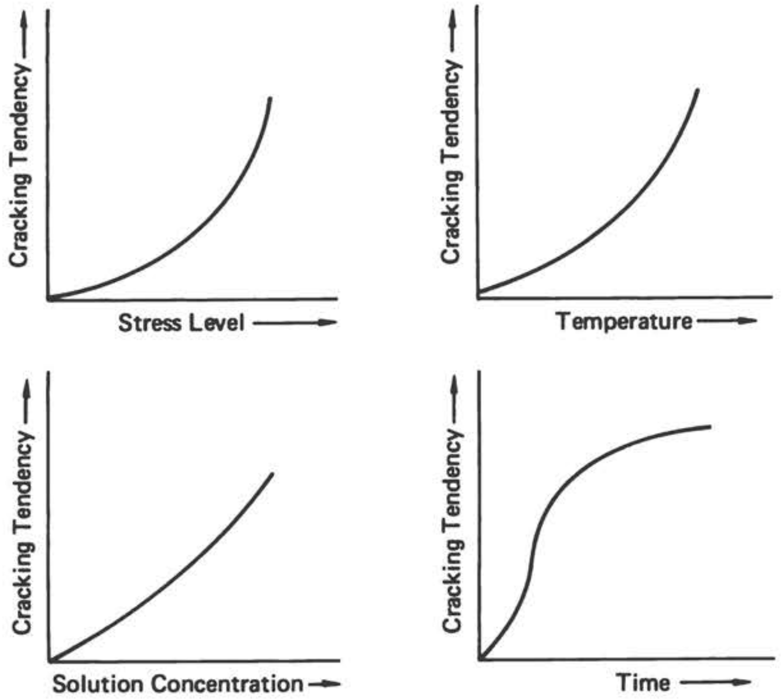


Figure 6.16 General Dependences of Stress-Corrosion Cracking

Once the crack has begun, the rate of cracking may be similar for a number of alloys. In those systems (i.e., stainless steels, aluminum, copper, and plain carbon steels) where corrosion processes are the dominant factor, velocity of cracking may be as high as 1 mm/hr. For titanium and high-strength steels, the rate of crack propagation may be higher; 10 mm/hr. or higher.

The theory of stress-corrosion cracking is poorly developed at this time; since the phenomenon was first observed in brasses, many theories and models have been proposed. Descriptions of theories of stress-corrosion cracking are listed in references 53-62.

Since the mechanism of stress-corrosion cracking is not well understood, the techniques for controlling it are general and empirical. In practice, stress-corrosion cracking can be prevented by controlling the metallurgy of the alloy, the chemistry of the environment, and/or the stress loads. Careful attention must always be given to avoiding conditions which might accidentally incite stress-corrosion cracking, i.e., the adventitious arrival of an aggressive ion.

6.3.7 Liquid Metal Embrittlement

Liquid metal embrittlement is the decrease in strength or ductility of an alloy caused by contact with a liquid metal; low melting metals may enter incinerators easily in the rubbish from shipboard activities. Embrittlement may begin instantaneously upon contact of the alloy and the liquid metal, or may be delayed until the alloy is wet by the liquid metal. No detailed and comprehensive explanation of the mechanism of liquid metal embrittlement has been advanced. In general, current theories postulate a reduction in the surface energy of the alloy by the liquid and access of the liquid to the crack tip.

Susceptibility of alloys to embrittlement by various liquid metals differs [46, 62]. Carbon and low-alloy steels are susceptible to liquid metal embrittlement in a number of molten metals. The degree of embrittlement is greater for steels that have been heat treated or alloyed to produce higher strength. For example, mercury-sodium amalgams embrittle high-strength steel at room temperature but have no effect on plain carbon steels such as 1010.

Studies conducted on several low-carbon and low-alloy steels at temperatures from 260°C to 815°C reveal that these steels are embrittled by contact with the following metals in the liquid state: brass, aluminum, bronze, copper, zinc, lead-tin solders, and indium. In addition, the embrittling effect of lithium at its melting point (180.5°C) is well documented. Failure of welded 4130 steel occurs within one minute at an applied stress of only 15,000 psi in the presence of molten lithium.

Stainless steels generally are resistant to liquid metal embrittlement and sustain little or no degradation when contacted by liquid metals that severely embrittle plain carbon and low alloy steels.

Although liquid metal embrittlement of aluminum alloys is not common, it can result in rapid failure. Mercury, gallium, indium, tin, and alkali metals (except lithium) are embrittling agents, whereas lead, bismuth, and cadmium are not. Several aluminum alloys, including 1100, 2024, 3003, 5083, 5454, 6061, 6063, 6066, 7001, 7075, and 7079, are susceptible to embrittlement by mercury. In general, the higher the strength of the alloy, the more severe the embrittlement. Exposure to mercury of aluminum alloy structures containing even low tensile stresses can result in failure by liquid metal embrittlement. Failures result from accidental spillage of mercury from pressure gauges or broken thermometers. In structures not subject to fatigue loading, components made of 5xxx and 6xxx aluminum alloys that are not susceptible to stress-corrosion cracking may fail catastrophically if exposed to mercury. After such a failure, mercury contamination of other components or adjacent structures must be eliminated. In failure analysis when the presence of mercury is suspected, visual and macroscopic examination of the corroded or fracture surfaces helps to detect the presence of tiny globules of the liquid metal.

Brasses and bronzes are particularly susceptible to liquid metal embrittlement by mercury. In general, cracking follows an intergranular path. The time to failure depends on the stress level. No effective inhibitor of embrittlement of brass and bronze by mercury has been found, but additions of tin or silicon appear to lessen the degree of embrittlement. Brasses also are susceptible to liquid metal embrittlement by tin, lead, and their alloys, even at very low stresses. Copper and copper alloys other than brass are embrittled by bismuth, bismuth-lead alloys rich in bismuth, lithium, and under some conditions, mercury. These cracks caused by exposure of these metals in the solid state to liquid metals are usually intergranular. Stress-corrosion cracking in copper alloys may be either intergranular or transgranular, depending on pH, alloying concentrations, and variations in environmental species.

Magnesium alloys are relatively insensitive to embrittlement by liquid metals. Liquid sodium and liquid zinc are the only low-melting-point metals that embrittle magnesium.

Nickel and nickel alloys, although rapidly corroded by mercury or lead, show little or no embrittlement. Similar observations have been recorded for cobalt exposed to bismuth and cadmium exposed to high-temperature water. Small amounts of lead will embrittle nickel alloys.

Mercury embrittlement of titanium has occurred when titanium was deformed while immersed in mercury. Molten cadmium embrittles titanium; in addition, brittle fracture of several titanium alloys in intimate contact with solid cadmium has occured at ambient temperatures. The oxide film on titanium must rupture before embrittlement can occur.

Table 6. 6 shows the effects of some different liquid metals on the embrittlement of various alloys [62].

TABLE 6. 6 Behavior of Various Liquid Metals on Common Engineering Alloys.

Engineering Metal	Test Temp. (°C)	Liquid Metal			
		Aluminum Alloys	Magnesium Alloys	Steel	Titanium Alloys
Mercury (Hg) (3% Zn Amalgam)	30	E	N	N	E
Gallium (Ga)	50	E	N	N	N
Sodium (Na)	125	E	E	N	N
Indium (In)	180	E	N	E	N
Lithium (Li)	210	N	N	E	N
Selenium (Se)	250	N	N	N	N
Tin (Sn)	260	E	N	N	N
Bismuth (Bi)	300	N	N	N	N
Thallium (Tl)	325	N	N	N	N
Cadmium (Cd)	350	N	N	E	E
Lead (Pb)	380	N	N	N	N
Zinc (Zn)	450	E	E	E	N
Tellurium (Te)	475	--	--	E	N

Key: E = embrittlement
N = nonembrittlement

Source: Reference 62.

6.4 Metallic Materials of Construction

6.4.1 Introduction

Severe corrosion of common materials of construction can occur in incinerator environments. For the most part, materials selection for existing and preliminary systems has been based upon the technology developed for fossil fuel fired boilers and for gas turbines. In municipal incinerators and similar systems, the environmental conditions within the incinerators are more corrosive than originally expected. The complex nature of the waste and refuse materials and the relatively poor control of combustion in an incinerator combine to increase the possibility for aggravated corrosion. The contributors to attack are corrosive gasses, low-melting chloride, and sulfur-containing salts which exert a fluxing action on the protective oxide films formed on the metal surfaces. These low-melting salts contain heavy metal chlorides such as zinc and lead, as well as sodium and potassium chlorides and potassium bisulfates. Incinerator deposits containing 4 to 8 percent chromate are very corrosive. Only 0.5 percent chloride in the deposit will accelerate the attack of plain carbon steels. Gases such as SO_2, SO_3, HCl, and Cl_2 also accelerate corrosion. Recent unpublished data by Battelle suggest that, when combined with refuse, high-sulfur coals result in reduced amounts of chlorides in deposits; and corrosion is no more severe than that for coal alone [63]. This effect of sulfur requires further study.

Alternate oxidizing and reducing conditions caused by intermittent flame contact may also cause corrosion in waste incinerators because Fe_2O_3 reacts with HCl under reducing conditions to form $FeCl_2$, which changes to $FeCl_3$ at slightly elevated temperatures.

In stationary boilers using residual oils containing vanadium, the corrosion by the sulfate-chromate salt system is further accelerated by the presence of V_2O_5, which readily fluxes protective oxide films. However, for Navy incinerator service the vanadium pentoxide is not expected to be a problem since only distillate oils will be burned in the incinerator.

Corrosion is not limited entirely to high temperatures. Rapid attack can occur during downtimes under humid conditions. Under such conditions the pH under deposits may be 4 and below, leading to rapid attack of most common materials of construction. In the absence of deposits, corrosion is reduced both during downtimes and at operating temperatures. Typical compositions of alloys which are considered for incinerators are summarized in Table 6.1.

Section 6.4.2 and the remainder of 6.4 consider the performance of alloys which might be useful for linings in incinerators. The alloys are treated generally in the order of their increasing corrosion resistance. Most of these data are taken from studies developed for municipal incinerators, for gas turbines or fossil fuel power plants.

6.4.2 Carbon and Low-Alloy Steels

Carbon and low-alloy steels are the preferred materials of construction of fossil-fueled steam power plants. The oxidation resistance of carbon steels in contact with products of combustion is adequate if metal temperatures do not exceed 430°C. Low-alloy chromium-molybdenum steels are required for higher temperatures. For superheater and reheater tubes which operate at metal temperatures of 560°C to 600°C, Fe-1.25Cr-0.5Mo steels are commonly used. In some instances, steels containing up to 5 percent chromium are preferred.

Sulfur-bearing compounds play an important role in boiler-tube corrosion in fossil-fueled furnaces. Sodium and potassium sulfates, pyrosulfates, and bisulfates formed as a result of the reaction between fly ash and gaseous combustion products collect on the tube surfaces to flux the protective oxide films and cause excessive metal wastage in the temperature range 315°C to 650°C [51]. The presence of vanadium pentoxide and chlorides in the deposit further accelerate the corrosion. In practice, sulfate formation can be controlled by using low excess air; however, for incinerator operation, such a technique may be impractical.

Similar types of corrosion processes have been observed in water-wall incinerators burning municipal wastes. However, because of the presence of chlorides (3 to 7 percent) and heavy metal ions (i.e., zinc and lead) in the incinerator environment, corrosion rates are as much as an order of magnitude higher for carbon and low-alloy steel than those in commercial fossil-fueled furnaces.

In municipal water-wall incinerators, corrosion for both plain carbon (A106, Grade B) and low-alloy steel (A213, Grade T11, 1.25Cr-0.5Mo) ranges from about 10 mils per month at metal temperature of 260°C to more than 25 mils per month at 510°C [51].

Metal wastage rates for specimens exposed in a refuse incinerator in Miami County, Ohio, are shown in Figures 6.17 and 6.18. These data pertain to a number of alloy systems exposed at temperatures ranging from 150°C to 815°C. While the metal wastage rates represent short exposure periods (up to 400 hours), they do show the relative corrosiveness of incinerator environments (see also Figure 6.18). Probe Runs 13 and 15 have very high metal wastage rates because of overheating.

As the flame temperature is increased, even though specimen temperatures are held constant, corrosion rates of carbon and low-alloy steels increase (compare Figure 6.19 with 6.17 and 6.18). This is further illustrated in Figure 6.20 which indicates that reactions taking place within the deposit are affected by flame temperature, and influence the rate of corrosion. Other results for a T11 steel showed identical results to Figure 6.20 [64].

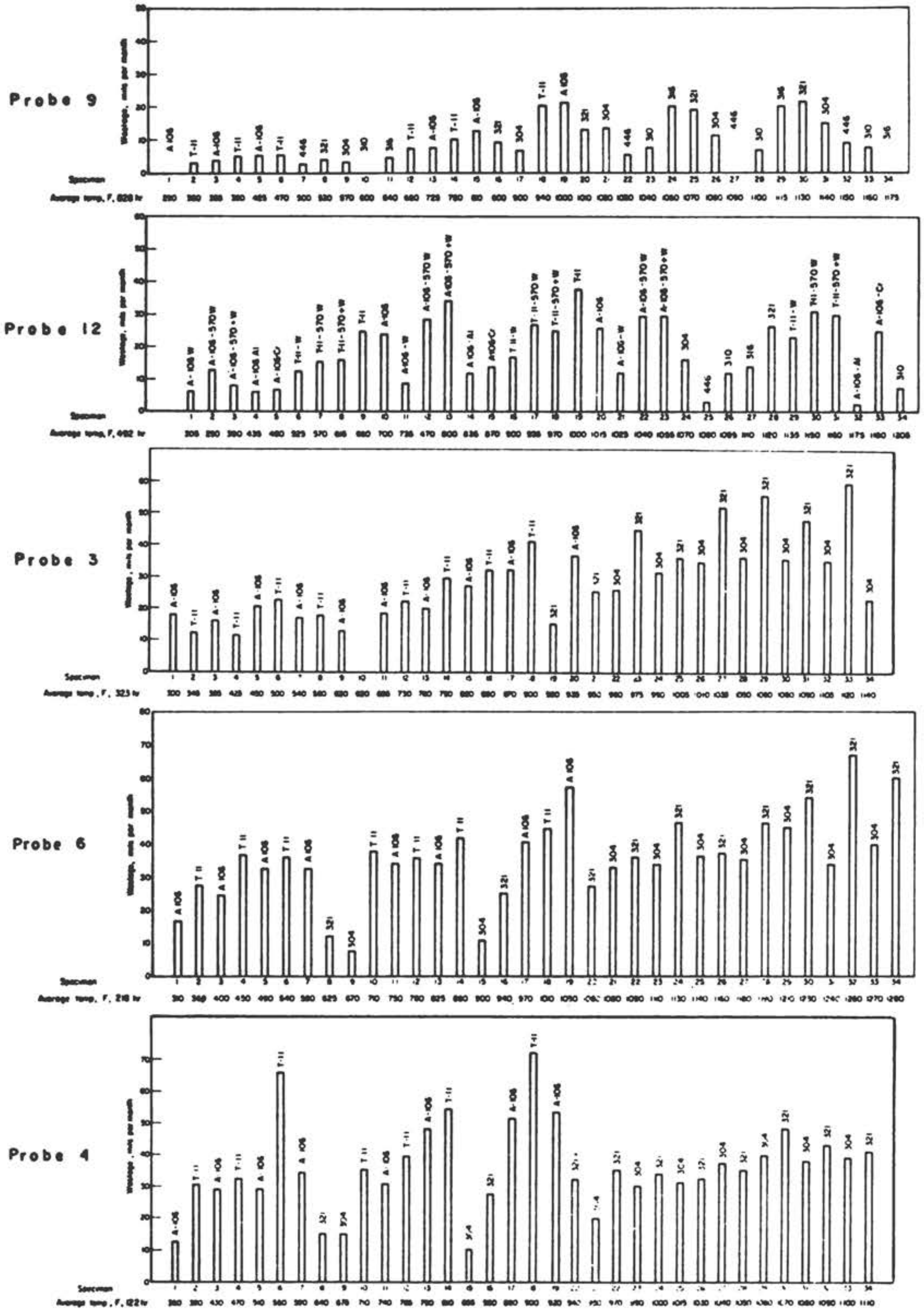


Figure 6.17 Tube Wastage Rates for Probes Exposed at Miami County, Ohio. (Alloy designations at top of each bar correspond to Table 6.6.) [51]

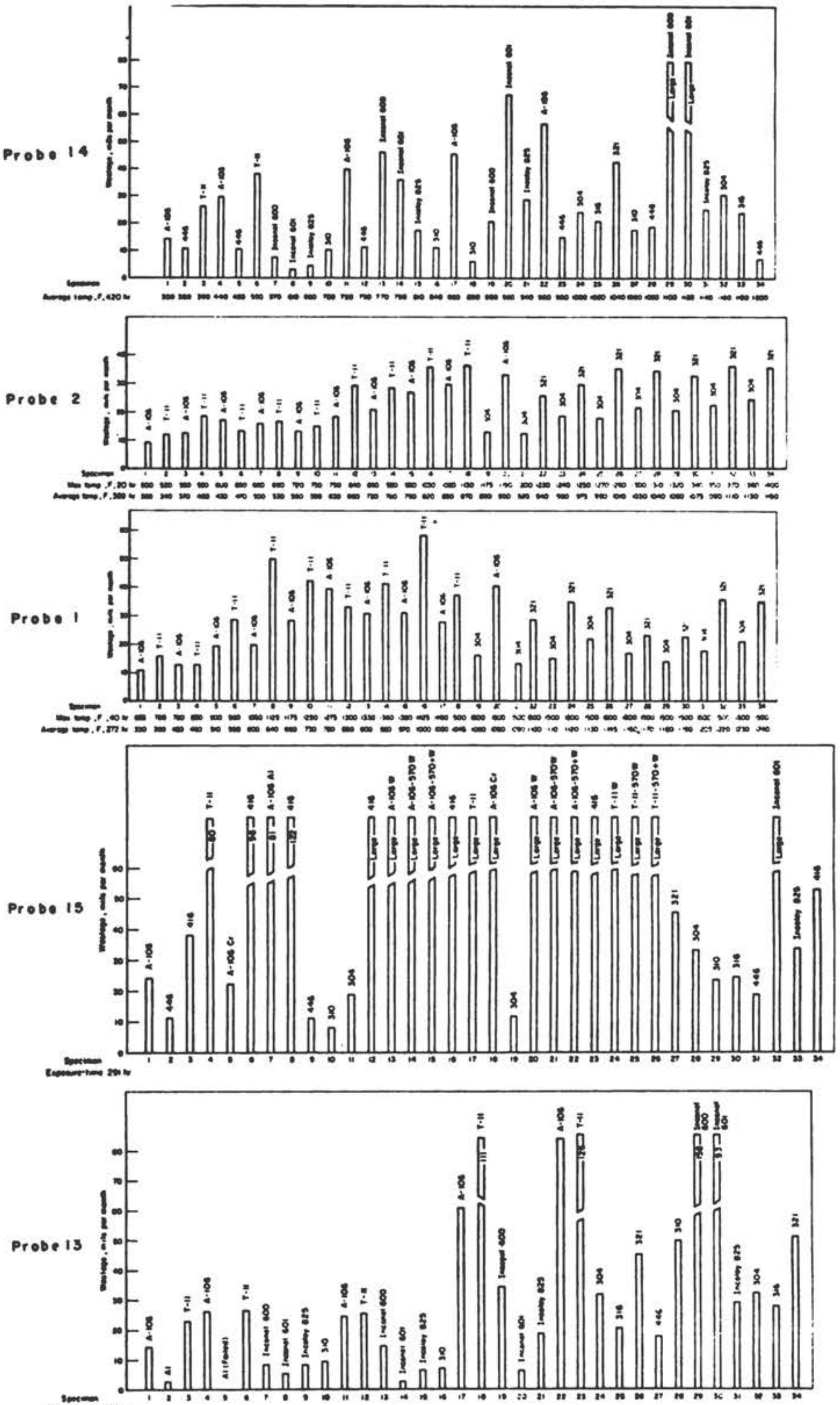


Figure 6. 18 Tube Wastage Rates for Probes Exposed at Miami County.[51]

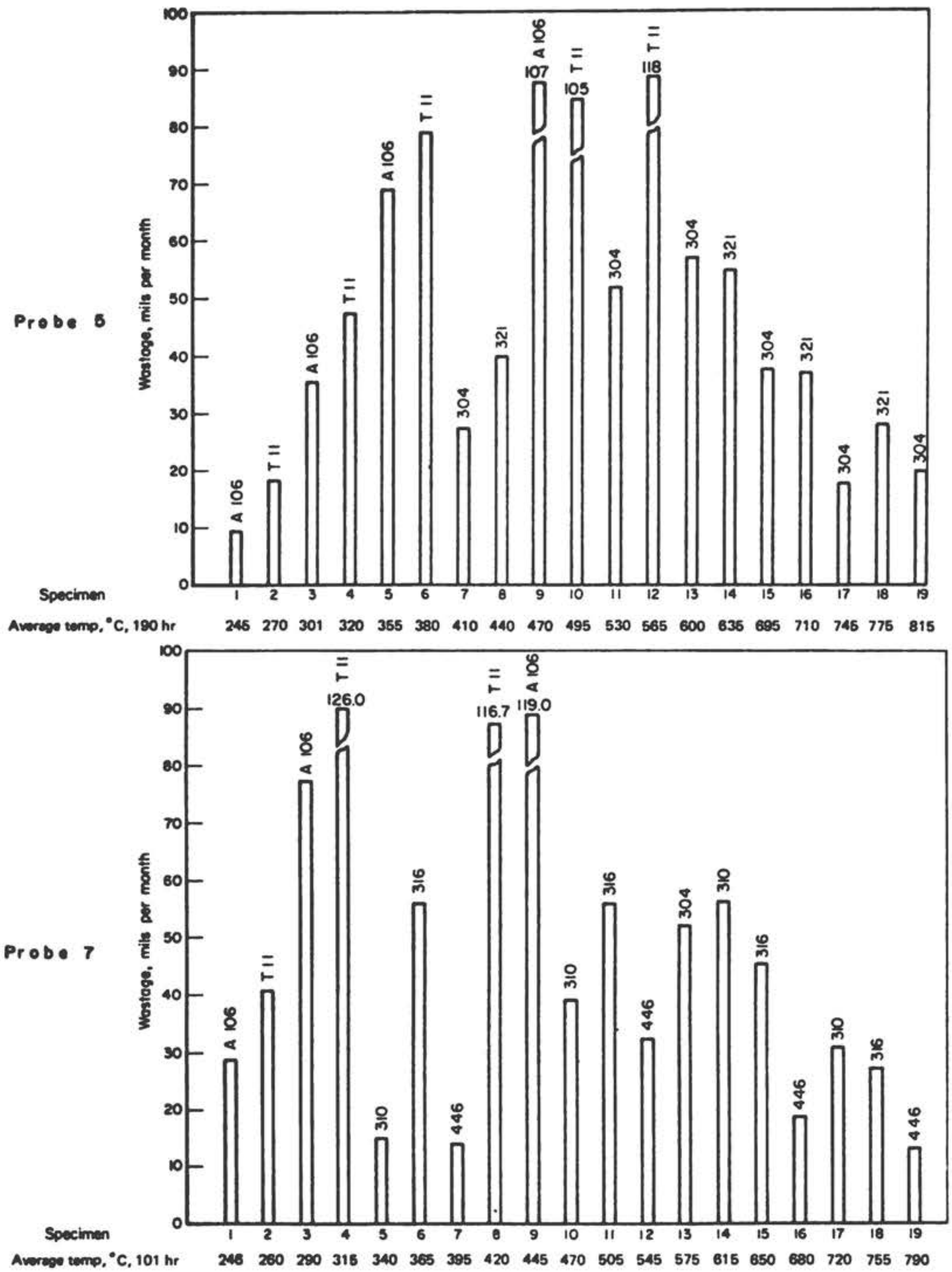


Figure 6.19 Tube Wastage Rates from Exposure in Flame Area [51]

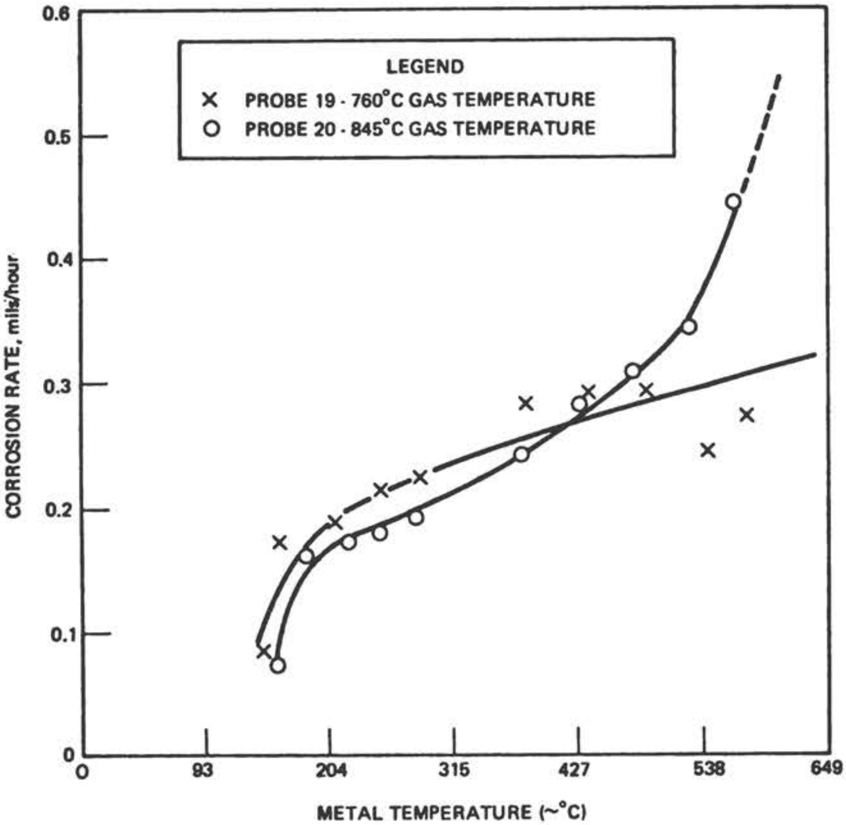
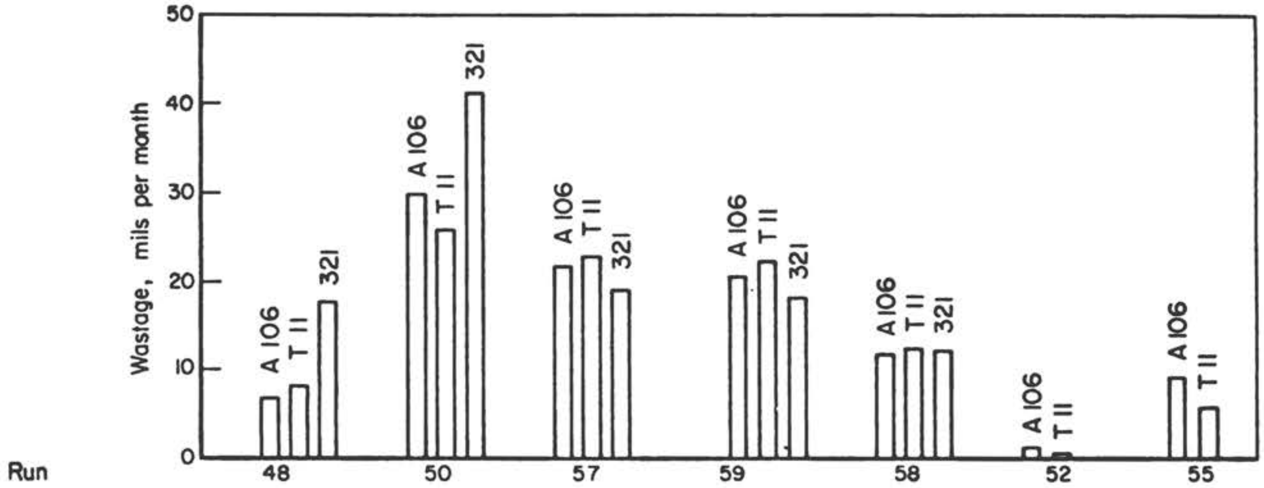


Figure 6. 20 Corrosion Rate of A 106 Steel Versus Metal Temperatures [64].

Metallized and ceramic coatings applied to the surfaces of the carbon-steel tubes were also evaluated (see data in Figures 6. 17 and 6. 18, Specimen A106-570W). For the most part, the ceramic coatings flaked off. Similar results were obtained with chromicized and aluminized coatings, but these coatings were quite protective when they remained on the surface.

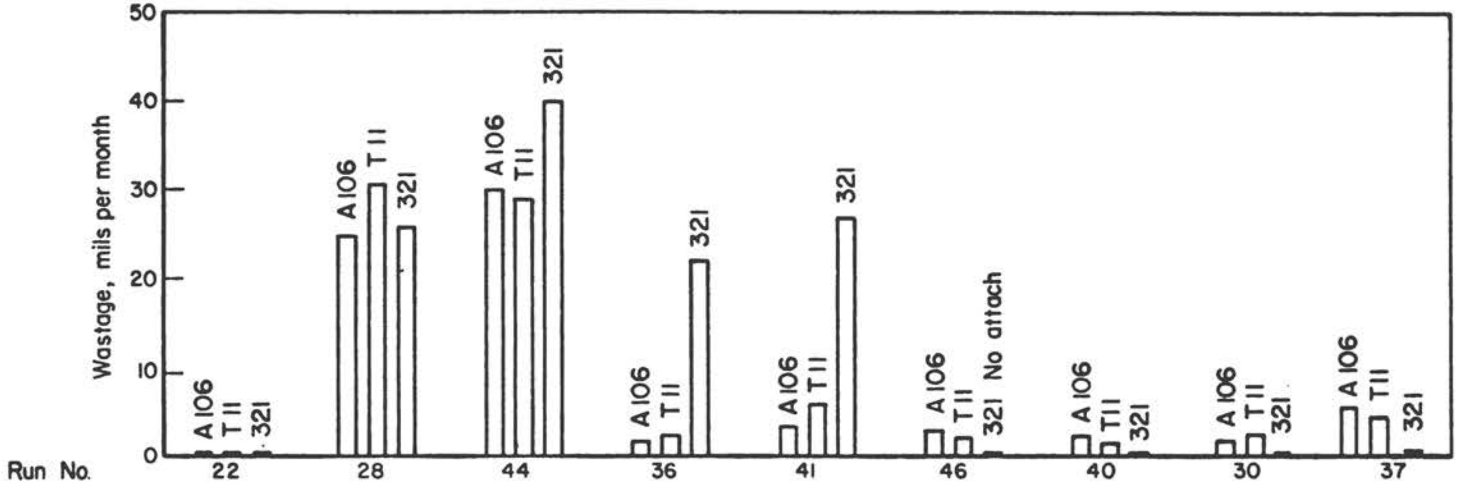
Laboratory data obtained by exposing metals to mixtures of corrosive salts representing those found in incinerator deposits are shown in Figure 6. 21, 6. 22 and 6. 23. For these studies, the environment of the furnace contained SO_2 and HCl. Corrosion rates as high as 40 mils/month were obtained for both carbon steel and austenitic Type-321 stainless steels.

In addition to high temperature metal wastage, carbon and low-alloy steels are subject to attack under deposits at ambient temperatures. The sulfate-chloride containing deposits are hygroscopic which results in the formation of acidic liquids with pH values as low as 2. Under such conditions metal attack is very rapid.



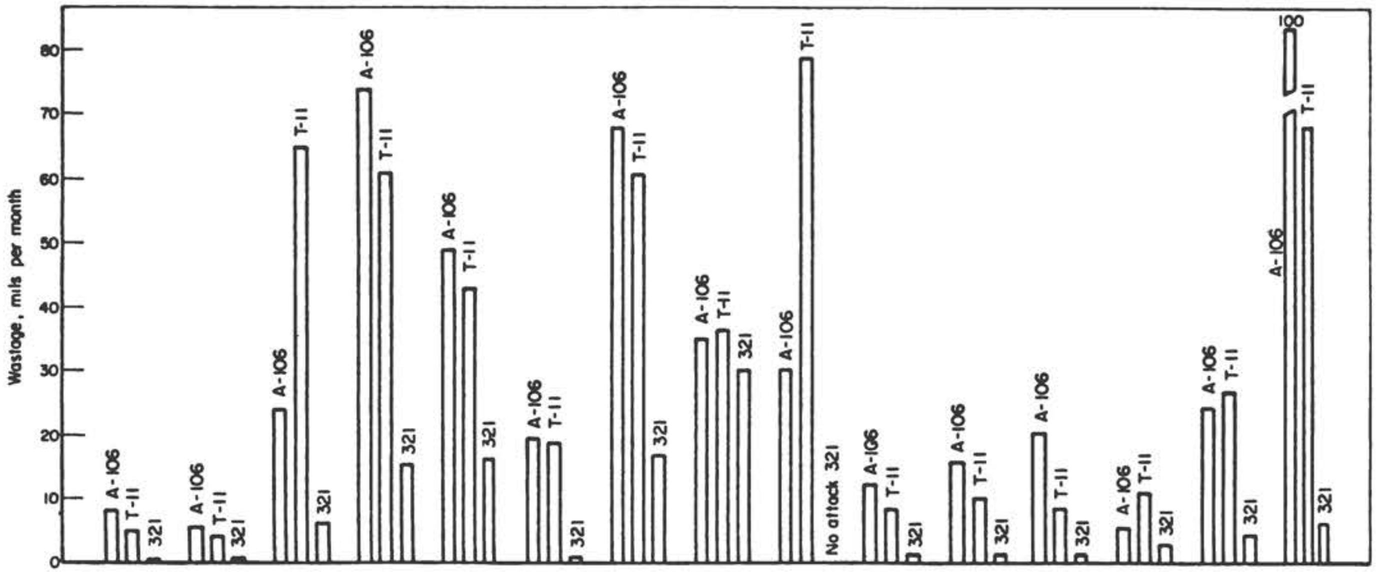
Run	48	50	57	59	58	52	55
KH SO_4 %	100	95	90	90	80	50	50
NaCl %	–	5	5	5	10	5	5
Zn Cl_2 %	–	–	5	5	10	–	30
Misc %	–	–	–	–	–	30 Zn SO_4	15 Pb Cl_2
Misc %						15 Pb O	–
SO_2 ppm	250	250	250	250	250	250	250
H Cl ppm	–	–	–	2000	–	–	–
Azide	+	+++	+++	+++	+++	+++	+++
Physical state	Fused	Fused	Fused	Fused	Fused	Fused	Part fused

Figure 6.21 Effect of Potassium Acid Sulfate ($KHSO_4$) on Corrosion at 316°C [51].



Run No.	22	28	44	36	41	46	40	30	37
$K_2S_2O_7$ %	–	100	95	95	95	65	50	5	5
K_2SO_4 %	75	–	–	–	–	–	–	71	67
Na_2SO_4 %	20	–	–	–	–	–	–	19	19
NaCl %	5	–	5	–	–	5	ZnO, CaO	5	5
Misc %	–	–	–	5 $ZnCl_2$	5 $ZnCl_2$	30 Fe_2O_3	Al_2O_3	–	5 $ZnCl_2$
SO_2 ppm	250	250	250	250	250	250	250	250	250
HCl ppm	–	–	–	–	–	–	2000	–	2000
Azide test	+	+++	+++	+++	+++	+++	+++	+	+++
Physical state	Agglom	Fused	Fused	Fused	Fused	Agglom	Caked	Caked	Caked

Figure 6.22 Effect of Potassium Pyrosulfate ($K_2S_2O_7$) on Corrosion at 316°C [51].



Run	0	3	1	5	20	7	10	11	13	15	16	18	17	19	21
K_2SO_4 %	-	59	58	78	78	99	75	75	-	-	78	78	78	78	75
Na_2SO_4 %	-	16	16	21	21	-	20	20	-	-	21	21	21	21	20
NaCl %	-	-	1	1	1	1	5	-	100	100	1	1	1	1	5
Misc %	-	25 Fe_2O_3	25 Fe_2O_3	-	-	-	-	5 KCl	-	-	-	-	-	-	-
Atmosphere	F.G.	FG	FG	FG.	FG	F.G.	FG	FG	FG	No SO_2	No SO_2	No SO_2	Helium	He + SO_2	FG. Hi SO_2
Azide test	-	?	++	+++	++	+	+++	+++	+++	-	-	-	-	-	+++

Figure 6.23 Laboratory Corrosion Results at 540°C. Exposure time was 50 hours. [51]

6.4.3 Chromium-Iron Alloys

Chromium-iron alloys containing 12 percent chromium have satisfactory oxidation resistance to 600°C. At higher temperatures, increasing chromium concentrations are required to form protective Cr_2O_3 scale. Studies of incinerators burning municipal wastes show that 25 percent chromium steels have adequate resistance to sulfur-chloride deposits at temperatures up to 650°C (5 to 10 mils per month). Under deposit conditions, corrosion increases with increasing gas temperatures. An increase in furnace gas temperature of 80°C from 760°C to 840°C produces a three-fold increase in corrosion rate.

Studies in Na_2SO_4- NaCl [65] salt mixtures suggest that at 900°C, 25 percent chromium was needed for satisfactory corrosion resistance. At 1050°C, as much as 40 percent chromium was needed for protection. Similar results were also obtained for Na_2SO_4- V_2O_5 mixtures.

Under humid conditions when the incinerators were shut down, the 13 to 25 percent chromium-iron alloys severely pit under deposits. Other factors which must be considered with chromium-iron alloys containing sufficient chromium for good corrosion behavior are lack of high temperature strength and the possibility of forming sigma phase which can embrittle the materials.

6.4.4 Austenitic Stainless Steel

The oxidation resistance of the austenitic stainless steels, like the binary iron chromium steels, depends strongly upon chromium content [66-68]. Chromium concentrations of about 15 percent or more are sufficient to develop the protective Cr_2O_3 barrier. Certain environmental conditions can rapidly remove the chromium from the stainless steels; this causes severe oxidation. Cyclic oxidation conditions under which the Cr_2O_3 barriers crack and spall eventually produce severe oxidation. The time required for the onset of the severe oxidation decreases as the temperature and frequency of the thermal cycles increase. The presence of SO_2 in the gas causes chromium sulfides to form within the steels, and this condition leads to reduced useful lives of the steels. The effectiveness of the SO_2 in increasing oxidation depends on the SO_2 pressure at temperature. At temperatures above about 800°C, most of the stainless steels are not sufficiently resistant to gases containing SO_2. Sodium sulfate-sodium chloride mixtures, or sodium chloride alone, are especially effective in removing the chromium from alloys and therefore causing rapid oxidation of stainless steels. Rapid deterioration is commonplace with such deposits at a temperature of 540°C or above.

The austenite in these types of steels is supersaturated with carbon, and chromium carbide precipitation will occur upon use of these materials at temperatures in the range of 500°C to 800°C. The carbide precipitation occurs at the grain boundaries of the alloys and may result in intercrystalline corrosion because the grain boundaries of the alloys are depleted in chromium as a result of the carbide precipitation. Susceptibility to intercrystalline corrosion of the stainless steels can be avoided by adding metals such as titanium or columbium, which have a great affinity for carbon.

Although experience with austenitic stainless steels in incinerator service is limited, some data are available from gas turbine and fused salt studies to provide an indication of the behavior to be expected in naval incinerators' service. In the Battelle studies [51] samples of Types 304, 310, 316, and 321 stainless steels were exposed in actual operating incinerators. Metal temperatures ranged from about 315°C to 820°C. Metal waste rates for the most part increased with increasing temperatures ranging from less than 10 mils per month at 315°C to 820°C to about 40 mils per month at 650°C. (See Figures 6.17 and 6.18.) Higher rates of wastage were obtained for a given metal temperature as the temperature of the gases in contact with the metal surface increased (Figure 6.19). In general, Type 310 was superior to Types 304, 321, and 316, in that order. Stainless steel appears to sustain a maximum corrosion rate in the temperature range 535°C to 650°C (Figure 6.18). At higher temperatures, metal wastage rates decrease. This may be the result of carbide sensitization which occurs rapidly in the 535°C to 650°C range.

As previously noted, the corrosion resistance can be impaired by cyclic operation and by the presence of salt deposits containing chlorides and sulfates. In a mixture of 75 percent Na_2SO_4, 25 percent NaCl salt mixture, an Fe-20 Cr-15 Ni alloy corroded at a rate of 200 mils per month at 1035°C (see Table 6.7). Corrosion of the austenitic stainless steels appeared to be a maximum at 870°C. Laboratory studies with simulated waste deposits from incinerators in the temperature range 315°C to 535°C indicate that the most corrosive salts to stainless steels are bisulfates and pyrosulfates. Under these conditions, with 250 ppm SO_2 in the combustion gas, metal wastage rates for Type 321 stainless steel were of the order of 40 mils per month at temperatures of only 315°C as shown in Figures 6.21 and 6.22. Lead chloride, found in incinerator deposits, causes rapid attack of Type 321 stainless steel at 535°C.

In vortex incinerator studies, the Navy [69] found that Type 309 stainless steels exhibit low corrosion rates under operating conditions. Metallographic examination of the Type 309 stainless steels revealed intergranular oxidation up to 2 grains deep. This experience seems to confirm laboratory studies [65] which suggest that 25 percent chromium in iron-chromium nickel alloys imparted good resistance at 900°C to a Na_2SO_4 and NaCl salt mixture. However, the lack of sigma phase formation in the incinerator material suggests that wall temperatures during operation may have been lower than anticipated, and this fact may account for the good behavior of the Type 309 material.

TABLE 6.7 Half-Immersion Corrosion Tests on Nickel-Chromium-Iron Alloys

Material				Weight Loss, mg/cm^2, after exposure to[a]														
				75% Na_2SO_4 - 25% NaCl[b]							80% V_2O_5 - 20% Na_2SO_4[c]							
				Duration of Test in Hours														
Nickel %	Chromium %	Iron %	Test Temp. °C	16	32	48	64	96	144	288	4	8	16	32	48	64	96	144
65	10	25	700	77	--	--	--	--	--	--	--	--	13	--	--	--	--	--
			800	88	--	--	1800	1800	--	1800	--	--	288	288	492	462	423	539
			900	1006	--	--	--	--	--	--	--	--	--	--	--	--	--	--
			1050	815	1314	1351	--	1800	1800	--	--	656	1203	--	--	--	--	--
80	20	--	700	2.4	--	--	--	--	--	--	--	--	26.2	--	--	--	--	--
			800	5.1	--	--	14.8	17.6	--	17.4	--	--	98.5	154	262	314	218	272
			900	8.0	--	--	--	--	--	--	--	--	187	--	--	--	--	--
			1050	17.9	18.8	36.1	--	32.7	39.4	--	416	358	789	--	--	--	--	--
68	20	12	700	3.5	--	--	--	--	--	--	--	--	19.7	--	--	--	--	--
			800	7.3	--	--	96.1	75	--	49.8	--	--	134	193	403	418	487	609
			900	10.6	--	--	--	--	--	--	--	--	344	--	--	--	--	--
			1050	14.7	36	235	--	120	97.3	--	527	500	788	--	--	--	--	--
50	20	30	700	10.1	--	--	--	--	--	--	--	--	15.8	--	--	--	--	--
			800	14.4	--	--	1082	1113	--	860	--	--	161	248	509	590	574	678
			900	832	--	--	--	--	--	--	--	--	267	--	--	--	--	--
			1050	535	870	712	--	622	1070	--	601	765	994	--	--	--	--	--
35	20	45	700	7.9	--	--	--	--	--	--	--	--	14.9	--	--	--	--	--
			800	11.2	--	--	1036	761	--	566	--	--	202	345	564	683	839	969
			900	456	--	--	--	--	--	--	--	--	473	--	--	--	--	--
			1050	10.3	459	779	--	972	582	--	774	1340	1800	--	--	--	--	--
15	20	65	700	9.3	--	--	--	--	--	--	--	--	11.8	--	--	--	--	--
			800	24	--	--	564	619	--	184	--	--	214	487	1144	1389	1394	1671
			900	53	--	--	--	--	--	--	--	--	794	--	--	--	--	--
			1050	15.8	349	655	--	535	921	--	566	820	1373	--	--	--	--	--
70	30	--	700	1.7	--	--	--	--	--	--	--	--	14.3	--	--	--	--	--
			800	8.1	--	--	23.5	33.6	--	57.7	--	--	90.3	143	261	236	251	303
			900	12.7	--	--	--	--	--	--	--	--	232	--	--	--	--	--
			1050	11	15.9	20.6	--	47.7	39.4	--	342	396	460	--	--	--	--	--
50	30	20	700	5.8	--	--	--	--	--	--	--	--	13.9	--	--	--	--	--
			800	25.9	--	--	46.3	206	--	64.6	--	--	130	196	477	961	.487	600
			900	201	--	--	--	--	--	--	--	--	336	--	--	--	--	--
			1050	70.7	89.2	122	--	425	297	--	486	884	1016	--	--	--	--	--
45	30	25	700	3.5	--	--	--	--	--	--	--	--	12.2	--	--	--	--	--
			800	13.9	--	--	29.2	79.1	--	57.6	--	--	107	149	554	625	553	728
			900	217	--	--	--	--	--	--	--	--	269	--	--	--	--	--
			1050	12	12.8	146	--	683	660	--	579	745	763	--	--	--	--	--
40	30	30	700	5.6	--	--	--	--	--	--	--	--	16.2	--	--	--	--	--
			800	9.4	--	--	756	856	--	--	--	--	135	232	592	682	713	833
			900	20.4	--	--	--	--	--	--	--	--	254	--	--	--	--	--
			1050	6.7	13.6	17	--	99.7	888	--	604	920	1620	--	--	--	--	--
25	30	45	700	10.7	--	--	--	--	--	--	--	--	9.5	--	--	--	--	--
			800	16.7	--	--	21.5	114	--	126	--	--	119	179	438	556	801	653
			900	630	--	--	--	--	--	--	--	--	324	--	--	--	--	--
			1050	165	348	231	--	94	163	--	416	844	1270	--	--	--	--	--
20	40	40	700	7.2	--	--	--	--	--	--	--	--	2.7	--	--	--	--	--
			800	11.8	--	--	23	35.9	--	54.5	--	--	35.3	30.6	135	219	136	229
			900	16.4	--	--	--	--	--	--	--	--	139	--	--	--	--	--
			1050	10.8	19.8	13.9	--	23.5	46	--	46.6	42.5	42.6	--	--	--	--	--

[a] Weight loss measured after descaling cathodically in molten sodium hydroxide.

[b] Simulated coal ash and oil ash of high sulfur content contaminated by seawater environment.

[c] Simulated high vanadium oil ash environment.

Source: Reference 65

In addition to high temperature corrosion, austenitic stainless steels are susceptible to pitting and stress-corrosion cracking in the presence of chloride-containing deposits at low temperatures. Stress-corrosion cracks have been observed in solution-annealed Types 310 and 304 stainless steels in contact with incinerator deposits in moist air at 75°C. Sensitized materials also exhibit a high degree of sensitivity to stress-corrosion cracking (see Figures 6.14 and 6.15). Some stress-corrosion cracking was also observed for Type 316 stainless steel and a 22 Cr-13 Ni-5 Mo alloy. Data obtained for a number of alloys exposed to moist air in contact with actual incinerator deposits are summarized in Table 6.8.

6.4.5 Fe-Cr-Ni, Ni-Cr, Ni-Cr-Co Alloys

The oxidation resistances of Fe-Cr-Ni, Ni-Cr, and Ni-Cr-Co alloys are all based upon the formation of continuous Cr_2O_3 scales [67]. Alloys with compositions such that Cr_2O_3 films are not stable (e.g., less than about 15 to 25 weight percent Cr) cannot be considered to be oxidation resistant. While all of these alloys rely upon Cr_2O_3 barriers for protection, their specific corrosion rates may differ. These differences are attributable to varying adhesion of the Cr_2O_3 to the alloys, and to the amount of oxidation which takes place before the Cr_2O_3 barrier becomes continuous.

Data from hot corrosion tests must be cautiously presented since the results are influenced by the type of test [68-70]. Generally, in the case of Na_2SO_4 or Na_2SO_4-NaCl deposits [65], the resistance of all the alloys to hot-corrosion attack increases as the chromium concentration increases. The hot-corrosion process appears to follow an Arrhenius relationship: more severe corrosion occurs as the temperature is increased. It has been found that cobalt in alloys either produces beneficial effects on hot-corrosion behavior or is innocuous.

Aluminum can produce either beneficial or deleterious effects. At aluminum concentrations where Al_2O_3 scales are developed on these alloys, increasing the aluminum content apparently improves the hot-corrosion resistance. When Al_2O_3 scales are not formed on the alloys, however, aluminum can produce undesirable effects on hot-corrosion behavior. Molybdenum and tungsten usually produce adverse effects on the hot corrosion of alloys. It must be emphasized that usually about 4 weight percent or more of these latter two elements are required before the decreased hot-corrosion resistance is evident; but, depending on the alloy composition, undesirable effects may be observed at lower concentrations.

Phase changes in Fe-Cr-Ni alloys can occur with long exposures at elevated temperatures. These changes usually impair the mechanical properties; no dramatic influence of phase changes on hot corrosion has been reported.

TABLE 6.8 Corrosion Results of Stress Specimens Exposed to Induced Draft Fan Housing Deposits Under Hot Humid Conditions

Alloy Type	Specimen	Corrosion[a] Found at Indicated Week					Pit Depth, mils
		1	2	3	4	5	
Ti-6Al-4V	J	G-0, P-0, C-0	G-0, P-0, C-0	G-0, P-0, C-0	G-0, P-0, C-0	G-1, P-0, C-0	0
Inconel 625	N	G-0, P-0, C-0	------	G-0, P-0, C-0	G-0, P-0, C-0	G-0, P-0, C-0	0
Hastelloy C	D	G-0, P-0, C-0	G-0, P-0, C-0	G-0, P-0, C-0	G-1, P-0, C-0	G-1, P-0, C-0	0
S-816	F	G-0, P-1, C-0	------	G-0, P-1, C-0	G-1, P-2[b], C-0	G-1, P-2[b], C-0	2
Incoloy 800	W	C-1, P-1, C-0	------	G-1, P-1, C-0	G-1, P-1, D-2, C-0	G-1, P-2, D-3, C-0	6
Incoloy 825	A	G-0, P-2[b], C-0	G-0, P-3[b], C-0	G-0, P-3[b], C-0	G-0, P-3[b], C-0	G-0, P-4[b], D-2[b], C-0	15
Carpenter 20	C	G-0, P-2[b], C-0	------	G-0, P-2[b], C-0	G-0, P-2[b], D-2[b], C-1[b]	G-0, P-3[b], D-3[b] C-1[b]	9
316L	H	G-1, P-4, D-2, C-0	G-1, P-4, D-2, C-0	G-2, P-4, D-3, C-1	G-2, P-4, D-3, C-1	G-2, P-4, D-4, C-2	16
USS-18-18-2	U	G-3, P-3, C-0	G-4, P-3, C-0	G-5, P-4, C-0	G-5, P-4, C-1	G-6, P-4, D-1, C-2	7
Armco 22-13-5	T	G-1, P-3, C-7	G-1, P-3, C-8	(removed)	------	------	8
304	G	G-5, P-5, C-0	G-8, P-5, C-0	(removed)	------	------	--
Plain-Carbon Steel	V	G-8	G-9 (removed)	------	------	------	--

[a] Magnitude of corrosion increasing 0-9 by surface examination

G = General Rust
P = Surface Pitting
D = Deep Pitting
C = Cracking

[b] Major attack where specimens contact deposits

Source: Reference 68

Deposition of acid salts such as those which occur in naval incinerators produces corrosion for all ranges of compositions of Fe-Cr-Ni, Cr-Ni, and Cr-Ni-Co alloys. The results of immersion tests in 75 percent Na_2SO_4-25 percent NaCl over the temperature range 700°C to 1050°C are shown in Table 6.9. Of the Ni-Cr alloy studies, the most promising commercial alloys are the Ni-50Cr and Ni-35Cr. Corrosion rates were of the order of 5-6 mils per month. The addition of 10 to 20 percent cobalt to the Ni-Cr alloys did not significantly influence the corrosion behavior (see Figure 6.24). On the other hand, the substitution of cobalt for 10 to 20 percent iron or nickel in Ni-Cr-Fe alloys reduced the amount of chromium required for acceptable corrosion rates at 900°C from about 40 to 25 percent.

TABLE 6.9 Half-Immersion Salt Tests on Nickel-Chromium Alloys

Material			Weight Loss[a] mg/cm^2 after Exposure to								
			75% Na_2SO_4 - 25% NaCl[b]				80% V_2O_3 - 20% Na_2SO_4[c]				
		Test Temp.	Time in Hours								
Nickel %	Chromium %	°C	1	16	48	300	1	16	48	120	300
100	0	700	--	14.3	--	--	--	29.2	--	--	--
		800	--	10.0	--	1240	--	23	24.1	31.3	34.9
		900	--	382	--	--	--	29.6	--	--	--
		1050	7.9	157	>1800	>1800	34.2	73.3	154	158	228
90	10	700	--	6.9	--	--	--	37.8	--	--	--
		800	--	10.2	--	154	--	82.5	156	270	391
		900	--	18.8	--	--	--	199	--	--	--
		1050	18.5	83	294	531	196	205	761	1370	>1800
80	20	700	--	3.1	--	--	--	32.4	--	--	--
		800	--	3.8	--	25.8	--	107	184	417	525
		900	--	4.8	--	--	--	247	--	--	--
		1050	3.6	22.7	62.1	174.8	182	490	1528	>1800	>1800
70	30	700	--	2.7	--	--	--	14.6	--	--	--
		800	--	6.9	--	59	--	90.5	165	430	580
		900	--	12.2	--	--	--	309	--	--	--
		1050	2.9	16.2	37.7	98	192	660	926	1195	>1800
60	40	700	--	4.8	--	--	--	8.2	--	--	--
		800	--	14.6	--	58.6	--	38.2	83.4	213	259
		900	--	20	--	--	--	176	--	--	--
		1050	2.0	33.9	24.4	35.6	113	545	469	484	655
50	50	700	--	6.7	--	--	--	2.7	--	--	--
		800	--	17.9	--	84	--	18.3	44.6	137	164
		900	--	17.9	--	--	--	93	--	--	--
		1050	5.5	35.8	24.4	46.6	44	48.5	151	185	409
40	60	700	--	10.6	--	--	--	2.7	--	--	--
		800	--	15.5	--	47.5	--	8.6	27.8	57.1	134
		900	--	25.6	--	--	--	49.6	--	--	--
		1050	4.0	34.5	31.9	39.2	8.8	11.9	81.1	150	200

[a] Weight loss determined after descaling electrolytically in molten sodium hydroxide

[b] Simulated coal ash, and oil ash of high sulfur content contaminated by seawater environment

[c] Simulated high-vanadium oil ash environment

Source: Reference 65

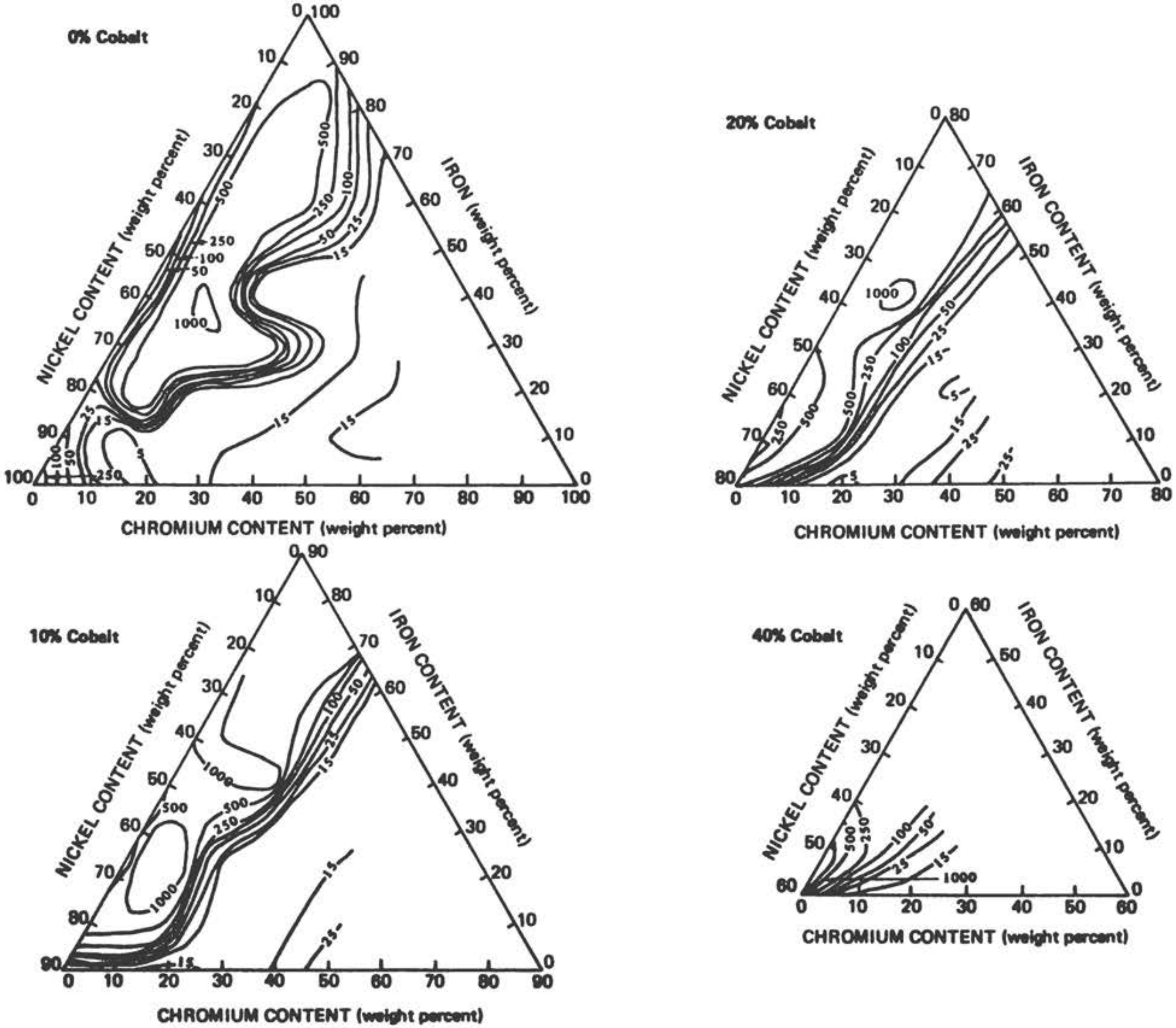


Figure 6.24 Isocorrosion Contours for Nickel-Chromium-Iron-Cobalt Alloys Exposed to a 75 Percent Na_2SO_4-25 Percent NaCl Salt Mixture. Exposed for 16 hours at 900°C (corrosion in mg/cm^2 weight loss) [65]

A number of Ni-Cr and Ni-Cr-Fe alloys are being studied in coal gasification pilot plant environments containing concentrations of N_2-CO_2-CO-H_2S at temperatures of 980°C to 1000°C [70]. Under these conditions, the 50 Cr-50 Ni alloy corroded rapidly. While the environments in the coal gasification pilot plant and shipboard incinerators are different, the data suggest some limitations for even the 50-50 alloys.

Little data are available for super alloys in incinerator environments. In the Battelle studies [51], Incoloy 825, Inconel 600, and Inconel-601 exhibited good resistance at temperatures up to 315°C. As the temperatures were increased to 650°C, metal wastage rates increased to about 20 mils per month. As would be expected, the higher chromium Incoloy 825 was more resistant than either Inconel-600 or 601. Inconel 601 performed poorly in vortex incinerator applications of the Navy and Coast Guard in both field and laboratory studies [71].

As noted in Tables 6.2 and 6.3, the Navy is evaluating a number of candidate incinerator liner materials in a simulated incinerator environment. The environment contains by-products of high sulfur diesel fuel and natural urine. The alloys being studied include Haynes-25, 150, and 188; Hastelloys S and X; Inconel 601, 617, 671, and 690; RA-333; two titanium alloys and several stainless steels (Types-304, 310, 446, and RA-330). Based on preliminary results, the alloy rankings are similar to that prediced from gas turbine studies. The most resistant alloys were Inconel 671, 690, and Haynes-150.

Coatings improve corrosion resistance in the super alloys used for gas turbines. Aluminide coatings can be deposited on these alloys by a number of processes. Such coatings impart resistance to corrosion by forming an Al_2O_3 barrier. Aluminide coatings impart improved resistance to virtually all alloys. Nickel or chromium coatings may be formed on alloys. Nickel coatings have never been used to develop corrosion resistance. There are instances, however, where chromium coatings have been used, but such coatings usually are not as effective in protecting alloys as are aluminides.

Overlay coatings are beginning to be used extensively to protect alloys. These coatings, while more expensive than the diffusion aluminide coatings, are not limited by the composition of the alloys upon which they are deposited. CoCrAlY and overlay coatings (e.g., Co-17 percent; Cr-12 percent; Al-0.5 percent; and Y) are especially resistant to hot-corrosion degradation. The Ni-50Cr alloy with the CoCrAlY overlay coatings should be resistant to hot-corrosion attack induced by Na_2SO_4. Less resistance is found when NaCl is present in the deposits.

6.4.6 Relative Advantages of Metallic Materials

While more specific data on candidate alloys in actual naval incinerator environments are needed, available data suggest that the most resistant alloys will be (1) Inconel 671 (50 Cr-50 Ni) and (2) Inconel 690 (30 Cr-60 Ni-10 Fe). These alloys have been found to be resistant in a variety of high temperature applications under both oxidizing and carbonizing conditions. Their resistance to molten sulfate, chloride, and vanadium salts is well documented. It is expected that these alloys will have satisfactory life at temperatures up to 980°C. They are also very resistant to the acid conditions which may occur under deposits during shutdown of the incinerator.

Cladding such alloys with MCrAlY coatings should produce more resistant materials and might extend the useful life of the Ni-Cr alloys to 1100°C or for much longer times at lower temperatures.

Substitution of cobalt for nickel and iron in most alloy systems does not appear to produce alloys with significantly increased resistance to sulfate and chloride salt mixtures at chromium level above 30 percent. At lower chromium concentrations, cobalt may be beneficial. Thus, alloys such as Haynes-188 and 150 are not expected to be as resistant as the higher chromium alloys. In addition, for alloys containing both chromium and chloride, replacement of nickel with cobalt results in more corrosion resistant alloys.

Although the high chromium austenitic alloys such as Type-309 and 310 exhibit satisfactory service in vortex incinerators, their performance in other applications involving Na_2SO_4-NaCl salts has been only fair. These alloys, unlike the Ni-Cr alloys, have been found to be susceptible to chloride stress-corrosion cracking when in contact with moist deposits from incinerators. Care must be exercised in the use of these materials in marine environment service.

The iron-chromium alloys, while possessing good resistance to oxidation and chloride stress-corrosion cracking, appear to have only limited application in naval incinerators. They are difficult to weld and may become embrittled with prolonged heating between 370°C and 650°C.

Carbon and low-alloy steels cannot be considered for service in incinerators at temperatures above 260°C. Applications of aluminum, chromium, and the super CoCrAlY and NiCrAlY coating have been shown to improve corrosion behavior. However, more data are needed to establish their long-time serviceability. During shutdown under condensing conditions, carbon and low-alloy steels suffer rapid corrosion by the acid condensates found in incinerators. For service under these conditions they would have to be protected.

6.5 Ceramic Materials of Construction

6.5.1 Introduction

Refractory ceramic materials offer the possibility of higher temperature stability and chemical inertness over greater ranges of conditions than most metals. A number of ceramic materials are being evaluated for Navy incinerator service. Preliminary thermal shock and chemical reactivity data with salt deposits are shown in Tables 6.10 through 6.12.

TABLE 6.10 Behavior of Selected Refractory Materials in Cyclic Salt Spray Test.

Material	Temp. °C	Time, Hours	Weight Change[a] Percent	Observations
Mineral wool	705	140	-17.0	Excessive degradation and spalling
	760	140	-22.5	Excessive degradation and spalling
Fiberfrax hotboard	705	100	-21.4	Excessive spalling
	760	24	-25.0	Excessive spalling
Y_2O_3-stabilized ZrO_2, low density	760	100	- 4.5	Specimen fractured
	870	110	- 9.3	Specimen fractured
	980	110	- 5.9	Specimen fractured
Y_2O_3-stabilized ZrO_2, high density	760	140	- 0.2	Specimen fractured
	870	100	- 7.0	Specimen fractured
	980	100	- 2.8	Specimen fractured
Mullite ($3Al_2O_3 \cdot 2SiO_2$)	760	300	+ 1.2	No visible deterioration
	870	300	+ 0.5	No visible deterioration
	980	312	- 0.3	No visible deterioration
SiC (18% Si_3N_4)	540[b]	300	- 0.5	No visible deterioration
	760[b]	300	+ 0.5	No visible deterioration
	980[b]	312	+ 2.3	No visible deterioration

[a] Average of two specimens

[b] Synthetic sea salt + synthetic urine

Source: Reference 72

TABLE 6.11 Penetration of Castable Ceramics in Contact with Metallic Oxide Ash

Material	Temp., °C	Observations[a]
Lightweight castable ($60Al_2O_3$-$30SiO_2$)	760	——
	870	——
	980	Superficial reaction—wetting
Castable ($65Al_2O_3$-$26SiO_2$)	760	——
	870	——
	980	Superficial reaction—wetting
Castable($76Al_2O_3$-$17SiO_2$)	760	——
	870	——
	980	Superficial reaction—wetting
Castable ($97Al_2O_3$-$0.1SiO_2$)	760	——
	870	——
	980	Superficial reaction—wetting
Super-rigidized Kaowool	760	——
	870	Shrinkage and fracture
	980	Shrinkage and fracture, localized penetration

[a] For 300 hour exposure at indicated temperature

Source: Reference 72

TABLE 6.12 Penetration of Castable Ceramics in Contact with Shipboard Incinerator Sludge

Material	Temp., °C	Penetration Depth,[a] inches		
		Primary[b]	Secondary[c]	Total
Lightweight castable ($60Al_2O_3$-$30SiO_2$)	760	--	--	--
	870	--	0.03	0.03
	980	0.08	0.31	0.39
Castable ($76Al_2O_3$-$17SiO_2$)	760	--	--	--
	870	--	0.01	0.01
	980	0.08	0.40	0.48
Castable ($65Al_2O_3$-$27SiO_2$)	760	--	--	--
	870	--	0.04	0.04
	980	0.06	0.23	0.29
Castable ($97Al_2O_3$-$0.1SiO_2$)	760	--	--	--
	870	--	0.11	0.11
	980	0.08	0.2	0.28

[a] Average of two specimens

[b] Due to melt reactions

[c] Due to vapor phase transport

Source: Reference 72

In cyclic tests, 10.2 x 5.1 x 2.5 cm thick corrosion specimens were subjected to a periodic spray of water solution containing synthetic sea salt and/or urine. Cycles were 0.5 hour in the furnace followed by a 3 second spray of the test residue. Exposure time for the screening tests was 300 hours (1600 cycles), followed by 600 to 1,200 hour exposures. The temperature drop during thermal cycling in the spray test was limited to about 95°C at the surface to simulate incinerator operations and to avoid excessive thermal shock failure of the ceramic.

Weight change data for 300 hour screening tests in the cyclic spray test are contained in Table 6.10. The low density materials, mineral wool and Fiberfrax hotboard, failed by spalling even at 705°C. On the other hand, yttria-stabilized zirconia failed by fracture in about 100 hours at all exposure temperatures. High-density mullite and silicon-nitride bonded silicon carbide were essentially unaffected after a 300 hour exposure. Permeation of the surface for mullite and silicon carbide results in the measured weight gains. Tests of 600 and 1,200 hours at 760°C to 980°C, like that of the 300 hour tests, showed no visible deterioration.

Castable ceramics are being evaluated by crucible tests in which the castable is the crucible. Included in this test is a commercial super-rigidized Kaowool. Slip cast specimens 6.4 cm in diameter by 6.4 cm long with a 1.9 cm diameter by 5.1 cm deep hole are used for these tests. The central hole was machined in the Kaowool. Screening tests consist of 300 hour exposures at 760°C to 985°C. After the 300 hour screening test, extended exposures for 600 to 1,200 hours will be conducted.

Two types of ash mixtures are being used for evaluating castable ceramics and super-rigidized Kaowool: (1) a high metallic oxide ash refuse, and (2) incinerator residues from a current shipboard incinerator. The metallic ash represents refuse from solid garbage combustion, primarily CaO, aluminum, iron, and glass with minor amounts of sea salt. Shipboard incinerator ash consists of a mixture of chlorides, sulfates, and phosphates of calcium, potassium, and sodium. The softening point of the metallic ash is like greater than 1100°C, whereas that of the shipboard ash is about 955°C.

Penetration data for castables in contact with metallic oxide ash mixtures for a 300 hour exposure are given in Table 6.11. Little penetration of either high or low density castables occurred at 760°C to 985°C. Super-rigidized Kaowool exhibits shrinkage and fracture at 985°C.

Penetration data for castables with the shipboard ash for a 300 hour exposure are summarized in Table 6.12. No testing of Kaowool was conducted in this phase based on metallic ash results. Penetration of the castables was limited at 760°C to 870°C, i.e., below the softening point of shipboard ash. At 985°C, penetration by both liquid (primary penetration) and vapor phases (secondary penetration) occurred for all castables. The results suggest that penetration of the castables by alkali metal salts is potentially the greatest problem.

In progress are tests of the exposure of the high-alumina castables and the light-weight castable for 600 and 1,200 hours at 870°C and 985°C in contact with both types of ash.

6.5.2 Temperature Limit

Except for glass, almost all ceramic materials could be considered for incinerator design from the point of view of temperature range. Many ceramic materials have high melting points. As with metals, ceramic materials cannot be used near their melting points because they lose mechanical strength. For incinerators, maximum-use temperatures are probably limited to 1200°C by reactions with salt deposits. Possible refractory materials and maximum use temperatures in the absence of fused salts are shown in Figure 6.25.

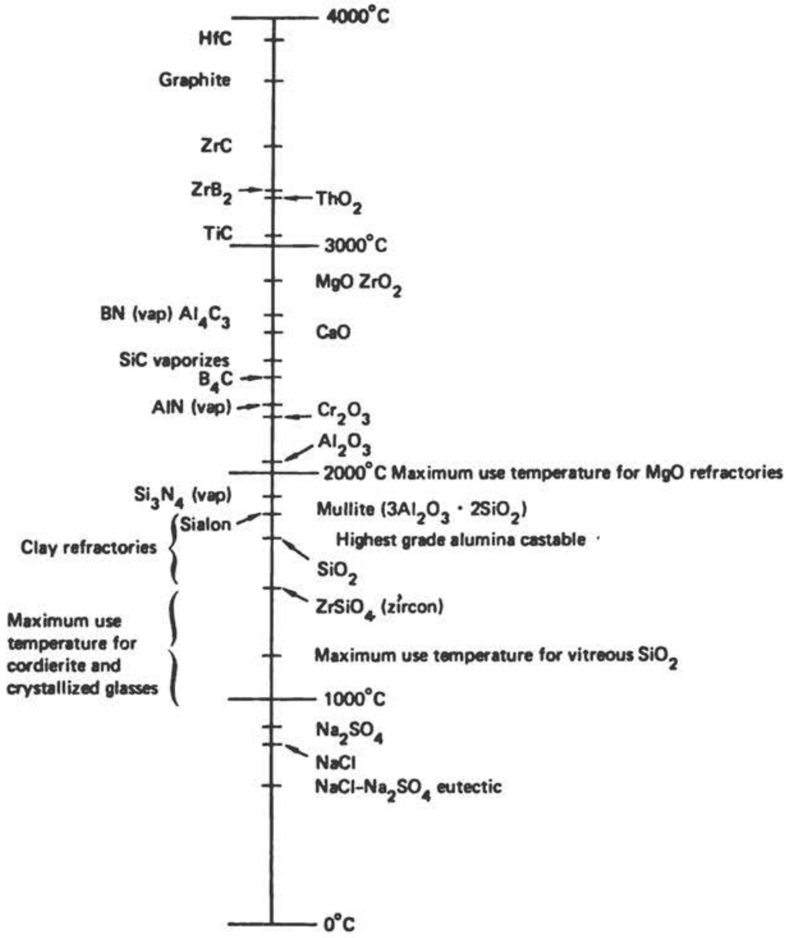


Figure 6.25 Melting Points of Ceramic Materials

6.5.3 Heat Shock Resistance

Lack of heat shock resistance of most ceramic materials is related to their brittleness. Thermal stresses may become severe enough to propagate critical flaws to catastrophic fracture. The only successful methods of avoiding thermal stresses are to minimize temperature gradients or to select materials with low coefficients of thermal expansion. The latter alternative is not often available in high temperature furnace design where chemical compatibility with corrosive glasses or slags is important (see Tables 6.13 through 6.15). It is nearly impossible to heat shock-fused silica and some glass-ceramic materials regardless of heating or cooling rates. With coefficients of thermal expansion below 5 x 10^{-6}/°C, resistance for thermal shock failure is very good. Ceramic materials with coefficients larger than 10^{-5}/°C are easily destroyed by heat shock. For the relatively low temperature of an incinerator, it is possible to select some materials with low coefficients of thermal expansion and avoid thermal shock. Consideration should be given to vitreous silica (fused quartz) either as a dense glass or sintered refractory and to cordierite (magnesium aluminum silicate). These materials could be fabricated in fairly large, thin panels of the size and weight needed; and their use temperatures (1000°C to 1100°C for vitreous silica and 1200°C for cordierite) are sufficient for incinerator operation.

If thermal stresses cannot be avoided, the alternative is to minimize crack propagation. Furnaces containing brick composed of mechanically held aggregates are often cycled without failure because the bricks do not easily propagate a crack. The crack is arrested at pores and interfaces between aggregates. An extreme example of this is a fiberous compact which has such a low modulus as to absorb thermal stresses and such large amounts of porosity that a fracture must proceed through one fiber at a time.

For a simple geometrical shape uniformly cooled through a temperature difference, ΔT, with the body external surfaces rigidly restrained to induce a uniform state of triaxial stress, S, of magnitude

$$S = \alpha E \, \Delta T/(1-2\nu) \tag{6.1}$$

where α is the coefficient of thermal expansion; E is Young's modulus of elasticity; and ν is Poisson's ratio. This represents the worst possible condition for thermal shock. The larger the ΔT, the larger will be the stress, S, until one of the Griffith cracks propagates to catastrophic failure. Hasselman [73] observed that the strength of a dense uniform ceramic material is not affected by ΔT until it becomes large enough (ΔTc) to initiate fracture by rapid growth of one of the numerous Griffith flaws in the surface of the ceramic. Under these conditions, the material parameters that produce the most thermally shock resistant ceramic are

TABLE 6.13 Potential Ceramic Materials for Incinerators

Materials	Use Temperature Limit °C	Heat Shock Resistance	Density g/cc	Size Limitation	Resistance to Molten Salts	Strength in 1000 psi (kpsi)	Custom Fabrication
Silicon Nitride:							
a. Reaction Type	>1200	good	~2.4-2.7	90cm x 90cm x 1.3cm	good	20	Hard to get
b. Hot Pressed	>1200	good	~3.2	30cm x 30cm x 2.5cm	very good	100	Hard to get
Silicon Oxynitride	>1200	good	~2.0-2.7	30cm x 45cm x 1.3cm	very good	5-30	Available
Silicon Carbide:							
a. Si_3N_5 Bonded	>1200	good	~2.5	30cm x 45cm x 1.3cm	moderate to 1000°C	5-10	Off Shelf
b. Recrystallized	>1200	----	2.6	same	same	20	Off Shelf
c. Reaction	>1200	good	~3.2	same	same	>20	Available
d. Silicate Bonded	~1200	fair	~2.5	Slabs and bricks	poor	~5	Off Shelf
Crystallized Glasses:							
a. Lithium Type	1000	excellent	2.5	Large pieces-0.6cm and thicker	limited	20	Available
b. Zinc Type	900	good	2.5	Stovetop size	expected to be better	20	Available
c. Magnesium Type (cordierite)	1000	excellent	2.5	Large pieces-0.6cm and thicker	somewhat better	20	Available
Cordierite	1200	excellent	1.6	~90cm	poor	1-2	Available
Fused Silica (fused quartz):	900-1000	excellent	2.2	up to 90cm x 0.6cm	moderate	5	Available
a. Dense	------	---	---	--------	----	--	----
b. Porous	------	---	1.5	up to 60cm x 1.3cm	poor	1	Available
Refractory Castable	>1200	fair	3.0	like concrete	moderate	5	Easily Fabricated
Refractory Brick[a]	>1200	good in small amounts	2.0	limited to small 30cm x 45cm x 2.5cm	moderate	5	Available
Sialon	>1200	good	3.1	still experimental	expected to be good	30	Yes, when available

[a] Possible to reinforce with stainless steel wire mesh or other metal.

TABLE 6.14 Linear Thermal Expansion Coefficients

Material	Coefficients (x 10^6/°C)[a]
Fire clay refractory	5.5
Mullite ($3Al_2O_3$-$2SiO_2$)	5.3
Silicon Carbide (SiC)	4.7
Si_3N_4	3.0
Si_2ON_2	3.2
Fused Silica	0.5
Glass-Ceramics	0 to 3.0
Cordierite	0.8 to 3.5
Zirconia (Stabilized)	10.0
Alumina	8.8
Alloy Steels	14.0 to 18.0
Inconel	16.7 to 17.0
Hastelloy^X	16.6

[a] Range = 0-1000°C

TABLE 6.15 Thermal Conductivity of Some Ceramic Materials

	Thermal Conductivity (cal/sec/cm^2/°C/cm) at	
Material	100°C	1000°C
Al_2O_3	0.072	0.015
BeO	.525	.049
MgO	.090	.017
$MgAl_2O_4$	.036	.014
ThO_2	.025	.007
Mullite	.014	.009
$UO_{2.00}$	.024	.008
Graphite	.43	.15
ZrO_2 (stabilized)	.0047	.0055
Fused silica glass	.0048	.006
Soda-lime-silica glass	.004	---
TiC	.060	.014
Porcelain	.004	.0045
Fire-clay refractory	.0027 to .008	.0037 to .01
TiC cerment	.08	.02
SiC-Silicated Bonded	.07	.04
Si_3N_4	.08 to .04	---
SiC Hot Pressed	.18	.09
Silicon Oxynitride (porous)	.014	.01
Cordierite (porous)	.0022	---

$$Rst = [k^2 \gamma/\alpha^2 Eo]^{1/2} \tag{6.2}$$

where k is thermal conductivity; γ is surface energy; and Rst is the resistance to thermal shock.

Refractory manufacturers note that a pre-cracked ceremic material does not easily propagate a catastrophic fracture. It is not as strong initially but does not suffer a drastic loss in strength as ΔT increases. It does not have a critical ΔT, but as ΔT increases, strength gradually decreases. Thermal shock resistance can be built into the ceramic material by using numerous microcracks and internal interfaces obtained by voids or polyphase microstructures. The material parameters important for this mode of failure are

$$R = E\gamma/S^2 (1 - \nu) \qquad (6.3$$

according to Hasselman [74]. Navy tests with fiber ceramics show they fail very quickly by delamination due to mechanical forces; and chemical attack appeared to be minimal at temperatures below 985°C.

6.5.4 Porosity

Porosity minimizes heat shock in ceramic materials. Porous brick and rigidized fiber board are examples of materials through which crack propagation is very difficult. However, as noted, Navy data indicate that fiber ceramics suffer delamination. Refractory brick usually contain 15 percent porosity to increase thermal shock resistance. As a general rule, however, porosity increases the possibility of failure by corrosion from slag attack. For incinerators, an impervious refractory would have many advantages over a porous refractory in contact with molten salts and/or abrasive solids. The real question is the relationship between the rate of corrosion and the porosity for various refractories. In contact with silicate slags and glasses in such furnaces as glass melting tanks and arc furnaces for melting metals, only dense alumina or $MgCr_2O_4$ are recommended. There is no experience for these materials exposed to $NaCl$-Na_2SO_4 melts. Dense MgO and Al_2O_3 hold up in molten Na_2CO_3 systems that contain some sulfates. Research in progress at the University of Utah with coal ash and potassium sulfate show $MgAl_2O_3$ to have reasonable life at 1500°C. Unfortunately those refractories that are dense also have poor thermal shock resistance.

6.5.5 Size Limitations

Few refractory possibilities are available in the thin, lightweight dimensions needed for shipboard incinerators. The exceptions are vitreous silica, cordierite glass-ceramic (crystallized from a glass melt) and the rigidized fiber insulations. The cordierite, made up like the paper board used in catalytic emission control devices for automobiles, presumably could be obtained in large sections (~ 1 m x 1 m x .01 m). Other materials would be more easily fabricated as tile with dimensions of the order of 0.5 m x 0.01 m x 0.1 m.

6.5.6 Salt Reactivity

Knowledge of slag attack on refractory materials in the metallurgical industries and the corrosion of refractories in the presence of molten glass can be used in designing ceramic materials to withstand the attack of molten salts in an incinerator. Refractory materials that withstand molten oxides in the form of slags or glasses must be impervious to these liquids; this is opposite to the trend for fabricating refractories purposely porous to withstand thermal shock. The constraint of impervious non-porous refractory is important. In areas of severe attack by corrosive slags and glasses, the respective industries have selected fused cast refractories because of their imperviousness. For application to shipboard incinerators emphasis should probably be placed upon imperviousness since heating and cooling rates can be minimized.

Fused salt electrolysis of magnesium and aluminum comes very close to duplicating conditions of incinerators for sewage. The sodium chloride-sodium sulfate molten salt is reasonably close to the molten magnesium chloride in magnesium smelting and the aluminum oxide-aluminum fluoride eutectic used in the aluminum electrolysis or smelting industry. In both cases, carbon is used. Neither carbon nor graphite is sufficiently resistant toward the oxidizing atmosphere of an incinerator to make an acceptable refractory material. An even more successful refractory material than carbon and graphite is the family of nitrides available from the ceramic industry. The most prominent of these is the silicon nitride bonded silicon carbide refractory which has shown promise in preliminary evaluations for incinerator service. This has been used extensively in the aluminum industry. Silicon oxynitride, though porous, is reported to be very good in its resistance to salts in their molten state [75].

A relatively new and unexploited refractory material, Sialon, should have excellent resistance to molten salts. It is essentially an oxynitride but is formed with silicon nitride and aluminum oxide. It has an advantage over the normal silicon oxynitride in that it can be sintered to a dense condition. It has a potential as a rather inexpensive refractory material, inasmuch as it can be obtained from clay [76].

In contrast to the nitrides, all of the oxides have a measurable rate of solution and corrosion in molten salts. The silicates tend to react more readily than the pure oxides because of a low melting eutectic between the alkali salts and silica. Of the oxides, aluminum oxide and magnesium oxide are the most readily available and will probably have the best resistance to the molten salts.

6.5.7 Mechanical Failure Processes

The vast majority of ceramic materials are subject to brittle fracture. Plasticity resulting from dislocation motion is impeded at grain boundaries and generates dangerous flaws. As a result of sensitivity to flaws, ceramic materials are subject to surface damage and catastrophic impact damage.

Some toughness can be built into ceramic materials by porosity as in a refractory brick or by fiber reinforcement in composite materials. Metal fibers in a refractory castable minimize the fracture event and, like conventional concretes, maintain the integrity of a cracked ceramic material.

Brittle ceramic materials often fail from thermal shock for the same reason that they fail from impact. Flaws are propagated catastrophically from thermal shock just as they are from impact. Some ceramic materials are immune to thermal shock. These are materials with low coefficients of thermal expansion. Materials such as vitreous silica have extremely low coefficients of thermal expansion. Some of the crystallized glasses of the lithium-aluminum-silicate variety (pyroceram) have negative coefficients of thermal expansion and are very resistant to thermal shock. For very high temperature applications, silicon nitride and silicon carbide with moderate coefficients of thermal expansion are reasonably resistant to thermal shock. Some degree of thermal shock resistance can be built in by use of porosity to minimize fracture propagation.

At very high temperatures, ceramic materials fail by creep failure mechanisms very similar to metallic materials; and some ceramic materials experience dislocation creep failure mechanisms. Often commercial ceramic materials that consist of crystalline materials bonded with some glassy grain boundary constituent fail by viscous creep failure.

6.5.8 Wear and Impact Resistance

Because of frictional wear from surfaces, wear in ceramic materials is hard to minimize. Metals are often coated with ceramic materials to reduce friction. Among the materials with the lowest coefficient of friction are the nitrides such as Si_3N_4, Sialon, and silicon oxynitride.

Impact resistance is not related to frictional wear. Velocity of impact and area of impact are the important criteria in the degradation of brittle materials. At high velocities, the amount of energy absorbed by dislocation motion is small, and most of the energy must be expended by elastic processes. Fracture occurs when the local stress exceeds the fracture strength at the grain boundaries or exceeds the cohesive strength; or, fracture will occur when the energy of the particle exceeds the cohesive energy plus the energy absorbed by dislocation motion. Repeated impacts of this nature can wear away brittle materials. This is one of the mechanisms involved in the grinding of brittle materials by abrasive materials.

6.5.9 Fabrication

For metals, ductile deformation allows fabrication by cold working processes that are not possible with ceramic materials that are brittle at room temperature. All deformation processes for ceramic materials are limited to hot processing. Often ceramic materials have such high deformation temperatures that even hot working is not applicable. Refractory materials are seldom hot worked, but glasses and glass ceramic materials are extensively fabricated by hot rolling, pressing, drawing, forging, etc.

For the refractory oxides, carbides, nitrides, etc., fabrication is limited to the following processes:

1. Powder Forming and Sintering: Finely divided powder is pressed to greater than 50 percent theoretical density and sintered with accompanying shrinkage. This shrinkage limits product sizes to generally less than 90 cm. Uniaxial pressing is used for simple shapes (plates, discs, etc.) and isostatic pressing for more complicated shapes (tubes, crucibles, etc.). Powder can be slip-cast to give complicated shapes or sludge-cast for larger shapes. Mixed with a suitable binder and vehicle, a plastic powder mass can be extruded to form shapes of axial symmetry. Injection molding can be accomplished by loading a polymer with powder and using a polymer molding procedure to form the ceramic part. The polymer may be oxidized or volatilized prior to sintering. Thin films may be formed by a paint-ceramic type formation.

2. Hot Pressing: Hot pressing of powders eliminates the sintering operation and minimizes the problem of shrinkage and porosity in the sintered piece. Hot pressing requires graphite dies and high temperatures. Shapes are limited to 30 cm x 45 cm plates and cylinders and tubes of limited height to diameter ratios.

3. Chemical Vapor Deposition (CVD): Forming by CVD is limited to coating the surface of a partially densified material. Some CVD single crystal shapes have been fabricated into dimensions up to a few inches in size.

Costs for fabricated parts of ceramic materials are determined to a great extent on the market or volume. High volume has cut the cost for light bulb glass envelopes to a few pennies. Glass in standard shapes is inexpensive. Custom fabrication costs considerably more. Table 6.16 lists fabricated costs for ceramic materials in approximate forms.

TABLE 6.16 Approximate Costs of Custom Fabricated Ceramic Material

Type of Material	Cost in Dollars per Cubic Inch
Clay Refractory	0.01 to 0.02 (.002 for standard brick)
Alumina Refractory	0.02 to 0.1 (.005 for standard brick)
Fused Silica	0.05 to .8
Alumina Castable	0.02 to 0.05
Fiber Insulation	0.01 to 0.03
Silicon Oxynitride	0.50 to 5.0
Si_3N_4 Bonded SiC	0.1 to 0.3
Reaction Sintered Si_3N_4	0.5 to 1.0
Hot Pressed SiC	20.0
Hot Pressed Si_3N_4	20.0
Stainless Steel	0.30
Super Alloys	0.85
50-50 Chromium-Nickel	1.4 to 1.7

6.5.10 Reactivity with Environments

For oxides or silicates only intimate contact with carbon and very low partial pressures of oxygen can cause deterioration by reduction. These conditions do not exist in an incinerator. Sulfur is no threat to ceramic materials because the oxides are generally more stable than the sulfides. All ceramic materials are expected to be thermodynamically stable in an incinerator atmosphere.

The most aggressive environment which can deteriorate ceramic, as in the case of metals, is fused salts. These attack the oxides protecting metals and for the same reason will attack the ceramic oxides and silicates used in refractories. Only silicon nitride, perhaps Sialon (silicon aluminum oxynitride) and silicon oxynitride are not wetted by molten NaCl-Na_2SO_4 at incinerator temperatures.

The thermodynamic stability of the oxides, carbides, nitrides, sulfides, sulfates, and chlorides can be readily evaluated from the series of Ellingham diagrams available from Rosenqvist [77]. The diagram showing thermodynamic stability of oxides is given in Figure 6.26. The oxides are very stable (large negative ΔG). By thermodynamic calculation it can be shown that $Na_2SO_4 + Al_2O_3 - 2SiO_2$ (clay) will react at moderate temperatures to form $Na_2OAL_2O_3 \; x \; SiO_2 + SO_3$ where x is 4 or 6 or the appropriate $Na_2 - Al_2O_3 - SiO_2$ glass. Thus, clay is a possible additive to diminish the adverse effect of NaCl - Na_2SO_4 eutectics.

6.5.11 Criteria for Insulation

For purposes of insulating at high temperatures with a lightweight, heat shock resistant material, ceramic fibers offer the greatest opportunity for satisfactory service. For low temperature insulation, glass fibers are adequate; intermediate temperature service requires mineral wool; for high temperature service, refractory fibers are used. The most widely used refractory fiber insulation is derived from kaolin clay by arc melting and blowing in a high pressure gas stream. The most prominent products are Kaowool by Babcok and Wilcox and Fibrefax by the Carborundum Company. These fibers have high melting points in the order of 1760°C, but have service temperatures in the order of 1200°C. The restricted service temperature 1200°C results from sintering and shrinkage that takes place with the micron size fibers ($\sim 3\mu$m in diameter) as the temperature is raised above the 1200°C limit.

A somewhat higher temperature fiber is the zirconia fiber, originally produced by Union Carbide under the trade name, Zircar. Although its melting point is much higher, 2480°C, its use temperature is still limited by sintering and problems of shrinkage of filaments contacting each other. Hence, its service temperature is limited to about 1300°C or 1400°C. Hitco, ICI, and 3M have high temperature fibers made as continuous filaments. Like Zircar, they are expensive and offer little additional advantage for insulation of shipboard incinerators.

All of the fibrous insulations may be obtained in a rigidized board form. In this configuration, the fibers are mixed with an inorganic binder (colloidal silica, for example) and the resulting structure is fairly rigid, yet the board has excellent heat shock resistance. Under these conditions, it is difficult to propagate a fracture through the porous insulation. Rigidized fibrous materials in an incinerator have the advantage of having good insulating qualities, lightweight, and good resistance against flame impingement; but, because of the porosity of these materials, they lack resistance to mechanical abrasion or slag attack from salts and ash. They are thus restricted to back-up insulation or to areas not subject to abrasion and salt attack.

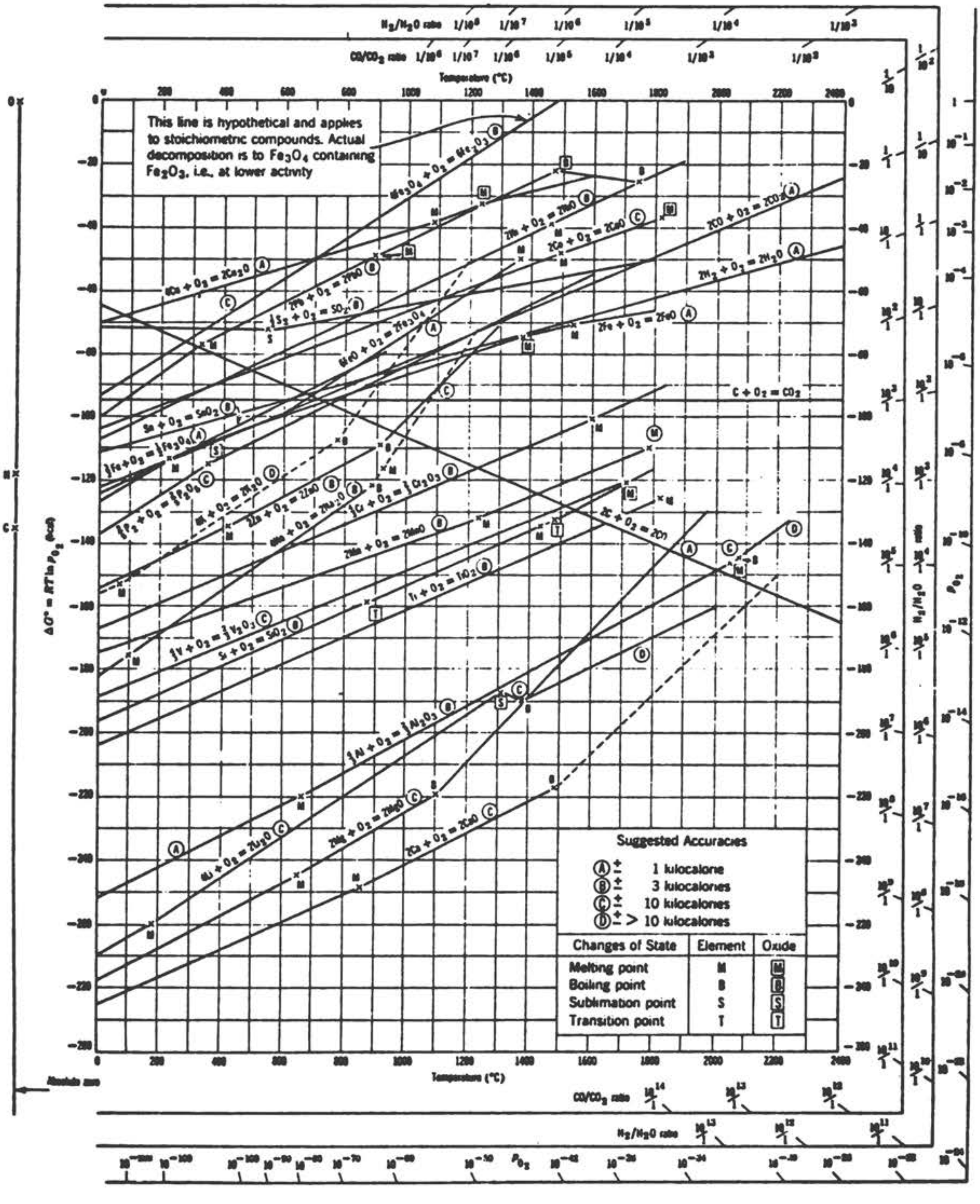


Figure 6.26 Standard Free Energy of Formation of Oxides as a Function of Temperature [78]

In the absence of abrasion or salt impregnation, rigidized board or blanket insulation may be readily installed and pinned into place with non-metallic pins spaced about a foot apart. Many kilns and furnaces have been successfully constructed in this manner. The rising cost of energy has increased the use of light weight insulating fibers in furnace construction.

6.5.12 Summary of Potentially Satisfactory Ceramic Materials for Shipboard Incinerators

Outlined below are the ceramic materials which appear to be the most promising for linings in shipboard incinerators. The techniques of fabrication and general composition are described.

1. Silicon Nitride: Silicon nitride (Si_3N_4) is prepared from silicon by nitridation near the melting point of silicon. It is fabricated by hot pressing, usually with magnesia as an additive. An alternative is to cold press silicon powder and nitride the porous compact in situ (reaction sintered).

2. Silicon Carbide: Silicon carbide is usually made by reaction of sand and coke at very high temperature. The silicon carbide powder may be bonded by heating the silicon carbide powder compacts as if they were to sinter. At high temperature, evaporation and condensation produce a bond without consolidation and shrinkage. The porous product is designated recrystallized silicon carbide.

   a. Silicon nitride bonded silicon carbide can be produced by mixing silicon carbide with silicon powder and heating the mixed and compacted powders in a nitrogen atmosphere. A similar product of silicon oxynitride bonded silicon carbide utilizes some silica in addition to silicon. This product is porous like reaction sintered silicon nitride.

   b. Reaction sintered silicon carbide uses silicon mixed with carbon or graphite and formed into the preferred shape. The shape is heated in a vacuum in the presence of silicon liquid which wicks into the porous structure by capillary action, reacts with the carbon or graphite, and produces a dense silicon carbide bonded silicon carbide ceramic.

   c. A porcelain composition mixed with silicon carbide forms a good bond for some purposes. This is called silicate bonded carbide.

3. Crystallized Glasses: Lithium aluminum silicates, zinc aluminum silicate and magnesium aluminum silicates may be melted and formed as a hot viscous glass by glass working equipment. After forming and cooling,

the glass articles are annealed near the softening point of the glass to produce crystals of low coefficients of thermal expansion. The magnesium aluminum silicate crystals (cordierite) are the most refractory of the crystallized glasses.

4. Cordierite: Cordierite (magnesium aluminum silicate) may be fabricated by sintering a mixture of talc and clay that has been previously formed into the desired shapes by any one of a number of ceramic forming operations. The sintered cordierite is porous but less expensive than the cordierite obtained by glass forming techniques.

5. Fused Silica: Fused or vitreous silica (dense SiO_2 glass), sometimes called fused quartz, is obtained by melting silica surrounding a graphite resistor. While the glass is hot (> 1500°C), some blowing and drawing may be applied. The advantage of this material is its near zero coefficient of thermal expansion. The temperature limit for vitreous silica is dictated by the crystallization of vitreous silica.

Porous fused silica is used as a sintered refractory in continuous casting of steel. It is made from fused silica powder shaped by conventional ceramic powder forming techniques followed by sintering.

6. Castable Refractory: A family of concretes suitable for refractory service can be fabricated by the usual concrete technology. The cement is a special calcium aluminate or iron calcium aluminate similar to portland cement but setting more rapidly by hydraulic activity. The aggregate may be sintered clay, fused or sintered bauxite, or sintered alumina depending on the service temperature of the castable refractory. Maximum service temperatures range from 1300°C to 1700°C.

7. Refractory Brick: Many compositions of refractory brick are available, but only clay refractory brick need be considered here. Tile made from refractory clay would be appropriate for consideration in incinerators. It is formed from a mixture of raw clay and clay sintered into an aggregate and shaped by the usual ceramic powder forming techniques. The formed tile is fired or sintered but yields a porous product of intermediate strength and slag or salt resistance.

8. Sialon: Sialon, a recent discovery, is an extension of silicon nitride. It is a sinterable solid solution of silicon nitride and aluminum oxynitride such as $Si_3N_4 \cdot Al_3O_3N$.

6.6 Fabrication of Metallic Materials

6.6.1 Fabrication of Complex Materials Systems

Materials used in the shipboard incinerators are selected to meet the widely varying conditions described in Chapter 5.0. For example, corrosion resistance is required both under high temperature operating conditions as well as the circumstances of moisture condensation at low temperatures. Further, there are rapidly varying thermal conditions. Such circumstances imply the use of various materials and fabrication techniques applied in close juxtaposition in the construction of the incinerator.

Discussed in the following sections are important considerations in fabricating candidate metallic materials.

6.6.2 Low Alloy Steels

Low alloy steels are candidates for incinerator sheet materials where temperatures do not exceed 260°C to 370°C. They can be easily fabricated by conventional techniques of forming and welding. The most probable failure mode for the low alloy steels is corrosion as a result of condensation during the time the incinerator is shut down. At temperatures in excess of 540°C, oxidation rates will be so rapid as to preclude their use. Weldable low alloy replacement liners for vortex incinerators which operate in the 650°C to 705°C metal temperature range have a short service life (4 to 6 months). The failure mode will most likely be rapid intergranular oxidation as a result of the presence of chlorides. During downtime, acid condensates will also contribute to early failure. Field weld repairs are probably impractical.

6.6.3 Cast Alloys

Incinerator grates are normally made from low alloy cast irons. Since these materials are not resistant at high temperatures, the common practice is to blow air through the grates to cool them to a safe operating temperature (less than 650°C). In spite of this, grate burnouts frequently occur.

The alloys normally used for furnace and incinerator grates are ductile iron and an Fe-1Cr. Cast alloys can be weld-repaired if special techniques involving high preheat temperatures, nickel alloy weld rods, and slow cooling are employed. It is doubtful that field weld repair of Naval incinerator grates would be economical. For some applications, heat-resistant casting of the HK-40 (25 Cr-12 Ni) type are used. These materials are usable at temperatures of 870°C and above, but most incinerator service temperature limitations probably are below 650°C. Weld repair of the HK-40 is difficult.

6.6.4 Chromium-Nickel Alloys

Of particular interest for Navy incinerator service are the 50Cr-50Ni and the high chromium-metal alloys, Inconel 671 and 690. These alloys, while possessing excellent high-temperature corrosion resistance to $NaCl-Na_2SO_4$ salt mixtures, are difficult to fabricate. Small additions of titanium are necessary to insure satisfactory rolling and forging of the Inconel 671 type alloys.

The high chromium-nickel alloys are also difficult to weld. However, a wire-rod composition for Tungsten Inert Gas (TIG) welding of the Inconel 671 alloy has been developed. This alloy (Huntington Alloy designation R-122) is somewhat lower in chromium than the base material (43 percent chromium as compared with 48 percent chromium). Satisfactory welds can be made, but it remains to be seen whether the weld material will have the same corrosion-resistant properties as the base metal.

Inconel-690 can be welded with either Inconel 625 or R-122. However, experience suggests that Inconel 625 does not have sufficient chromium for resistance to the $NaCl-Na_2SO_4$ salts. Therefore, if Inconel 625 weld wire is used, a final overlay pass can be made with R-122.

6.7 Ceramic Materials' Design and Fabrication

Designs with thin cross-sections are required. A thin tile with either high thermal conductivity and/or low coefficient of thermal expansion would make this configuration attractive because it insures freedom from fracture and from thermal strains. There is no reservoir of experience for incorporating thin tiles into incinerator designs. The problems can only be estimated on the basis of past experience.

6.7.1 Problem of Monolithic Structures

Fabrication of monolithic, thin-walled ceramic liners larger than 30 cm in diameter appears to be very difficult. Slip-casting followed by sintering is the only method of fabrication for such shapes. Thermal stresses and fracture with large shapes of this size and larger add to the hazards of this design.

The use of self-interlocking tiles offers the most reliable and inexpensive construction. They do not have to be attached with hangers to a metallic shell. Interlocking tiles could be compressed into a stable configuration with back-up fibrous insulation.

Ceramic hangers or pins have been used to secure fibrous blankets to furnace walls. Although a porous liner cannot be tolerated as would be the case with a fibrous blanket, the ceramic hanger or pin concept for tile attachment can be used. This requires a design, perhaps spring-loaded, that will not fracture small diameter pins under the load of strains developed from thermal stresses.

Metallic hangers would need to have the same corrosion resistance previously described for the requirements of a metallic monolithic liner.

6.7.2 Size of Ceramic Tiles

Fabrication by sintering is the least expensive method of fabrication, but tolerances are sometimes difficult to maintain. Shrinkage and reproducibility of flatness or curvature must be considered. Experience suggests that the maximum size of these tiles would be 30 cm x 45 cm.

REFERENCES

1. Courtesy of P. Schatzberg, Naval Ship Research & Development Center, Annapolis Laboratory, Annapolis, MD.

2. Doving, H. Von E. and Bergmon, P., Construction and Operation of Hot Corrosion Test Facility, Materials Research and Standards, ASTM Vol. 9, No. 9, page 35.

3. Wacker, G. A., Naval Ship Research & Development Center, Annapolis Laboratory, Annapolis, MD; letter to D. G. Groves, National Materials Advisory Board, 10 Feb 1976.

4. Alloy and Microstructural Design, J.K. Tien and G. Ansell, Editors, Academic Press, NY, (1976).

5. Goebel, J.A. and Pettit, F.S., "Na_2SO_4-Induced Accelerated Oxidation (Hot Corrosion) of Nickel," Met. Trans., Vol. 1, p. 1943, (1970).

6. Goebel, J.A., Pettit, F. S. and Goward, G.W., Hot Corrosion Mechanisms in Stationery Gas Turbines, Proceedings CEBG Conference on Corrosion and Deposition in Gas Turbines, held in London, 1972, Editors, A.B. Hart and A.J.B. Cutler, Applied Science Publishers, Essex, England (1973).

7. Chang, R.N., Ph.D. Thesis, Northwestern University, 1973.

8. Wagner, C., "Reaktionstypen bei der Oxydation von Legierungen," A. Elektrochem, Vol. 63, p. 772, (1959b).

9. Wagner, C., "The Formation of Composite Scales Consisting of Oxides of Different Metals," J. Electrochem. Soc., Vol. 103, No. 11, p. 627, (1956a).

10. Wagner, C., "The Oxidation of Alloys Involving Noble Metals," J. Electrochem. Soc., Vol. 103, No. 10, pp. 571-580, (1956b).

11. Wagner, C., "Theoretical Analysis of the Diffusion Processes Determining the Oxidation Rate of Alloyw," J. Electrochem. Soc., Vol. 99, p. 369, (1952).

12. Rapp, R.A., Acta Met., Vol. 9, pp. 730-741, (1961).

13. Wagner, C., "Diffusion and High Temperature Oxidation of Metals," Atom Movements, American Society for Metals, (1951).

14. Kubaschewski, O. and Hopkins, B.E., Oxidation of Metals and Alloys, Academic Press, Inc., New York, NY, (1962).

15. Hauffe, K., Oxidation of Metals and Alloys, Plenum Press, New York, NY, (1965).

16. Kofstad, P., High Temperature Oxidation of Metals, John Wiley & Sons, New York, NY, (1966).

17. Failure Analysis and Prevention, Metals Handbook, Vol. 10, American Society for Metals, Metals Park, OH, (1975).

18. Hart, A.B. and Cutler, A.J.B., Deposition and Corrosion in Gas Turbines, Halstead Press, Essex, England, (1973).

19. "Hot Corrosion Problems Associated with Gas Turbines," ASTM Publication 421, American Society for Testing and Materials, Philadelphia, PA, (1967).

20. Stringer, J., "Hot Corrosion in Gas Turbines," Metals and Ceramics Information Center Publication No. 72-08, Battelle-Columbus Laboratories, Columbus, OH, (1972).

21. Wright, I.G., "Oxidation of Iron-Nickel and Cobalt-Base Alloys," Metals and Ceramics Information Center Publication No. 72-07, Battelle Columbus Laboratories, Columbus, OH, (1972).

22. Evans, U.R., The Corrosion and Oxidation of Metals, Edward Arnold Ltd., London, (1960).

23. Sahm, P.R. and Speidel, M.O., High Temperature Materials in Gas Turbines, Elsiver Scientific Publishing Co., New York, NY, (1974).

24. Giggins, C.S. and Pettit, F.S., "Oxidation of Ni-Cr-Al Alloys Between 1000 and 1200°C," J. Electrochem. Soc., Vol. 118, p. 1782, (1971).

25. Daniels, P. and Rapp, R.A., "Halidation of Metals," Advances in Corrision Science and Technology," Vol. 5, Plenum Press, New York, NY, (1976).

26. Bruchman, A. and Mrowec, S., Werk. und Korr, Vol. 25, p. 502, (1974).

27. Lund, C.H. and Wagner, H.J., "Oxidation of Nickel and Cobalt-base Superalloyws," DMIC Report 214, Defense Materials Information Center, Columbus, OH, (March 1, 1965).

28. Stringer, J., Corrosion Sci., Vol. 10, p. 513, (1970).

29. Giggins, C.S. and Pettit, F.S., "Oxide Scale Adherence Mechanism Program," Final Report, (Contract F33615-72-C-1702), Pratt Whitney Aircraft for Aerospace Research Laboratories, WPAFC, OH, (January 1976).

30. Dils, R.R., "Materials Responses to Combustion Dynamics," Materials Problems and Research Opportunities in Coal Conversion, Vol. II, p. 345, (April 1974).

31. Wukusick, C.S. and Collins, J., Mater. Res. Stand., Vol. 4, p. 647, (1964).

32. Goebel, J.A. and Pettit, F.S., Hot Corrosion of Cobalt Base Alloys Program," Final Report, (Contract F33615-72-C-1757), Aerospace Research Laboratories, WPAFC, OH, (January 1976).

33. Tien, J.K. and Pettit, F.S., Met. Trans., Vol. 3, p. 1587, (1972).

34. Pettit, F.S., Effects of Oxide Dispersions and Rare Earth Type Elements on the Osication of Cr and Al-Containing Alloys," Introductory Paper No.120 for the Proceedings of AGARD Conference on High Temperature Corrosion of Aerospace Alloys, Specialist Meeting held at the Technical University of Denmark, Lyngby, Denmark, (1972).

35. Giggins, C.S., Felten, E.J. and Pettit, F.S., "Growth Stress Induced Features of Al_2O_3 Scales Developed on Alloys During Oxidation," Stress Effects and Oxidation of Metals, J.V. Cathcar, editor, The Metallurgical Society, (1975).

36. Goebel, J.A., Felten, E.J. and Pettit, F.S., "Hot Corrosion Mechanisms for Nickel and Cobalt Alloys," Proceedings of the 1974 Gas Turbine Materials in the Marine Environment Conference, pp. 93-114, MCIC-75-27, NTIS, U.S. Commerce Department, Springfield, VA, (1974).

37. Hurst, R.C., Johnson, J.B., Davies M. and Hancock, P., "Proceedings CEGB Conference on Corrosion and Deposition of Gas Turbines held in London, 1972, A.B. Hart and A.J.B. Cutler, Editors, Applied Science Publishers, Essex, England, (1973).

38. Adler, W.F., "Analysis of Multiple Impacts on Brittle Materials," Report AFML-TR-74-210, WPAFB, OH, (1974).

39. Finnie, I., Wolak, J. and Kabil, Y., "Erosion of Metals by Solid Particles," J. Mater., Vol. 2, p. 682, (1967).

40. Materials Engineering and Research Laboratory, Pratt & Whitney Aircraft, Middletown, CN, (Feb. 1975).

41. Localized Corrosion, Editors R.W. Staehle, B.F. Braun, J. Kruge, A. Agrawal, National Association of Corrosion Engineers, Houston, TX, (1973).

42. Localized Corrosion, STP-516, American Society for Testing of Materials, Philadelphia, PA, (1972).

43. Fontana, M.G. and Greene, N.D., Corrosion Engineering, McGraw-Hill Book Company, New York, NY, (1967).

44. Uhlig, H. H., Corrosion and Corrosion Control, Wiley & Sons, NY, (1963)

45. Cook, R.H. and Skelton, R.P., "Environment-Dependence of the Mechanical Properties of Metals at High Temperature," International Met. Rev. IMRVBH 19, 199, (1974).

46. Metals Handbook, Failure Analysis and Prevention, Vol. 10, American Society for Metals, Prak, OH, (1975).

47. Cotterill, P., "The Hydrogen Embrittlement of Metals," Progress in Materials Science, Vol. 9, Chalmers and Kind, eds., Pergamon, Longon, (1961).

48. Bernstein, I.M and Thompson, A.W., Hydrogen in Metals, American Society for Metals, Metals Park, OH, (1974).

49. Bernstein, I.M. and Thompson, A.W., Effect of Hydrogen on Behavior of Materials, Transactions of the Metallurgical Society, American Institute of Mining, Metallurgical and Petroleum Engineers, New York, NY, (1976).

50. Doherty, J.E., Giamei, A.F. and Kear, B.H., Canadian Met. Quarterly, Vol. 13, p. 229, (1974).

51. Corrosion Studies in Municipal Incinerators, Report No. SW-72-3-3, U.S. Environmental Protection Agency, (1972).

52. Proceedings of Conference on Fundamental Aspects of Stress Corrosion Cracking held at Ohio State University, R.W. Staehle, A.J. Forty and D. Van Rooyen, editors, National Association of Corrosion Engineers, Houston, TX, (1969).

53. Stress Corrosion Cracking and Embrittlement, Electrochemical Society, Symposium, W.D. Robertson, ed., John Wiley & Sons, Inc., (1956).

54. Physical Metallurgy of Stress Corrosion Fracture, Metallurgical Society Conference, T.N. Rhoden, Interscience Publishers, New York, NY, (1959).

55. Proceedings of Second International Congress on Metallic Corrosion, New York, NY, (1959).

56. Logan, H.L., The Stress Corrosion of Metals, John Wiley & Sons, New York, NY, (1966).

57. Nielsen, N.A., "Observation and Thoughts on Stress Corrosion Mechanism," Corrosion, Vol. 27, No. 5, pp. 173-189, (May 1971).

58. Parkins, R.N., "Stress Corrosion Cracking," Metall. Review, Vol. 9, No. 35, p. 201, (1964).

59. "The Theory of Stress Corrosion Cracking in Alloys," Proceedings of a Research Evaluation Conference, J.C. Scully, NATO, Science Affairs Division, Brussels, (1971).

60. "Stress Corrosion Cracking in Metal," Report NASA-SP 8082, National Aeronautics and Space Administration, (August, 1971).

61. Brown, B.F., "Stress Corrosion Cracking in High Strength Steels and Titanium Alloys," Naval Research Laboratories.

62. Rostoker, W., McCaughey, J.M. and Marcus, H., Embrittlement by Liquid Metals, Reinhold Publishing Cor., New York, NY, (1960).

63. Krause, H.H., Vaughn, D.A., Cover, P.W., and Boyd, W.K., "Firing of Refuse with High Sulfur Coal," Corrosion and Deposits From the Combustion of Solid Waste, Part V, ASME Paper No. 76-WA/CD-1, ASME J. of Engrg for Pwr., (January 1977).

64. Vaughan, D.A., Krause, H.H., Boyd, W.K., "A Study of Corrosion in Municipal Incinerators Versus Refuse Composition," NTIS Report No. PB-238-747, (December 1974).

65. Fontaine, P.I., and Richards, E.G., "Hot Corrosion of Nickel-Iron-Chromium-Cobolt Alloys by Sulfate-Chloride and Sulfate-Vanadate Simulated Fuel Ashes," Hot Corrosion Problems Associated with Gas Turbines, ASTM STP 421, American Society for Testing and Materials, New York, NY, (1967).

66. Kubaschewski, O., and Hopkins, B.E., "Oxidation of Metals and Alloyw," Academic Press Inc., New York, NY, (1962).

67. Wright, I.G., "Oxidation of Iron-Nickel, and Cobolt-Base Alloys," Metals and Ceramics Information Center 72-07, Battelle-Columbus Laboratories, Columbus, OH, (1972).

68. Stringer, J., "Hot Corrosion in Gas Turbines," Metals and Ceramics Information Center 72-08, Battelle-Columbus Laboratories, Columbus, OH, (1972).

69. Private communication from S. Zerrik.

70. Hancock, P., "Corrosion of Alloys at High Temperatures in Atmospheres Consisting of Fuel Combustion Products and Associated Impurities," Her Majesty's Stationary Office, (1968).

71. Private communication. Letter from George Wacker to Don Groves, National Materials Advisory Board, (Feb. 10, 1976).

72. Letter report. Navy Contract No. N00600-75-D-0465, Task 14, IITRI, (February 20, 1976).

73. Hasselman, D.P.H., "Unified Theory of Thermal Shock Fracture Initiation and Crack Propagation in Brittle Ceramics," J. Am. Ceramic Soc., Vol. 52, No. 11, p. 600, (1969).

74. Hasselman, D. P. H., "Thermal Stress Crack Stability and Propagation in Severe Thermal Environments," Materials Science, Vol. 5, Ceramics in Severe Environments. W. W. Driegel and H. Palmer, III, Editors. Plenum Press, New York, NY, (1971).

75. Washburn, M. E., "Behavior of Silicon Oxynitride Refractories in Molten Alkali Halides," presented to the New England section of the American Chemical Society at a special Symposium at MIT, October 21, 1970 and available from Norton Co., Worcester, Mass. "Silicon Carbide Refractory with a Complete Nitride Bond Containing Silicon Oxynitride," M. W. Washburn, and Robert W. Love, American Ceramic Society Bulletin, Vol. 41, No. 7, p. 447, (1962). "Behavior of Silicon Oxynitride in Contact with Molten Cryolite," M. E. Washburn, presented at the Symposium on Refractories for the Aluminum Industries, Seattle, Washington, October 17, 1969, available from the Norton Co., Worcester, Mass.

76. Lee, J. G., Casarini, R. and Cutler, B., "Sialon Derived from Clay as a Refractory Material," presented at the Fall Meeting of the Refractories Division of the American Ceramic Society, (October 3, 1975).

77. Rosenqvist, T., Principles of Extractive Metallurgy, McGraw-Hill, New York, NY, (1974).

78. Richardson, F. D. and Jeffes, J. H. E., J. Iron Steel Inst., 160, 216(1948). Modified by L. S. Darken and R. W. Gurry, Physical Chemistry of Metals, McGraw-Hill, New York, NY, (1953).

CHAPTER 7.0

FAILURE MODES, SYSTEMS RELIABILITY, AND SAFETY

7.1 Introduction

The primary reason for addressing the question of materials performance is the desire to maximize systems reliability. In order to favor the materials, in view of the aggressive conditions within the incinerators, this report has considered, in Chapter 8.0, various options for ameliorating conditions of operation. Following from these ideas, the primary objective of the overall materials-design effort is to optimize the reliability of the shipboard incinerator systems. Thus, if any of the components in the main or auxiliary systems fail, the whole system is jeopardized.

In view of overall concern for the reliability of the system, this chapter considers various failure modes which could vitiate the incinerator system as easily as a failed liner. Further, it is constructive and stimulating to integrate the question of materials reliability with all aspects of reliability. We hope that this would incite the reader to consider other eventualities, involving such diverse aspects as design and operation, which could cause failure.

The shipboard incinerator is not a critical system whose failure would automatically disable a ship. Malfunction at sea would not force return to port since the waste normally processed could either be dumped overboard, as an emergency measure, or bypassed into a holding tank. Malfunction in port would present certain legal or political problems but would not cause loss of the ship nor compromise its functioning.

However, the failure mode could have a bearing on the magnitude of the effect. In the worst case, an explosion could produce casualties or result in damage to the ship. On the other hand, a malfunction which caused local hot-spots in the liner could be handled by reduction of combustion temperature with some undesirable effects such as odors and reduced processing rate. Failure of an auxiliary subsystem would result in a temporary shutdown until repairs could be made or until such time as the vessel reached a Naval facility. These latter failures would be an inconvenience but would not affect the performance of the ship significantly.

While this report addresses itself to the problem of materials of construction with primary emphasis on the combustion chamber, these auxiliary components and subsystems cannot be ignored. Fortunately, most of these operate in an environment less hostile than that encountered in the combustion chamber. Furthermore, extensive Navy experience with motors, pumps, and plumbing in shipboard applications should minimize problems with these components, provided that components suitable for these applications are specified. Sealed motors requiring minimal maintenance and possibly Monel and Cupro nickel sludge feed lines are examples of preferred components.

Reliability must be designed into the system and cannot be treated as an "add-on" item. Design constraints such as space, weight, and location generally mitigate against reliability. An incinerator which would function reliably for the life of the ship is probably impossible. On the other hand, if the mean-time between failures (MTBF) is three or four years, the goal is probably attainable, and this would permit overhaul or replacement on a time schedule compatible with normal overhaul of the ship.

Maintainability of equipment is also important in assuring reliability. Motors, valves, and all other components requiring regular service or check-out must be in readily accessible locations. Motors, blowers, pumps, and plumbing components should be items of standard design which are readily available at forward bases and, when installed, are readily accessible.

In addition to reliability, an equally important consideration is safety, with respect to both personnel and the ship. The incinerator component should incorporate fail-safe features and damage control devices such as sprinkler systems. The incinerator system must operate reliably under the shock and vibration conditions normally encountered; and bypass circuits for the wastes must be incorporated to handle extended interruptions.

In addition to the failure modes which may be anticipated in the design of the incinerator proper, the incinerator auxiliaries, and the incinerator controls, failures which may result from personnel training inadequacies and incomplete or deficient repair manuals must also be anticipated. Appropriate manuals are especially critical because they serve as both training and repair manuals.

Subsequent sections describe failure modes which must be considered to achieve reliable performance of the full incinerator system. Figures 7.1, 7.2 and 7.3 illustrate failures which may occur inadvertently or by design oversight or by insufficient attention to an internal or external operating environment.

Material damage which may be expected by low temperature acid attack is shown in Figure 7.1. Both general deterioration and severe localized attack are evident.

A catastrophic failure with no external evidence of corrosion is shown in Figure 7.2. This failure appears to be stress-corrosion cracking, probably hastened by vibration.

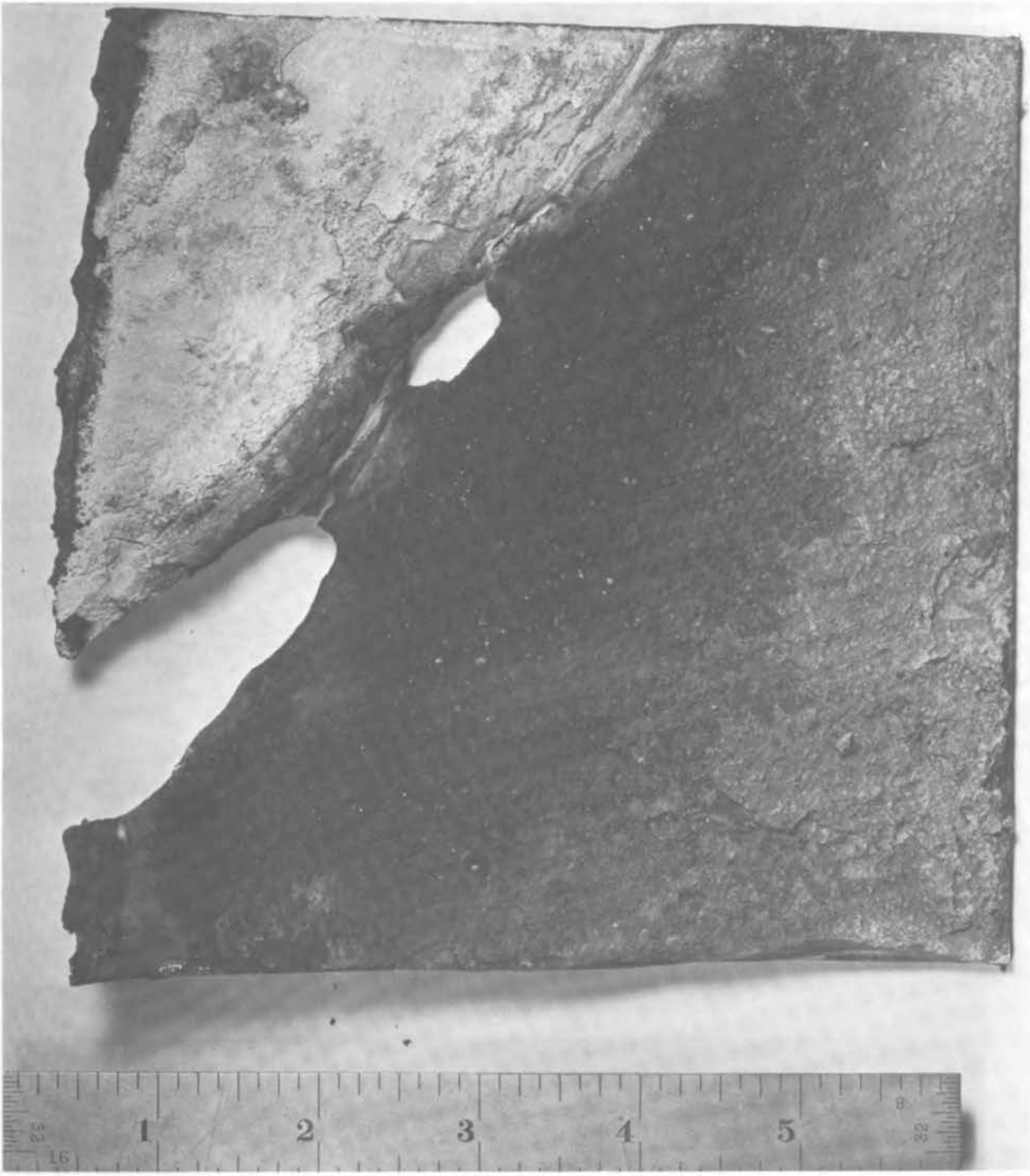


Figure 7.1 Material Damage from Low Temperature Acid Attack. (1X Magnification)

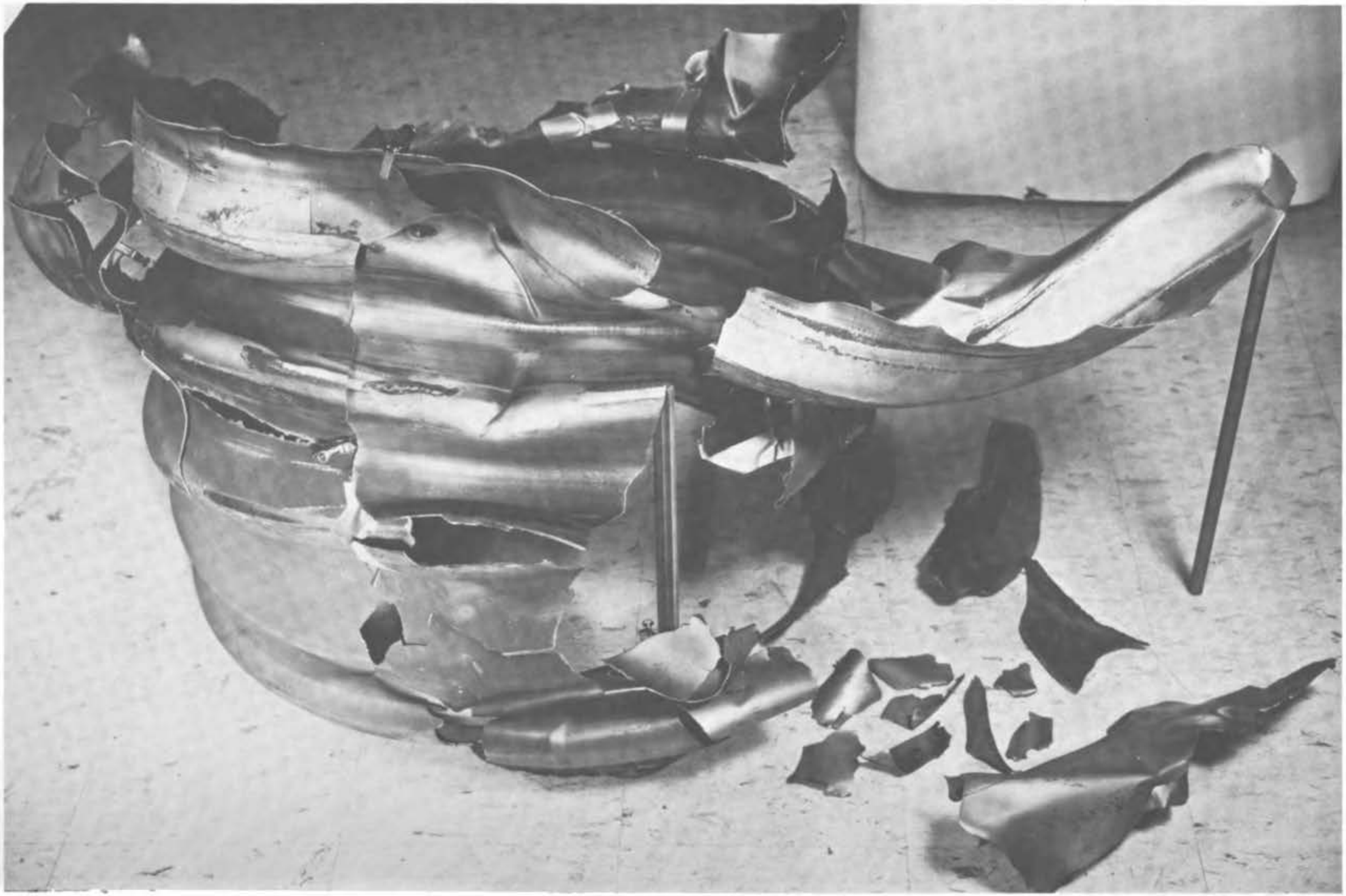


Figure 7.2 A Catastrophic Failure With No External Evidence of Corrosion. The appearance of the submitted sections of an expansion joint, after assembling a number of pieces with tape and clamps, is shown.

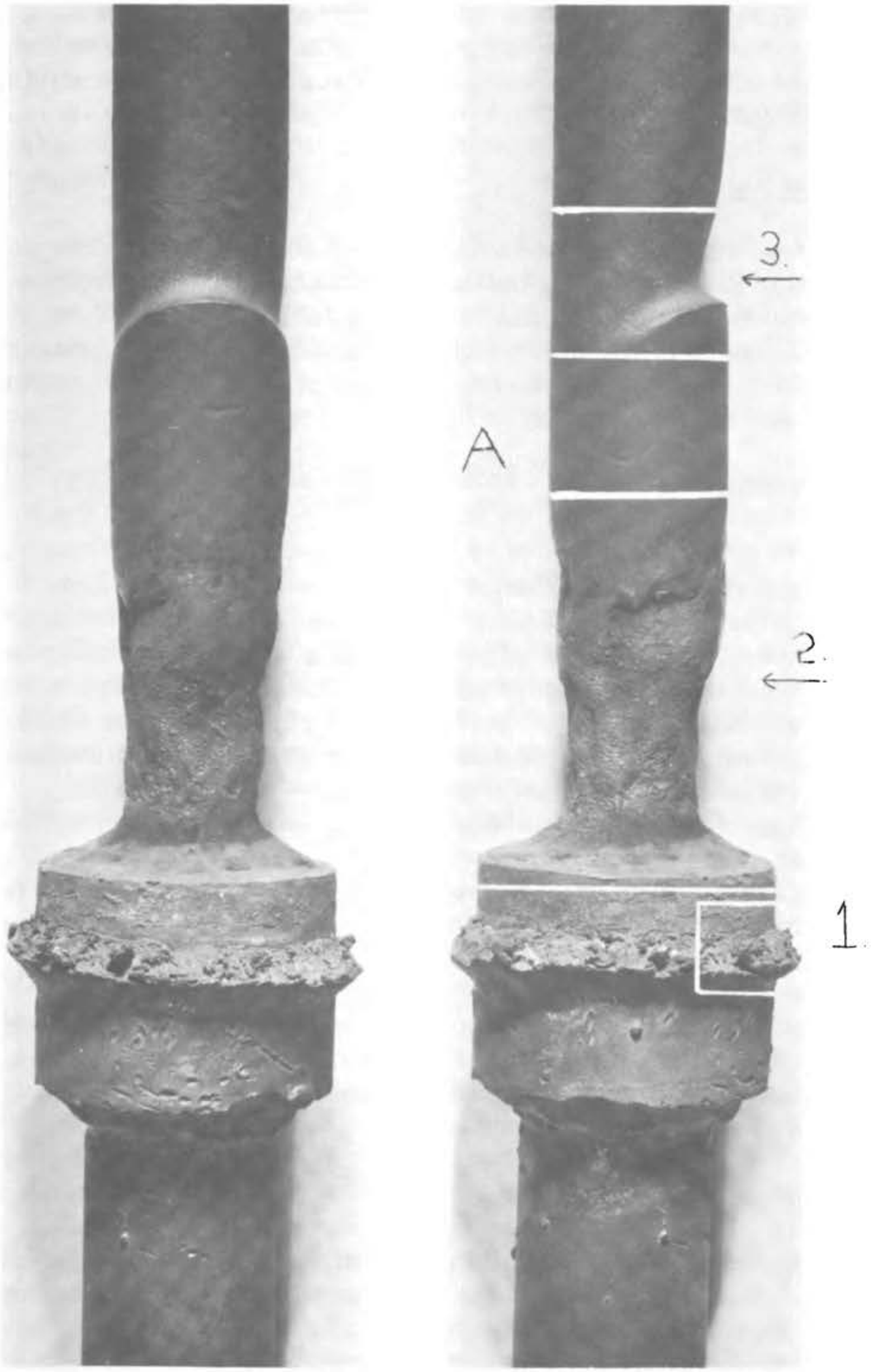


Figure 7.3 Loss of Protective Film Caused by Erosion Followed by Corrosion. Photograph shows two positions of the as-received thermowell removed from the "G" furnace. (1X magnification.)

Figure 7.3 shows a material failure caused by exposure to an erosive or abrasive environment carried by a flowing stream of hot gas. Similar failures should be anticipated when there is direct contact of solid moving trash within containing chamber walls.

7.2 Estimates of Reliability

There are few, if any, really useful data for predicting the lifetime of fabricated incinerator lines except for the data for Chapter 6.0. Nevertheless, an attempt to be semi-quantitative furnishes useful guidelines.

A recent discussion of reliability and maintainability requirements for shipboard incinerators arbitrarily assumed that one failure in 60 ten-hour daily operating cycles would be allowable [1]. Thus,

$$\text{Reliability} = \frac{\text{Number of successful missions}}{\text{Total number of missions}} = \frac{59}{60} = 0.983$$

Applying the exponential failure distribution $R = e^{-t/\theta}$, where $R = .98$ and $t = 10$ hours, the corresponding mean-time between failures (MTBF) for an incinerator is 500 hours. This MTBF of 500 hours at a 90 percent confidence level can be achieved if the system operates continuously for 1150 hours with no critical or major failures. Here, a critical failure is any malfunction which causes system shutdown, while a major failure is any malfunction which would, if not corrected, preclude processing of waste.

Test data suggest that a major overhaul (e.g., welding a crack, replacing a castable refractor section) is not expected before 2000 hours of operation. Since this estimate substantially exceeds the requirement of a MTBF of 500 hours, materials of construction are not expected to cause failure in liners which are short relative to scheduled repair availabilities.

A maximum repair time of 5 hours for system maintainability is expected [1]. Since maintenance for liner materials is not expected to occur before 2000 hours, it can be performed once a year, when the ship is in port. This type of maintenance thus lies outside the 5 hour maximum repair time during regular ship operations.

7.3 Explosion Hazards

The primary safety consideration is uncontrolled combustion or detonation. Such a detonation could occur perhaps as frequently as once per year in the incinerator in any of the following ways:

1. A power failure resulting in air and fuel flow cessation. Hot waste material would pyrolize releasing toxic and combustible gases. Re-ignition could produce a detonation.

2. A flame-out followed by fuel leakage into hot primary chamber. Fuel is gasified and detonates upon re-ignition.

3. A closed container of a combustible liquid is accidentally introduced into the incinerator resulting in detonation. This detonation could occur in the feed chambers.

In view of the probability of detonation, it is essential that incinerator design provide adequate safety protection for personnel and equipment. Adequate material strength to withstand detonation and/or proper relieving of the detonation must be provided. However, this requirement does not relate to this investigation, which deals with materials of construction to withstand environmentally induced deterioration caused by temperature, chemistry, and thermal cycling.

Explosions have also been reported in refuse shredders in commercial practice [2]. The survey of reference 2 reported 95 explosions in municipal solid waste shredding plants. Of the 41 explosions where a probable cause could be clearly identified, 30 were caused by common flammable gases or vapors (gasoline, propane, paint, thinner, etc.). Eleven others were caused by commercial or military explosives such as dynamite or gun powder. Combustible dust was suspected as one cause.

In cases where liquid sewage is stored, consideration should be given to explosions which would result from the accumulation of methane.

Various preventive procedures can be used to ameliorate such explosions including water spray and improved venting.

7.4 Safety

Since designs for land-based incinerators are not sufficiently compact, the development of a successful shipboard incinerator system requires extension of the state of the art. Four factors are especially significant: the mission of the ship; its space and weight limitations; its status as a self-contained unit like a town or city; and its generation of all types of wastes which must be converted on board. Since we are dealing with a new technology and owing to the hazards already discussed, special attention is needed to anticipate malfunctions which may affect the safety of the ship and its personnel.

There are three broad situations that affect safety. The first of these is fire. Means of escape from an incinerator compartment must be direct and at least in two different directions.

It is presumed that the incinerator will be installed in a ship's compartment and that the compartment will require ventilation, forced, induced or both. In this ventilated compartment are fuel pumps, fuel burners, fuel piping, and combustion equipment. It should be axiomatic that any such space must be either manned or be under direct observation and equipped with appropriate fire extinguishing apparatus. Every consideration must be given to insure the integrity of the entire fuel system within the compartment and without the compartment; special concern must be directed to four fuels—primary oil, waste oil, sludge, and trash.

These concerns should include such matters as fuel drips from joints, fuel sprays, leaking joints and fittings, fuel control system sensor failures causing fuel drips or sprays, and means to accommodate and assure complete fuel drainage from piping when beginning maintenance and overhaul procedures. Fuel spills during repairs not only create a fire hazard but also a personnel hazard due to a slippery deck. The primary fuels have low viscosity, and a small spill would quickly cover a large deck area. There must be positive means to determine the presence of fuel prior to the loosening of any piping joint including that which may occur from a hydrostatic head from elevated piping. To further control mechanical failures of fuel systems, hull and equipment vibrations should be considered in the design of piping and support facilities.

The second broad problem is caused by sewage sludge, which presents a potential biological hazard. Personal sanitation and bathing should follow repair operations. Mixing of potable and polluted water systems must be avoided. Goggles and other protective clothing should be available for those repair jobs requiring the use of these devices.

The third broad problem is the handling of the residual ash. Residues must be removed without increased manpower, exposure to dust, and failure of auxiliary appurtenance. The residues may contain potential toxicants, broken glass, nails, pieces of sharp metal, razor blades, and the like. The presence of these materials may be masked by ash.

Residue removal under these circumstances warrants concern to provide ready access to the appropriate location in the incinerator to enable safe removal. A container in which to collect and transfer obstructing unburned refuse and a container in which to store the residues should be available to control flash ignitions.

The necessary space and weight limitations require the incinerator to be compact and yet capable of high performance. Such limitations include accepting that outside surface temperatures may be on the order of 140°C. Direct human contact with surface temperatures of this order is painful and should be avoided. Wire screens should be caused to guard personnel from accidental contact with hot surfaces.

7.5 Soots and Their Interaction with Moisture

Soots are finely divided carbonaceous materials resulting from incomplete combustion or may also be formed as a result of rapid changes in thermal conditions. These load changes are conducive to the formation of soots which deposit in gas ducts depending upon prevailing gas flow patterns. The time-average of these load changes in a variable such as produced by gas temperature is constant, but the load change excursions may be large. The necessary small volume of the combustion chambers requires nearly instantaneous response of all combustion components to minimize formation of soots. The resulting soots may be mixed with salts which are either directly fired or formed in the combustion process. These soots with ingested salts occur in a soft and fluffy condition and are often hygroscopic. The soots include constituents which are acidic.

As the moist soots are dried, the aqueous acid concentration increases. Sources of moisture include rain falling into an idle stack, ambient air, and the products of combustion cooled below the dew point.

The attack of metals upon which soots deposit depends on the composition and the manner of deposition of the soot. The attack may be general; but, more often, the general attack is accompanied by pitting to such an extent that actual failure occurs by penetration of a metallic wall by pitting rather than by uniform loss of metal. In addition to the prevailing humidity at a given moment, consideration must be given to the effect of day-to-night temperature variation, which affects the relative humidity of the gas within the unit. Moisture condensation in air-cooled zones of the incinerator, causing possible subsequent rusting, should not be ignored.

Crevices between metallic parts or between metals and refractory materials provide pockets for soot deposition as well as sites for crevice corrosion. Cursory examination without attention to such crevices may overlook a condition of advanced deterioration and imminent failure.

Failures from these causes may be minimized by rapid combustion, avoiding crevices, avoiding sharp bends in gas passages, avoiding ingress of moisture from rains which approach being torrential in the tropics, and continuous ventilation of an idle incinerator using a source of hot air inside the ship.

7.6 Shut-down and Warm-up Procedures

These procedures should be consistent with the thermal shock and fatigue behavior of the materials used in the incinerator. Expansion coefficients and time-temperature lags of the various components affected by warm-up and shut-down should be considered. Severe thermal stresses may be encountered by differential absolute expansion or contraction of an assembly caused by expansion coefficient differences, assembly component temperature differences, and by component dimensions.

The shut-down procedures must also recognize a probable need for multiple purging. The internal thermal energy of the unit in operation may be of sufficient magnitude to cause an operating failure at the next start up. Oil burners may require purging to avoid carbonization of fuel on burner tips and in small oil passages leading to the burner tip. Although the carbonization may be insufficient to cause light-off failure, it may interfere with the expected fuel spray patterns during operation and cause fuel impingement on the walls of the combustion chamber which will upset the gas chemistry in the chamber wall vicinity. Also, depending upon the burner design, the amount of fuel within the burner may be sufficient to cause, by expansion, the drip of fuel from the burner into the hot combustion chamber. Sufficient fuel vaporization may form an unsuspected explosive mixture within the unit, including cooling air passages. Both the primary fuel burner or burners and the waste oil burner are suspect.

The sewage feed line into the combustion chamber may cause difficulty in the same manner as oil burners. The sewage entrained in the injection assembly may become baked and stop the flow. Problems of partial blocking are similar to that mentioned in regard to oil burners.

It is essential to purge the unit with air after shut-down and prior to start-up to dilute and remove any possible explosive mixture in the combustion chamber, air cooling passages (if fitted), and in the stack. However, the effect of purging on thermal shock on the hot incinerator must be considered; the purge rate during shut-down should be minimal to avoid thermal shock, but should be relatively high to avoid explosive mixtures.

7.7 Fuel Supply

Primary fuel supply must be assured and appropriately regulated during firing rate changes because primary fuel flameout may cause thermal shock of the unit assembly and also create an explosive fuel mixture within the unit. The thermal shock may be intensified with continued sewage feed into the hot incinerator in the event of flameout. Assuming that an otherwise undetected flameout would be detected by a gas temperature controller, the action of such a controller would create a demand for more fuel, which intensifies an already dangerous situation.

Detection of flameout must be rapid. Such detection should cause an immediate shut-off of all fuel and initiation of the shut-down purge procedure applicable to the incinerator unit. Any restart procedure must follow the full purge procedure.

The entire fuel system requires careful attention to assure an uninterrupted supply of clean fuel at all times. To this end, maintenance procedures and the effect of long time idle period duration should be considered to provide the capability to bleed entrained air from the fuel system.

7.8 Permanent Dimensional Changes

Materials show varying evidence of permanent dimension change when repeatedly heated and cooled. Such changes may produce buckling of components, distress at joints and fastenings, and dislocation and misalignment of components. Because these dimensional changes may not be sufficiently severe to cause obvious component failure, the component may remain in service. However, the changes may be sufficient to preclude proper assembly following a dismantling procedure.

7.9 Hull Vibration

Hull vibration has a broad spectrum of frequencies and amplitude. The consequences of such vibrations upon piping systems, equipment appendages of large mass with inadequate fastening, and instrument behavior require design attention.

An additional consequence of hull vibration may become evident if such vibration causes relative motion between a hard material such as an incinerator refractory and a soft but rigid one. Relative motion may cause a grinding away of the surface with loss of support and loss of refractory material. If a soft insulating material is used relative motion must be prevented at the bearing interfaces.

7.10 Complicated Assembly of Repair Procedures

Repair and assembly are routine activities on ship, and it seems redundant to mention them. Nonetheless, faulty repair and assembly often contribute to unexpected failures in all engineering equipment. Little of a specific nature can be said, but the high intensity of processes which is necessary in view of limited space together with the psychological bias of "non-criticality" raise to a more significant level the attention which is deserved by repair and assembly procedures.

An erroneous assembly may not preclude start-up, but a catastrophic failure may occur later. If, for example, special quality fasteners are required in a critical area of the incinerator, all like fasteners of the same special quality must be used. A requirement to identify like and similar fasteners by location and by quality invites assembly error.

The distinction between field welding and shop welding, with the lower quality of the latter, must be recognized. An assembly or procedure which requires extensive field welding techniques should be discarded.

Full attention should be given to the environment in which repair and assembly are conducted. The environmental considerations are space available, appendage interference, pipe and duct interference, and working conditions as influenced by ambient temperature and humidity.

Consideration should also be given to the motion of a ship at sea and the consequences of such motion upon the handling of heavy subassemblies or components.

7.11 Complicated Operating Procedures

Operating procedures include convenience of operation, visibility of all instruments, and ready and clear access to operation test and check points. The operating margins of a shipboard incinerator are narrow and critical. Full control of the incineration process must be maintained. The operator should be confident and should check instrumentation and controls. Sensors should be simple and reliable and subject to double checking. The use of fiber optics to permit visual observation of remote events, for example, may offer operational advantages.

7.12 Auxiliary Equipment

Failure may occur in any of the items of auxiliary equipment: pumps, blowers, instruments, controls, strainers, regulators, valves, fittings, and the like. The fitting of redundant auxiliaries to assure operation is generally prohibited by weight and space considerations. Selection of auxiliary equipment warrants as much attention as the incinerator proper. Because of the narrow operating margins of the incinerator, the effect of an auxiliary failure on the incinerator as a whole must be evaluated and appropriate compensation provided. This compensation includes ready access for routine test and maintenance and appropriate instrumentation and control.

Consequently, selection of auxiliary equipment is critical. The operating environment of the auxiliaries requires careful consideration, especially in regard to ambient temperatures which may be higher than normal. The possibility of high temperature in the incinerator enclosure after shut-down and the effect of these conditions on electrical and electronic components should be considered.

7.13 Waste Oil Properties

The viscosity and composition of waste oils directly influence atomization and subsequent combustion and it should be kept in mind that the small size and low weight of the incinerator limit operating margins. Waste oil may include mixtures in any and all proportions of ship's fuel, the various lubricating oils used on board, solvents, paint thinners, dissolved grease, hydraulic oils, and aviation fuels and oils. These, for the most part, are hydrocarbons, and their burnability, due to various mixtures will not be impaired. Further, the burnability of mixtures which may include vegetable oils used for cooking and salad dressings is similar to the mineral oils previously mentioned. However, the viscosity of the waste oil mixtures is unpredictable not only because of mixing composition but because of climatic changes over the oceans. The viscosity-temperature behavior of the lubricating oils and greases is markedly different from that of the fuel oils.

The effect of the viscosity of a fuel upon atomization and subsequent burning is well documented. Unless the viscosity is controlled, combustion may not occur. Depending upon the place of injection of the waste oil and the relative proportions of waste oil to primary fuel, material failure may also ensue.

Incineration of synthetic oils also warrants consideration. The behavior of mixtures of these with mineral oils in various proportions must be considered as to mutual solubility and viscosity effects. It is presumed that waste oils will be drained into a holding tank to obtain separation of entrained salt or fresh water prior to burning. The solubility of the synthetic oils in water and their water-emulsion forming effect in the presence of mineral oils must be evaluated. The motion of the ship while underway is sufficient to promote emulsification. Again, the effect of these on atomization, subsequent combustion, and exposure of incinerator construction materials to thermal shock is unpredictable.

7.14 Joints and Attachments

Failures of materials at joints and attachments in a corrosive environment are well documented, as is distress at welds. These appear mostly as localized pitting or cracks. Although the loss of bulk material and the structural impairment of the components may be negligible, the complete but narrow penetration of the walls is still a major failure. Penetrations which allow the combustion gases to escape into the shipboard surroundings produce failure, and those which allow the surroundings to enter the incinerator may or may not, depending upon location, constitute a failure.

Failure at unwelded joints of thin materials also warrants consideration. Joints of this nature may provide a large or small crevice. Dusts, soots, and other particulates deposit in these joints. Through alternate heating and cooling, the presence of the particulates may create a wedge effect at the joint and cause joint failure or a structural distortion to create a failure. Similarly, another mode of joint failure at joint crevices may occur by corrosion in which the corrosion products have a larger volume than the crevice. A wedge effect at the joint is again created to cause failure.

7.15 Overheating

The choice of the materials of construction for service in the combustion zones and hot gas passages fix the nominal operating temperatures within the incinerator. Temperature excursions above the nominal levels sometimes occur. Provided that the excursions are not gross and frequent, the mean time interval before failure may not be significantly shortened unless the nominal operating temperatures are near known material limits and control of the operation is poor.

Because the incinerator and the necessary auxiliaries may be located in a closeable compartment, the effects of overheating of controls and auxiliary components within the compartment must be considered. Unless ventilated, the internal thermal energy stored in the incinerator during operation may be sufficient to increase compartment temperature significantly. It may be necessary to limit purging to minimize thermal shock upon cooling. Prolonged purging would significantly reduce the amount of internal thermal energy transferred to the enclosing compartment.

The possible high compartment temperatures may be held to acceptable limits by ventilation, especially of electrical and electronic equipment and controls. These components must withstand high ambient temperature even when idle. Start-up of the equipment exposed to high ambients when idle is as harmful as prolonged operation in an unacceptably high ambient temperature.

7.16 Variation of Atmospheric Pressure

Assuming that the incinerator system is designed for operation in an atmospheric pressure ambient, the compartment in which the incinerator is located must be maintained at the appropriate pressure. Many compartments on board ship may operate at pressures different from the atmospheric ambient, which may adversely influence combustion-related processes; e.g., lighting-off difficulties, backflow through an idle incinerator, interference with combustion controls, interference with adequate cooling air flow and ventilation, and interference in operation of prescribed fire-fighting measures. As a consequence, operating difficulties may be caused by circumstances external to the incinerator system itself.

The multi-purpose incinerator is most vulnerable to nonambient air pressure conditions. Liquids introduced into the incinerator are pumped, and their supply is not strongly dependent upon air pressure within or without the incinerator. The trash may be moved through a feeding process of doors, traps, and seals to charge the incinerator. Inadvertent or reverse pressure differences across sealing methods and devices may not only cause incinerator malfunction but also create a hazard to operating personnel and to equipment.

7.17 Personnel Training

A shipboard incinerator or incinerator system is a complex device. Although a malfunction which affects the execution of one of its purposes may not require total shut-down, any operating disruption requires prompt attention.

Incinerator operations are not of the same importance as the primary mission of the ship. An incinerator failure will not abort a ship's mission. Still, incineration is important. The incinerator designer must assure that training procedures for operation and repair are simple and complete. He must make every effort to understand the operation and repair situations.

Maintenance personnel might well be considered as malfunction analyzers who make simple repairs and replacements. Repair and operating manuals should thus describe systematic procedures to allow rapid determination of malfunction causes. In particular, the control systems and interlock and the various safety interlocks must be fully detailed. Check points and test points should be clearly identified.

In the matter of repairs, the designer must consider the gap in available technology and facilities in making shop repairs ashore and at sea. Since good assistance is available in making shop repairs ashore, procedures requiring strict adherence to detail may be specified as appropriate. Field repairs are another matter. For example, a relatively simple procedure which requires either or both pre-weld heating and post-weld heat treatment becomes formidable on board ship.

These factors must be recognized throughout the incinerator design. Such recognition will aid in personnel training and in attaining the incinerator's objectives.

Parenthetically, the above discussion would seem trivial to a sophisticated engineer. Unfortunately, so many failures of equipment are associated with such considerations that these admonitions may well be as critical as the more sophisticated discussion in Chapter 6.0.

7.18 Loss of Power

The incinerator, incinerator operation, and operating personnel are vulnerable in the event of power loss. The multipurpose incinerator is particularly vulnerable if a loss of power occurs during the trash charging cycle. In such an event, combustion could occur in the incinerator and a partial charge of new trash could be exposed to the furnace environment. Since generation of noxious and explosive gases is likely, seals and traps and doors may be partially open with the result that the noxious and hazardous gases escape into the incinerator compartment.

7.19 Flooding

The necessary shipboard fire fighting procedures include water-based foams and sprays. There is chance of inadvertent discharge of these materials with the result that the incinerator could be damaged by flooding. Therefore, consideration should be given to providing adequate drainage or flood alarms or both.

REFERENCES

1. Wyatt, S. M., and Kemezis, R. J., Proceedings of 1976 Annual Reliability and Maintainability Symposium, p. 188 ff.

2. Zatosh, R. G., Wiener, S. A., and Budkley, J. L., "Assessment of Explosion Hazards in Refuse Shredders," Prepared for ERDA by Factory Mutual Research Center, No. E(49-1)-3737, FMRC Serial No. 22525 Apl., (1974).

CHAPTER 8.0

AMELIORATION OF CONDITIONS TO FAVOR MATERIALS PERFORMANCE

8.1 Introduction

The combination of aggressive environments, temperatures, and operations which are expected in incinerators is generally hostile to materials of construction. One way to achieve long and reliable life is to use more corrosion-resistant materials, which are usually more expensive. The alternative or perhaps supplementary approach is to reduce the severity of conditions in which the materials operate. The following discussion considers this latter approach. The former is considered in Chapter 6.0.

Any ameliorative process involves adjusting the influence and susceptibility parameters. Influence parameters include the chemical environment, temperature, erosive conditions, stress, and cyclic conditions. Thus, if the severity of these influences can be reduced, the materials can be expected to perform more reliably. Susceptibility parameters refer to the materials of construction: chemistry, structure, fabrication, and design. These also can be adjusted to reduce the likelihood of failure in a given environmental circumstance. Detailed dependencies of materials properties are considered in Chapter 6.0.

The influence and susceptibility parameters are usually applied by altering the system design, system operation, materials of construction, and requirements of specifications according to options possible within the framework of schedules and cost.

The influence parameters and possible ameliorative actions are summarized in Table 8.1; materials susceptibility parameters and ameliorative actions are tabulated in Table 8.2. This section emphasizes ameliorative options which are related to design and operation.

Certain options for amelioration are not available on shipboard. While Tables 8.1 and 8.2 show the full options, not all possible amelioration can be achieved. For example, the sulfur and chlorine contaminants cannot be eliminated from the environments since they are implicit in all wastes to be treated.

TABLE 8.1 Comparison of Parameters Which Influence Performance and These Actions to Ameliorate Aggressiveness.

External Influence Parameters	Ameliorations
Environmental Chemistry:	Operations:
• Major species: sulfur, chlorine, hydrogen, oxygen, carbon, nitrogen	• Prevent entry of aggressive environment impurities
• Aggressive impurities: silver, vanadium, lead, tin, zinc	• Minimize maximum steady state temperature
• Deposits and scales	• Remove deposits
• Cyclic alteration in oxidizing potential	• Controls to prevent thermal excursions
	• Add inhibitors
• Water absorbed in deposits at low temperatures and from rain down the stack	• Minimize rate of change of temperature increase and decrease
Temperature:	• Prevent cycling from oxidizing to reducing conditions
• Average	• Raise minimum temperature to prevent moisture condensation
• Transient increases	
• Flame impingement	Design:
• Cyclic frequency:	• Modify flame distribution to avoid hot spots
· rate of change · maximum temperature · minimum temperature	• Control process streams to avoid overheating or quenching
Stresses:	• Develop system controls which prevent exceeding performance envelope
• Applied	• Improved wall cooling
• Residual form fabrication	
• Cyclic	Modify Objectives:
Erosive Conditions:	• Relax odor requirements
• Particles' velocity	• Relax size and weight requirements
• Particles' properties	Education:
	• Manufacturer
	• Operating personnel
	• Failure mechanisms
	Prior Testing:
	• Establish more precise performance-failure envelope
	• Define accident circumstance

TABLE 8.2 Summary of Elements of Susceptibility of Materials and Methods for Reducing Susceptibility

Elements of Materials Susceptibility	Methods for Reducing Susceptibility to Failure
<u>Chemistry of Materials</u>: • Major alloy • Impurity <u>Structure of Materials</u>: • Grain boundary • Grain size • Brittle phase • Aging phenomena • Porosity • Anistropy <u>Configuration</u>: • Thickness • Crevices • Adjacent materials and compatibility <u>Susceptibility to Stress Corrosion Cracking</u>: • Welds • Complex Construction <u>Strength</u>	• Improve specifications for materials • Alloy additions for improving corrosion resistance • Coatings on alloy • Ceramic materials to replace metals • Improve quality of welding • Increase wall thickness • Modify alloy structure

8.2 Design Modifications

Factors that can be controlled or modified in incinerator design include the following: chamber size; wall design and materials; burner type and placement; injection; exhaust; and other factors such as shape, preheat, and staging.

8.2.1 Size

Chamber size is a nominally significant design variable over which the designer has relatively little control. The lack of control results from specific space limitations on ships. With no space limitation, as on land, all corrosion problems are theoretically controllable by removing the walls to a large distance away from the flame. This, clearly , is uneconomic, but it does illustrate the dilemma and the nominal potential for trade-offs as the chamber size is reduced at a given incineration rate. This can be expressed in terms of firing density, or combustion intensity, which is the average heat release rate per cubic foot of combustion space per hour. As this is increased and the combustion chamber volume is reduced, the thermal and other stresses on the walls would obviously increase to the point that the stresses finally become too great, and the combustion chamber is then too small.

A minimum size for incinerating a particular waste may well be time dependent—that is, if the incinerator is used on a continuous basis, or very frequently, then the time averaged thermal stresses on the walls will be greater, and the walls will have to be removed to a greater distance. The minimum size that can be used over a long period of time without unacceptable deterioration of walls must be determined. However, the question of minimum size is more likely to be determined by policy or educated guess, rather than strictly technical ones. That is to say, if a certain quantity of waste is to be destroyed per day, and only a certain fixed volume of space on ship can be allocated to the incinerator, then the incinerator must be designed to fill that space. If that is a given, and there are serious materials problems (which, of course, is the present case), then the technical solutions must be found elsewhere, and there is no real chance for altering the chamber size.

8.2.2 Wall Design

Considering the range of possible materials for walls, it is reasonable to say that they can be of metal, which must be maintained at a relatively low temperature—say, 500°C or lower for preference—or of some refractory or ceramic, which can operate at a significantly higher temperature. Where space and weight have not been considerations, a refractory wall has usually been preferred. The prime objection to refractory in this context has been jointly the weight and the reduced combustion chamber capacity. Also, ceramic walls are not easily cooled.

The principal alternative of metal alloy construction, however, presents a variety of potentially severe corrosion problems. The potential for corrosion is, of course, reduced if the metal can be effectively cooled from the outside; but in that event, there is the probability of quenching the incineration reactions near the wall. If the quenced products are not swept back into the main combustion stream, they can escape as wholly or partially unburnt smoke or odor. Even so, it may still not be possible to keep the wall cool enough since water tubes in incinerator boilers may sustain substantial corrosion.

Since water cooling offers the advantage of significantly lower wall temperatures, this technique should be explored. Another possible cure would then seem to be some sort of film cooling by air slots in the walls that would jointly cool the wall and help protect it. As already noted, this could still create additional problems from wall quenching. In that event, care must be taken to assure that the chamber shape will force the wall gases back into the main combustion stream.

8.2.3 Burners

There is considerable opportunity to change the burner type, location, and number, and, possibly, the direction of flow. Burner types may be classified in this context as interactive and noninteractive. Interactive burners are those in which the flame can be influenced by the waste injection. Noninteractive are those in which the flame is separately and independently stabilized in such a way that waste injection cannot interfere with stabilization. Examples of the noninteractive burners are tileport or tunnel burners, in which the flame is stabilized inside a refractory tube, and only the combustion products, or partly burned combustion products, emerge into the incinerator combustion chamber itself. Vaporizing burners generally also come under this heading. By comparison, the interacting burner designs are those like the gun type, in which atomization is produced either by a pressure jet, by air, or by steam, although this is not thought to be a suitable choice on ship. Such burners produce conical sprays, and quite a substantial volume is required to accommodate the expanding spray. Such sprays impact the walls in tileport burners, followed by pyrolysis and coke formation that can partially block the tunnel.

If the waste is sprayed directly into an interacting type flame, there is always a possibility of upset conditions. For example, if excessive water is injected, flameout may result. To avoid this, it is necessary to inject waste downstream of the burner, or at some location where significant quantities of waste cannot be drawn back into the incinerating flame. Unfortunately, because of the large volume required for the incinerating flame, the volume left for the waste incineration itself is very often a surprisingly small proportion of the total combustion chamber volume. The higher intensity tileport or tunnel burners are therefore preferred choices on the two counts of utilizing smaller volume in the incineration chamber, and being unaffected by waste injection. On the questions of direction of flow from the burner and number of burners, one can say that these are likely to influence behavior considerably; but there is unfortunately no available experience that can be suitably generalized. These factors need to be explored experimentally.

8.2.4 Injection

Liquid waste injection generally uses a method very similar to that used in an oil burner. The waste liquid must be atomized in one of two ways: pressure jet atomization if there are no suspended solids (a rare solution), or fluid atomization (where pressure air is the most suitable atomizing fluid). As with burners, questions arise about location relative to the burner flame, cone angle, injection pressure, drop size, and so forth. Drop size is governed substantially by the liquid and the atomizing air pressures in addition to factors, such as liquid viscosity, that are not controllable.

Other factors being satisfactory, the atomizing pressures must be increased to the point that there is total vaporization with total burning inside the combustion chamber; there should be no impaction and condensation of liquid on the fireside wall of the incinerator. If these objectives are not achieved, then either the incinerator chamber is too small, the rate of waste incineration is too large, or the atomizing nozzle design is inadequate. There are then no clear guides to action in these cases; one can only experiment with different atomizing nozzles, lower waste flow rates, and, if possible, test in larger combustion chambers. This might include arbitrary changes in injection point, or direction of injection. At issue here is the possible alteration of the mixing pattern; here again, there are virtually no guides to the best approach. Cold model studies of the mixing patterns may aid in interpreting the combustion results. Based on such studies, it may be possible to make better than arbitrary changes to burner and injection point location and direction. The only general guide that can be advanced now for interacting burners is to make sure that the method of waste injection does not interfere with the stabilizing flow required for the incinerating burner.

8.2.5 Exhaust

The location and design details of the exhaust port can also sometimes have a surprisingly large influence on the mixing pattern. Here again, it is very difficult to generalize. An exhaust port near the top of the chamber encourages the natural buoyancy of the flame and increases the heat at the top of the chamber close to the exhaust port. By the same token, an exhaust port near the bottom of the combustion chamber draws the flame off the top of the combustion chamber, so that it will generally tend to run cooler than in the previous instance. It also appears that the rotation of gases due to swirl in a cylindrical combustion chamber may be interfered with to some degree if the exhaust port is off axis. The exact effect of different locations can only be determined by direct experimentation and by judicious use of cold models.

8.2.6 Other Factors

Other factors that may be considered briefly include combustion chamber shape, use of preheat, and staging.

8.2.6.1 Combustion Chamber Shape. The shape of the combustion chamber is another factor that, like the exhaust location point, can unexpectedly influence the mixing pattern. General rules regarding shape are again hard to come by. However, it appears that simple and symmetrical shapes are best. One caveat on symmetry may be mentioned: flames themselves tend to be asymmetrical. One cause of asymmetry is the return of hot combustion gases from downstream to upstream; this return flow nudges the flame to an asymmetric configuration. Since flames are likely to exhibit asymmetries, it may be best to design the combustion chamber with some preset degree of asymmetry in the first place. It could mean that a square section combustion chamber is better than circular, and a rectangular section is better than a square. If problems are found in an existing design, a solution might be achieved simply by changing the shape or dimensions of the chamber cross-section. Here again, cold models might provide a valuable guide to the best approach.

8.2.6.2 Preheating. Preheating of the oil used for thermal support, the waste stream, or combustion air is not easily achieved in a shipboard incinerator. Little or nothing is gained by preheating the waste stream; also, this may cause decomposition and depositions that would block the line and atomizing ports. Preheating the oil for the thermal support burner is likewise not particularly appropriate if the oil used is Number 2, which flows and atomizes well enough without heating. If heated, it could cause vapor blocks in the line, and/or coking at the burner nozzle. There may be something to be gained from air preheat to the extent that it would raise the general levels of temperature inside the combustion chamber. This would provide some margin of reserve against flameout from upset conditions. However, a design incorporating an air preheater in the stack would be too clumsy and use too much valuable space. The only real source of air preheat seems to be the use of the air to cool the combustion chamber shell. However, increased heat transfer to the shell is then reflected in higher temperatures throughout the combustion chamber, which can, in turn, increase heat transfer to the shell. This is not necessarily advantageous and in many circumstances could be decidedly adverse. It means that it then becomes difficult or impossible to decouple the cooling of the shell from the combustor itself. A compromise might be a design that incorporates closures that permit air to flow either way: in parallel flow with the combustion products in the combustor, finally flowing into the stack at the exhaust end of the combustion chamber; or alternately traveling in counterflow to the combustion products, to enter the combustion chamber at the upstream end through the burner. If wastes were very variable from one day to another, this might provide the additional flexibility that would enable the incinerator to cope with wider fluctuations.

8.2.6.3 Staging. Staging in a burner is a process by which fuel is burned fuel-rich near the injector and the additional required combustion air is added downstream to complete the combustion. The advantage of staging is that it spreads out the reaction zone which makes the average temperatures throughout the reaction zone somewhat lower than would be true without staging. There is no particular advantage for staging so far as the thermal support burner in an incinerator is concerned. However, in a sense the split into a thermal support flame followed by waste injection is itself a form of staging. Beyond that, no advantage of staging can be seen at this time. This does not exclude a future discovery of some advantage to injection of part of the thermal support fuel along with the waste. In that case, staging of the primary thermal support burner would be one way of supplying hot fuel to the waste stream mixing point.

8.3 Operational Modifications

8.3.1 Combustion Modifications

There are relatively few modifications which can be made to the combustion process. The only controlled factors are firing density (rate of fuel supply to the thermal support burner), rate of waste supply, and excess air (ratio of air to fuel and waste). These reduce the combustion intensity, but at the expense of incinerator capacity. If one is willing to reduce incinerator capacity to something very small, this is certainly a viable option; but, if the incinerator capacity is reduced too far, it will not be able to keep up with the rate of waste generation. This is certainly an option in an emergency, but it is clearly of little long-term value if the incinerator is properly sized for the waste generation that occurs daily.

One other possible, but marginal, option might be the use of combustion additives like oil or water-soluble organics and/or inorganics that will catalyze or accelerate the reactions in some way. In the past, most attention has been given to additives to control smoke. Although appropriate additives might be developed in the future, at present nothing is available for application in shipboard incineration.

8.3.2 Cyclic Thermal Operation

Cyclic operation of shipboard incinerators may be dictated by the the demand design of the system and/or by vessel operational procedures. In any event, cyclic thermal operation accelerates corrosion in the following ways: thermal shock and stresses, condensation of corrosive gases, and moisture at the lower temperature range. Continuous operation at constant temperature is the preferred mode to ameliorate these damaging effects. However, since design and practical conditions may not allow this desirable option, cyclic frequency should be kept to a minimum, and minimum temperature should be kept above 150°C to avoid condensation of SO_2 and waste vapor according to the data in Figure 4.23.

8.3.3 Controls

Reliable operation will be most likely achieved if it is nearly as automatic as possible. Some high-temperature limit control is particularly needed. Automatic controls should establish a flow and temperature pattern that minimizes the following:

1. Excess temperatures at vulnerable points;

2. High-temperature reducing gases caused by impaired air flow or excess waste flow; and

3. Low-temperature attack by corrosive condensates during the off period.

8.3.3.1 Excess Temperature. The choice of the materials of construction for service in the combustion zones and hot gas passages fixes the nominal operating temperatures within the incinerator. (Of course, if cooling is used this choice can vary.) Temperature excursions above the nominal levels will occur occasionally. Provided that the excursions are not gross and frequent, the mean time interval before failure may not be significantly shortened unless the nominal operating temperatures are near known material limits and process control is deficient.

8.3.3.2 Flameout. Primary fuel supply must be assured and appropriately regulated during firing rate changes because primary fuel flameout may cause thermal shock of the unit assembly and also create an explosive fuel mixture within the unit. Thermal shock may be intensified with continued sewage feed into the hot incinerator in the event of flameout. Continued addition of raw fuel after the flameout would also accelerate the quenching. Assuming that an otherwise undetected flameout would be detected by a gas temperature controller, the action of such a controller would create a demand for more fuel which intensifies an existing dangerous situation.

Detecting flameouts must be rapid. Such detection should cause an immediate shut-off of all fuel and should initiate the shutdown purge procedure applicable to the incinerator unit. Any restart procedure should incorporate a full purge.

The entire fuel system requires careful attention to assure an uninterrupted supply of clean fuel. To this end, maintenance procedures should be organized to assure that fuel lines are clean. Special attention should be given to cleaning these lines after prolonged downtime.

8.3.3.3 Warm-Up and Shut-Down. These procedures should minimize adverse thermal cycle and fatigue behavior of the materials used for the construction of the incinerator. Consideration should be given to expansion coefficients and time-temperature lags of the various components affected by warm-up and shut-down.

Shut-down procedures must also recognize a probable need for mutiple purging. The internal thermal energy of the unit in operation may be of sufficient magnitude to cause an operating failure at the next start-up. For example, oil burners may require purging to avoid carbonization of fuel on burner tips and in small oil passages leading to the burner tip. Although the carbonization may be insufficient to cause light-off failure, it may be sufficient to interfere with the expected fuel spray patterns during operation and cause fuel impingement on the walls of the combustion chamber; this will upset the gas chemistry in the chamber wall vicinity. Also, depending on the burner design, fuel may drip from the nozzle into the hot combustion chamber and fuel vaporization may occur to form an unsuspected explosive mixture. Both the primary fuel burner and the waste oil burner are suspect in the matter.

The sewage feed line into the combustion chamber may cause difficulty in the same manner as oil burners. The sewage entrained in the injection assembly may become baked and cause flow stoppage. The ramifications of partial blocking may be similar to that previously mentioned for oil burners.

Purging of the unit with air after shut-down and prior to start-up is considered mandatory. All passages which could contain such mixtures should be purged. However, this purging must take into account possible thermal shocks produced by cold purging gases on the hot incinerator walls. On the other hand, the purge rate on start-up does not require consideration of thermal shock and the purge rate may be large.

8.3.3.4 Temperature Recording Systems. Rapid failure of high-temperature metallic components has been experienced in developmental shipboard incinerators. Since operating temperature is so critical, the temperature history of operating units should be recorded to show whether safe temperature limits have been exceeded. At least two or three points of expected maximum temperature in the incinerator should be equipped with rugged thermocouples connected to a reliable recorder. Progress toward more reliable incineration will be promoted by the collection and analysis of such detailed knowledge of the temperature history of the most threatened components. No attempt should be made to measure flame temperature as no known thermocouple would survive. Metal temperatures can be reliably measured if the thermocouple junction is imbedded in the wall through holes drilled from the cooled side.

8.3.3.5 Automatic Operation. Shipboard incinerators for solid wastes have been hand-fired for many years without any particular training for the operators and without automatic combustion controls. Liquid wastes and sewage were disposed of elsewhere. Now all wastes must be stored for later land disposal or all must be incinerated. This new requirement cannot be handled entirely by hand-fired incinerators operated by untrained crews.

Reliable operation will most likely be achieved if it is nearly as automatic as possible. High-temperature limit control is particularly needed with a suitable time delay to prevent extensive temperature overruns. Automatic controls should establish a flow and temperature pattern that minimizes the following: (1) excess temperature at vulnerable points; (2) high-temperature reducing gases caused by impaired air flow or excess waste flow; and (3) low-temperature attack by corrosive condensates during the off-period.

8.4 Pollutants in the Atmosphere

The incinerator must not produce pollutants in the atmosphere. This mandate provides an important boundary condition for operating the system.

Under some conditions, air pollutants may be generated from shipboard waste disposal by volatilization, evaporation, and combustion of liquid and solid waste materials. Potential sources include liquid waste storage tank vents, waste evaporator hotwell exhausts, and combustion chamber flue gases. The major emission occurs as a result of incineration by combustion of liquid and solid wastes. The types and amounts of pollutants generated depend on the characteristics of the fuel being burned, the combustion conditions, and the type of incinerator being used.

8.4.1 Particulate Air Pollutants

Particulate matter is emitted from the incinerator exhaust gases mainly as organic matter from incomplete fuel combustion or as inorganic matter entering as ash which derives from liquid wastes, solid refuse, and auxiliary fuel oil. The amount of particulate matter emitted from the shipboard waste incineration depends on the operating conditions as well as the type of incinerator. Particulate matter emissions from a vortex-type shipboard waste incinerator are presented in Table 8.3 which is based on a limited amount of stack test data [1]. These values were verified in subsequent tests by Schwartz [2], who determined particulate concentrations using a cyclonic ash collector on a vortex incinerator. He found 0.073 to 0.281 grains per standard cubic foot with emission rates of 1 to 5 pounds per ton of dry solid refuse burned.

A collection efficiency of approximately 83 percent is assumed for calculation of the controlled emission factors. Comparable uncontrolled particulate emissions from a fluidized bed incinerator used for municipal sewage sludge combustion are approximately 100 pounds per ton of sludge [3]. The variations in composition of shipboard waste depend on the relative amounts of solid refuses, sanitary wastes, galley wastes, waste oils, and auxiliary fuels, which influence the relative amount and composition of particulate matter. Operating variables such as combustion temperature, retention time, degree of turbulence, excess air concentration, and combustion chamber design also influence the composition and amount of particulate matter released.

TABLE 8.3 Particulate Matter Emissions From a Vortex-Type Shipboard Waste Incinerator

Control Status	CO_2 Content (% by volume)	Concentration (grains per standard cubic foot)	Emission Rate (lb particulate matter per ton of waste)[a]
No Control	4-5	0.088-0.130[c]	20-25
Control	4-5	0.010-0.015[c]	3-5
No Control	12[b]	0.244-0.715	20-25
Control	12[b]	0.042-0.122	3-5

NOTE: [a] Emission rates reported on a dry basis

[b] Corrected to 12 percent carbon dioxide

[c] Excess air levels of 90 to 110 percent of stoichiometric

Source: Reference 1

8.4.1.1 <u>Organic Composition</u>. The organic composition of the particulate matter released during combustion is directly related to variables of combustions: flame temperature, retention time, and excess air concentration. Generally, the organic content of the particulate matter leaving the incinerator combustion chamber is minimal under conditions favoring complete oxidation of carbon dioxide and water. The organic content of the particulate matter is generally significant only under conditions favoring incomplete combustion such as operating temperatures below 705°C, insufficient excess air, inadequate turbulence, and insufficient retention times [4].

No specific information is available on the chemical composition of the organic fraction of the particulate matter leaving the combustion chambers of shipboard waste incinerators. Elemental carbon can be formed as the result of incomplete combustion of the organic matter, as well as the partial oxidation products of organic alcohols, aldehydes, acids, and polycyclic aromatic hydrocarbons. Conditions favoring incomplete combustion such as excessive moisture in the fuel and insufficient excess air also favor the release of unburned organic compounds in the waste being incinerated. These include amino acids, sugars, peptones, lipids, and phenols [5]. These organic particles may potentially cause odor problems; or they may act as carriers for acid gas molecules which may deposit on surfaces to create possible corrosion hazards. No data are available regarding the particle size distribution of the organic particulate matter from shipboard waste incinerators. This information can be used to predict surface corrosion, visible plume formation, and possible problems for respiration. Additional organic particulate pollutants or potential interest include bacteria and virus from sanitary waste storage, evaporation and disposal, and solid waste incineration [6]. Under any reasonable incinerator operation, however, bacteria and virus are destroyed by the heat.

8.4.1.2 Inorganic Composition. The emission of the inorganic fractions of particulate matter from shipboard waste incinerator combustion gases is directly proportional to the ash content of the total input. The ash content of the combined waste material is typically 8 to 10 percent of the dry solids and 2 to 3 percent of the total input material including water [6]. Major components of inorganic particulates which may cause air pollution as well as corrosion, include: alkali metals, such as sodium, potassium, calcium, and magnesium; trace metal cations, such as copper, lead, zinc, and vanadium; and anionic constituents such as chloride, sulfate, nitrate, and phosphate.

Trace metal cationic constituents are important in that they may act as catalysts to enhance the formation of corrosion-producing constituents such as sulfur trioxide, which can be subsequently hydrolized to form sulfuric acid on ceramic and metal surfaces below the acid dewpoint temperature. Particularly important as potential catalysts for formation of sulfur trioxide are vanadium, copper, manganese, and iron, where the sulfuric acid formed enhances the corrosion by chloride salts. Raupuk and Van Ness [1], report on chemical analyses made of shipboard waste incinerator ash materials collected as particulate matter as listed in Table 8.4.

8.4.2 Gaseous Air Pollutants

The major class of organic gases released from combustion is hydrocarbons, while the major inorganic gases are sulfur oxides, nitrogen oxides, carbon monoxide, and hydrogen chloride. Emission factors have been developed for gaseous emissions for a vortex-type shipboard waste incinerator based on a limited number of stack tests by Raupuk and Van Ness [1], as listed in Table 8.5.

The relative types and amounts of gaseous pollutants released from shipboard waste disposal depend upon the system employed. The major emission source is the incinerator exhaust, but sanitary waste storage tank and liquid waste evaporator hotwell vents can also be the sources of odorous gases. The release of odorous gases may be minimized by thermal oxidation using combustion air from the ship's boiler or the waste incinerator. Possible adverse effects of gaseous emissions include corrosion, odors, photochemical air pollution formation, and acidic precipitation.

TABLE 8.4 Elemental Composition of Inorganic Flyash From Shipboard Waste Incinerators in Percent by Weight

Element	Freshwater Flush	Saltwater Flush
Aluminum	0.1-1.0	0.1-1.0
Barium	0.0-0.1	0
Calcium	1.0-5.0	5.0
Chromium	1.0-5.0	0.1-1.0
Copper	0.1-1.0	0.1-1.0
Iron	1.0-5.0	1.0
Lead	1.0	---
Magnesium	0.1-5.0	0.001-0.01
Manganese	1.0-5.0	---
Nickel	---	---
Phosphorous	---	---
Silicon	1.0-5.0	1.0-5.0
Sodium	1.0-5.0	1.0-5.0
Tin	---	---
Titanium	0.1-5.0	0.01

Source: Reference 1

TABLE 8.5 Gaseous Emissions from a Vortex-Type Shipboard Waste Incinerator

Air Pollutant	Concentration[a] (ppm by vol.)	Emission Rate (lb gas/ton waste)
Sulfur Dioxide	5-25	1-5
Nitrogen Oxides	32-224	5-40
Carbon Monoxide	40-700	5-70
Hydrocarbons	41-62	2-3
Hydrogen Chloride[b]	16-40	2-5

Notes: [a] Concentrations are reported in parts per million by volume at actual stack conditions at excess air levels of 90 to 100 percent of stoichiometric.

[b] Values have been estimated by the author from chloride levels in the input waste material.

Source: Reference 1

8.4.2.1 Organic Constituents. In terms of possible air pollution regulations, the major organic gaseous constituents emitted from shipboard waste storage, evaporation, and incineration are the volatile hydrocarbons. Olefinic hydrocarbons which may be present in waste oils, auxiliary distillate oils, or sanitary wastes which are not completely oxidized can be released to the atmosphere during shipboard waste incineration. Aliphatic and aromatic hydrocarbons may also be released during incineration or from storage and evaporation vent gases. Shipboard solid waste incineration can also result in the release of hydrocarbon emissions, in varying quantities. Hydrocarbon emissions tend to decrease with increasing flame temperature, retention time, turbulence level and excess air.

Other organic constituents may also be of interest as potential air pollutants. Organic sulfur compounds such as mercaptans and organic nitrogen compounds such as amines resulting from protein decomposition in sanitary wastewaters may cause significant local odor problems during storage. These compounds may also be released in varying quantities from shipboard waste incineration under conditions of incomplete combustion resulting from insufficient excess air, excessive moisture inputs, or insufficient auxiliary fuel. Polycyclic aromatic hydrocarbons may also be formed in trace quantities from shipboard waste incineration. Additional studies are needed to provide quantitative emission data.

8.4.2.2 Inorganic Constituents. The major inorganic constituents from shipboard waste incineration include sulfur oxides, nitrogen oxides, carbon monoxide, and hydrogen chloride. The sulfur dioxide may be eliminated by reaction with calcium if it is present in the ash. A small portion (1 to 10 percent) of the sulfur dioxide formed is oxidized to sulfur trioxide, where the amount formed depends upon the presence of trace metal catalysts, the excess oxygen concentration, and the reaction temperatures. Sulfur can also be reduced to hydrogen sulfide in oxygen-deficient atmospheres to enhance corrosion and accentuate odor problems.

Nitrogen oxides can be formed in substantial quantities from combustion processes. Nitric oxide can then be oxidized to nitrogen dioxide. Nitric oxide formation is primarily a function of flame temperature and excess air in the combustion zone; concentrations increase exponentially above 1315°C. The high moisture contents of shipboard wastes and the low combustion temperatures tend to reduce nitric oxide concentrations to below 100 parts per million by volume in the exhaust gases. However, the relatively high nitrogen contents (10 to 20 percent of the dry solids) of the sanitary wastes associated with urea from urine can produce significantly higher nitrogen oxide releases than would otherwise be expected at the low combustion temperatures. Ammonia can also be evolved from incomplete combustion of the nitrogenous materials in these temperature ranges. More research is needed to quantify the composition of the emissions.

The exit concentrations of carbon monoxide from shipboard waste incinerators generally vary from 0 to 0.2 percent by volume [7]. Carbon monoxide can be reduced by combustion temperatures above 705°C and with excess air. Hydrogen gas can also be formed from incomplete combustion of shipboard wastes.

Hydrogen chloride from shipboard waste incinerators is a pollutant of considerable interest because of its role as a corrosion agent. Hydrogen chloride can be produced during the combustion of the sanitary wastes containing seawater flush and waste oils, particularly at higher temperatures [8]. The relationship of hydrogen chloride emissions to sodium chloride content of shipboard waste as a function of combustion operating parameters requires further investigation. Lime in the material burned can act as a scavenger for hydrogen chloride [9].

8.4.3 Gas Flow Properties

Shipboard waste incinerators burn a nonuniform mixture of solid refuse, sanitary wastes and waste oils which generally have a moisture content of 50 to 95 percent by weight and require auxiliary fuel. Excess air requirements to assure complete combustion of the waste material vary widely from 3 to 250 percent [10].

The most important physical parameters regarding the exhaust gas streams from shipboard waste incinerators are the volume of gas per unit volume of waste material produced, the gas temperature, and pressure. Components of the gas stream which require determination are: carbon dioxide, oxygen, carbon monoxide, and moisture. Extreme ranges in values for these parameters and average values for a typical intermediate condition of 100 percent excess air are presented in Table 8.6.

8.4.4 Adverse Effects

Air pollutants generated from shipboard waste incineration can produce adverse environmental effects: respiratory ailments, water polluted with dissolved gases, acidic precipitation, photochemical air pollution and odor formation. The trace metals released from waste combustion can become part of the fine particulate matter in the respirable size range and can harm shipboard or shoreside personnel. Naturally, the volume of products produced from all incinerators on ships is small and their aggregate contribution to air pollution is not considered a major issue. There is, nontheless, a reasonable basis for eliminating emissions.

TABLE 8.6 Shipboard Waste Incinerator Flue Gas Flow Rates, Conditions and Composition

Parameter	Units	Average		Range
Excess Air	percent[a]	95		3-250
Flow Rate[b]	scf/lb Waste[c]	240		60-550
	scf/lb Waste[d]	500		130-1200
	scf/min/lb W/hr[e]	12		3-27
	scf/min/lb W/hr[e]	27		7-60
Temperature	°C	315		205-370
Pressure	in Hg	29.8		29.7-29.9
Carbon Dioxide	percent by volume[f]	4.2		2-16
Carbon Monoxide	percent by volume[f]	0.1		0.0-0.2
Oxygen	percent by volume[f]	14		2-17
Nitrogen	percent by volume[f]	73		68-77
Water Vapor	percent by volume[f]	8.7		7-15

Notes: [a] Excess air is reported as percent of stoichiometric requirement.

[b] Flow rates are reported on the basis of pounds of waste solids on a dry basis.

[c] Standard cubic feet are reported on the basis of 20°C, 29.92 in Hg, dry gas.

[d] Actual cubic feet are reported at stack conditions using a flue gas temperature of 315°C.

[e] Flow rates are reported as cubic feet of gas per minute per pound of dry waste solids burned per hour.

[f] Volumetric compositions are reported on a wet gas basis.

Source: References 1 and 2

Water quality can be affected by air pollutant emissions from waste incineration as trace metal constituents and acidic gases. Trace metal components of particulate matter can be incorporated into rainfall droplets as condensation nuclei with potential localized effects on fish and aquatic life in receiving waters. Acidic gas components such as sulfur dioxide, nitrogen dioxide, and hydrogen chloride can become absorbed by raindrops or converted to particles to enhance the formation of acidic precipitation over either land or water.

Photochemical air pollution results from the formation of hydrocarbons and nitrogen oxides in the presence of sunlight to form ozone and other reaction products. Both hydrocarbons and nitrogen oxides can be emitted from shipboard waste incinerators, but their potential contributions to photochemical air pollution would have to be established from specific emissions for specific locations under specific meteorological conditions.

Another impact of emissions of sulfur dioxide and nitrogen dioxide is the subsequent reactions to form their respective sulfate and nitrate aerosols to reduce atmospheric visibility. The release of trace metal-containing particles and sodium chloride aerosols in the size range from 0.1 to 1.0 micron in diameter can cause visible plume problems. The trace metal particulates can also act as catalysts to aggravate the formation of sulfate aerosols from sulfur dioxide.

A major onboard air pollution problem which may result from shipboard waste disposal is malodorous gas emissions during storage, evaporation, and incineration. The odorous gas emissions can result from anaerobic conditions in sanitary wastewater storage tanks, from waste evaporation vents, or from incomplete combustion during incineration. Amine compounds and mercaptans from protein decomposition in sanitary wastes and hydrogen sulfide formation from sulfur reduction in oil during oxygen-deficient combustion can lead to major localized odor nuisances aboard ships.

8.5 Odor Requirements

Most combustion-related odors come from hydrocarbons or organic gases and vapors resulting from incomplete combustion. Therefore, if the combustion process can be improved to assure complete oxidation of all such gases and vapors, odorous emissions are practically eliminated. In practice, it is found that when thoroughly mixed with oxygen and then maintained at a temperature of about 800°C for about one second, odor is eliminated.

With effective mixing in the incinerator, ample time must be allowed for completion of combustion of all organic compounds. This time has been roughly established as at least one-half second to one second; during this time the temperature of the oxidizing mixture should be high enough to assure combustion.

If some odorous gases slip through a cool or poorly mixed corner of the combustion zone, odor is very likely to result. Intense mixing of all vapors and gases with combustion air is essential so that all are held at a temperature of 800°C or above.

8.5.1 Catalysts for Odor Control

An alternative to using a high temperature for odor destruction is to utilize catalytic odor destruction. Combustion with air on the surface of a catalytic afterburner reaches completion at lower temperatures than those necessary for conventional flame burning. At lower temperatures, combustion is flameless. A thin film of catalyst is coated on a support material consisting of either thin, crimped, alloy ribbon, or porcelain rods. The support material is so arranged as to provide intimate contact of the catalyst with the gas stream at a reasonably low pressure drop. However, because catalytic combustion takes place on the exposed surface of the catalyst elements, it is important that these surfaces be kept clean and active to maintain satisfactory performance. Gas streams containing low concentrations of inorganic dust can be processed, if the elements are washed frequently; but at high dust loadings, washing becomes impractical. Another limitation is that catalyst surfaces become poisoned (inactivated) by metallic vapors, such as arsenic, lead, mercury, or zinc, when they are present in the gas stream. Thus, the potential for catalyst poisoning by the metallic compounds in incinerator exhaust appears to make them impractical for control of odor from most incinerators.

8.5.2 Air, Fuel Injection, and Mixing

The injection of fuel and air into an incinerator should direct the oxygen and the heat released toward the burning wastes while keeping the heat away from the walls. However, even with optimum flame distribution, the walls are likely to be heated above a safe operating temperature. Accordingly, in many metallic-walled combustion chambers, including some incinerators, air film cooling is utilized to keep the thin metal wall cool.

8.6 Alternate Flue Gas Discharge Methods

8.6.1 Stack Height

If ship structure permits the installation of a duct to carry the incinerator exhaust gas to one of the highest points on the ship, satisfactory dilution of the gas in the ambient air is probably quite feasible. An alternative is to discharge the corrosive gases near the top of the exhaust from the oil burning propulsion system, if available. In that case, the initial dilution would begin in the hot engine exhaust.

8.6.2 Liquid Scrubbing

At considerable additional cost, the exhaust gases could be rendered innocuous by means of liquid scrubbing. This has two advantages:

1. Flyash particles would be removed efficiently, and
2. Hydrogen chloride is easily removed.

There are five major disadvantages to liquid scrubbing of dirty gases:

1. High energy consumption for efficient scrubbing and hence high operating cost;
2. An additional system imposed on the ship in support of the incinerator;
3. Wet, cold gases leaving the scrubber stack which must be reheated to avoid their drifting downward in the ambient air and causing a corrosive vapor nuisance;
4. Disposal of corrosive waste liquor; and
5. High-energy scrubbers are heavy.

Obviously, if liquid scrubbing is considered a major problem, a design-feasibility study will be required. Since scrubbers are becoming widely used in industry, despite their evident drawbacks, pertinent design information is available.

8.6.3 Condensation and Heat Recovery

While it is highly desirable to conserve energy by recovering heat from the incinerator exhaust gases in the form of steam, heated water, or air, the corrosiveness of the acid gases requires that all heat recovery surfaces must be maintained above the dew-point. This requires auxiliary fuel burning during incinerator down-time to maintain sufficiently high system temperatures. Surfaces must also be maintained below some upper temperature limit to avoid high-temperature chloride corrosion associated with molten chloride. If all surfaces could be held within a temperature range of 200°C to 300°C, chloride attack on the heat exchanger would be negligible. This would require further optimization. However, heat recovery from the incinerator would not be economical in terms of the need for auxiliary equipment; also, the heat recovery is not significant relative to shipboard needs.

8.7 Deposit Removal for Shipboard Incinerators

Incinerators designed, built, and operated to burn materials which include food remnants, crating lumber, fuel and lubricating oil wastes, and human wastes, will generate corrosive gases and flyash particulates. Some vapors condense on the walls of the gas passages. The flyash adheres to the walls of the gas passages and reacts with the gases and condensed vapors, thus promoting attack upon the boiler metal surfaces. A great deal of information relating to these types of attack has been published during the last 15 years [11-20].

As deposits accumulate in the boiler, the gas flow is hindered, and heat transfer to the tubes is reduced. Hence, some method of deposit removal may be necessary. Soot blowers can be used for this purpose, but caution must be exercised. Soot blowing which is too frequent and at too high a pressure removes the protective oxides on the boiler tubes and thus enhances corrosion. Hence, both the frequency and intensity of soot blowing should be minimized to keep the convection passes open and maintain the steam temperature. Soot blowing techniques might be utilized to combat deposit buildup in naval incinerators.

It is important to maintain metal surfaces above the dew point of sulfuric acid (150°C) in order to prevent condensation of this acid with the flyash. Removal of the relatively light deposits which may accumulate might be accomplished by water lancing during scheduled maintenance or by mechanical means such as shovels and brushes.

In order to achieve easy removal of the ash, the floor of the incinerator should be made of castable, highly refractory material finished as smoothly as possible to permit puff blowing of compressed air from many points near the floor toward an opening in the center of the floor through which the ash can pass down and into a water-filled ash-transport pipe.

In order to provide ash which can be moved across floor surfaces by air-puffed blowers it is necessary to furnish substantial quantities of secondary air to the firing chamber since the nitrogen and the water vapor in the air passing through the incinerator are the only cooling or heat-transfer agents. Forced- and induced-draft fans driven by variable-speed motors are essential parts of the ash-removal system.

REFERENCES

1. Raupuk, H.W. and Van Ness, W., "Vacuum collection and Waste Incineration System for Shipboard Use," Enclosure to U.S. Department of the Navy correspondence, Naval Ship Research and Development Center, Bethesda, MD, (1975).

2. Schwartz, D.H., Orning, A.A., Snedder, R.B., and Demeter, J.D., "Development of a Vortex Incinerator with Continuous Feed," Proceedings of the 1972 National Incinerator Conference, American Society of Mechanical Engineers, New York, NY, (June 4-7, 1972).

3. Lahre, T., "Sewage Sludge Incineration," Compilation of Air Pollutant Emission Factors, pp. 2.5.1-2.5.2, 2nd Printing, U.S. Environmental Protection Agency, Office of Air and Waste Management, Research Triangle Park, NC, (March 1975).

4. Wall, C.J., Graves, J.T. and Roberts, E.J., "How to Burn Salty Sludges," Chemical Engineering, Vol. 82, No.7, pp. 77-82, (April 14, 1975).

5. "Treatment and Disposal of Vessel Sanitary Wastes," Maritime Research Information Service, National Academy of Sciences, Washington, D.C., (July 1971).

6. "Are Refuse-Fueled Power Plants Hazardous to Worker's Health?", Chemical Engineering, Vol. 82, No.26, p. 83, (December 8, 1975).

7. "The Shipboard Refuse Generation Survey," Naval Shipboard Refuse Study, U.S. Naval Ship Engineering Center, Hyattsville, MD, (1971).

8. Santoleri, J.J., "Chlorinated Hydrocarbon Waste Disposal and Recovery Systems," Chemical Engineering Progress, Vol. 69, No.1, pp. 68-74, January 1973).

9. Skinner, D.J., "Waste Oil as a Fuel for Cement Manufacturing," Presented at the Annual Meeting of the Pacific Northwest International Section of the Air Pollution Control Association, Vancouver, British Columbia, Canada, (November 19-21, 1975).

10. Singerman, H.H., Personal Communication to E.F. Gloyna, (February 7, 1975).

11. Hansen, W.A. and Kessler, G.W., "Fuel Ash Corrosion and Its Effect on Boiler Design," presented at the IEEE-ASME National Power Conference, Tulsa, Oklahoma, (September 27 - October 1, 1964).

12. Plumley, A.L., Jomkin, J., and Vuia, R.E., "A Review Study of Fire-Side Corrosion in Utility and Industrial Boilers," presented at Corrosion Seminar, McMaster University and Engineering Institute of Canada, Hamilton, Ontario, (May 19-20, 1966).

13. Fontaine, P.I. and Richards, E.G., "Hot Corrosion of Nickel-Iron-Chromium-Cobalt Alloys by Sulfate-Chloride and Sulfade-Vanadate Simulated Fuel," Hot Corrosion Problems with Gas Turbines, ASTM STP 421, pp. 246-269, American Society for Testing & Materials, Philadelphia, PA, (1967).

14. Regan, J.W., Mullen, J.F. and Nickerson, R.D., "Suspension Firing of Solid Waste Fuels," presented at the American Power Conference, Chicago, Illinois, (April 22-24, 1969).

15. Regan, J.W., "Generating Steam from Prepared Refuse," presented at Fourth National Incinerator Conference, Cincinnati, Ohio, (May 17-20, 1970).

16. Maritime Information Committee, National Research Council, National Academy of Sciences - National Academy of Engineering, "MRIS Report A Synthesis of Current Information on Treatment and Disposal of Vessel Sanitary Wastes," (July 1971).

17. Miller, P.D. with others from the Staff of Battelle Memorial Institute (Columbus, Ohio), "Corrosion Studies in Municipal Incinerators," published by Office of Research and Monitoring National Environmental Research Center, Cincinnati, Ohio, (1972).

18. Fernandes, J.H. and Shenk, R.C., "The Place of Incineration in Resource Recovery of Solid Waste, Combustion, (October, 1974).

19. Gunn, D. G., "Deposits and Corrosion in Boilers Fired with Domestic Refuse," Journal of the Institute of Fuel (England), (December, 1974).

20. Engdahl, Richard B., "Water Tube Wall Incineration," presented at International Symposium on Energy Recovery from Refuse, Louisville, Kentucky, (September 16-18, 1975).

CHAPTER 9.0

TESTING AND FUTURE EXPERIMENTAL WORK

9.1 Introduction

Two types of testing are considered in this chapter: the first part (Section 9.2) considers defining the environment, and the second (Section 9.3) considers testing of improved and alternate materials of construction.

Defining the environment is more crucial in these smaller and higher performance incinerators. Such improved definitions are useful for deciding upon effective testing procedures for qualifying alloys. In addition to defining environments to be used in testing, the determination of environmental conditions will be useful in assessing conformance with Federal emission standards.

Federal regulations governing emissions from incinerators are published in the Federal Register for December 23, 1971 [1]. At present, the regulations cover only emission of particulate matter. The provisions also apply only to incinerators having charging rates of more than 50 tons per day. They are not, therefore, expected to apply, at present, to shipboard incinerators. However, new regulations will probably be issued to cover smaller incinerators and a wider variety of emissions. The present regulation for emissions reads that particulate matter must not exceed 0.08 grains per standard cubic foot (scf) (0.18 grams/m^3), corrected to 12 percent CO_2 maximum for a two-hour average. The regulation also specifies test methods and procedures. Since the shipboard incinerators are expected to be used for commercial buildings, similar requirements will no doubt be developed for these smaller units.

Regarding the future testing of materials, it is likely that there will be several iterations of commercially built prototypes and final designs before a reliable system is developed. As failures or other difficulties develop, materials testing will be required and will be more or less continuous for several more years. Section 9.3 addresses principles and considerations in such testing.

9.2 Analyses of the Environments

9.2.1 General Requirements and Objectives.

In this context sampling means taking samples of gases in the stack, or inside the incinerator itself, and analyzing them to determine the load of particulates, unburned hydrocarbons, and normal combustion products. This procedure has two objectives: first, to determine emissions to insure that they are not excessive and do not violate any regulations; and second, to measure the performance and combustion behavior of the unit. The latter measurements would be made inside the incinerator combustion chamber as well as at the exhaust or in the stack. The prime concerns are the completeness of combustion and emissions loadings, including particulates, NO_X, SO_X, unburned hydrocarbons, smoke, etc.

Sampling and analysis generally require three necessary units: first, a sampling probe that will draw the gases out of the stack or the combustion chamber; second, a sampling train, which will collect particulates, absorb condensible or absorbable gases, and measure the flow rate of the gases, and being sampled; third, an analyzer or appropriate readout for such instruments as temperature pyrometers or velocity meters. Sampling problems have, or course, received considerable attention in the last few years.

The necessary sampling methods and sampling trains are described in the Federal Register for December 23, 1971 [1]. It should be noted, however, that in the majority of systems now under regulation, gases are exhausted at temperatures low enough to allow the use of metal probes that are not cooled. For sampling exhaust gases at high temperatures, or for sampling inside combustion chambers, refractory metals or water-cooled probes must be used. Information on the design and construction of such probes and alternatives to the EPA sampling trains is available, but is widely scattered and limited in scope. An important exception is Measurement in Flames by Chedaille and Braud [2]. Two other useful sources of information are References 3 and 4. Sampling from flame gases is technically complex; it provides an apt field for further innovation.

A full review of the sampling problem is beyond the scope of this report. What follows is an indication of some of the problems, equipment requirements, and related aspects of sampling. For further information, readers are directed to the list of references.

9.2.2 Probes

Probes are the point of contact between the investigator and the gases being investigated. Probes for velocity and temperature investigate the properties of the gases directly, with some appropriate readout attached to the end of the instrument. Probes for determining the composition gases merely remove the sample continuously or batch-wise for processing elsewhere.

The very simplest probe is a tube inserted into the gas stream. This would indeed suffice in many cases for sampling gases, or for sampling solids if there is a filter at the cold end of the probe, or a filter elsewhere in the line. The probe opening may be directed across the stream of flow, or for special reasons may turn up to face into the oncoming stream, or in some instances away from the oncoming stream. The rationale for probe design is given below.

All probes share certain characteristics, but they also differ depending on their function. If the probe is to be used in relatively cool gases, they differ substantially. If the probe is to be used in very hot gases, the probes must be water-cooled, and in this case, all probes have certain construction elements in common. Water must be supplied to the tip of the probe by internal or external pipes with flow back to the cold end of the probe through some sort of water jacket. This construction may be varied using either internal water-cooled "fingers" or single or multiple jackets.

9.2.3.1 Velocity. The most common method for measuring velocity is still the pitot probe. Like all other probes, this must be water-cooled if temperatures are high. The EPA-specified pitot is the Type S unit illustrated in Figure 9.1. Federal regulations do not seem to include provisions for water cooling such probes, and therefore they are restricted to lower temperature gases. Variations of common designs are illustrated by Chedaille and Braud [2]. Special designs for measurements in dust laden gases are also described by the same authors. Readout from such instruments is generally some form of manometer as for example that illustrated in Figure 9.1. Other manometers can be used: a furnace or boiler draft gauge, with high sensitivity is often a useful instrument for low velocities at air speeds generally below the normally considered range of pitot measurements.

Impact tube devices that are direction-sensitive or have multiple direction ports are also used to measure velocity. These and other alternatives, however, are used generally only for research.

9.2.3.2 Temperature. Gas temperature is most accurately measured by either the suction pyrometer or the venturi pneumatic pyrometers. Sheathed thermocouples are frequently used, but are often inaccurate.

The suction pyrometer uses two or more shields between the thermocouple or thermocouple sheaths and the surrounding gases, coupled with the increased heat transfer by convection by drawing gases rapidly through the spaces between the thermocouple shields. Since the shields are then closer to the true gas temperature, the sheath surrounding the thermocouple is less disturbed by radiating to them rather than radiating to hotter or colder

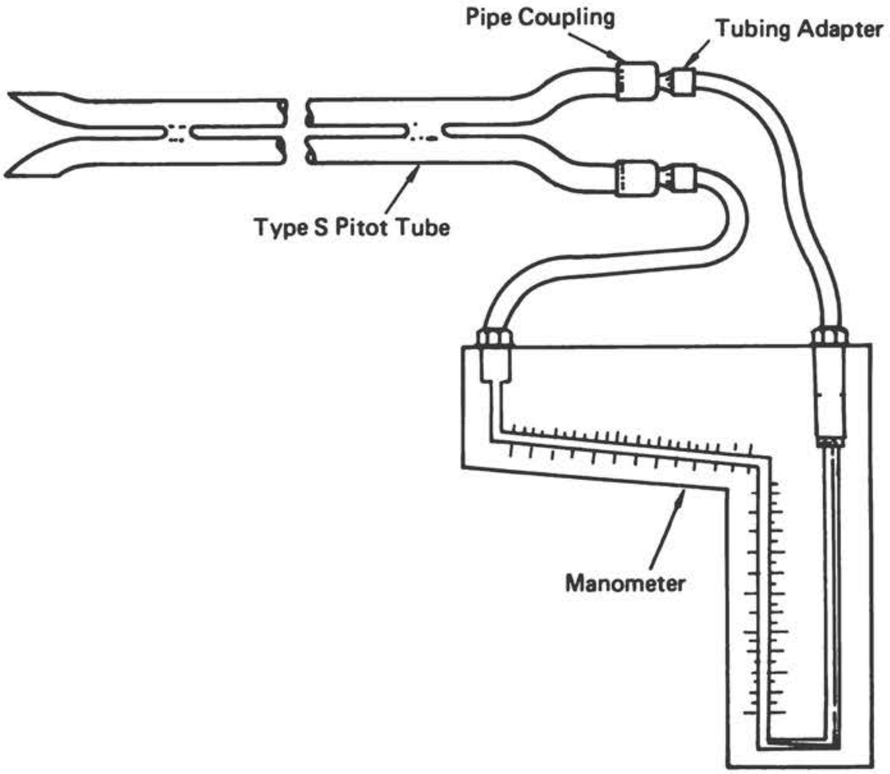


Figure 9.1 Pitot Tube-Manometer Assembly [1]

walls of the furnace. At the same time, the high velocity gases flowing between the shields and over the thermocouple sheath improve heat transfer between the gas and the solids, and again the approach of the thermocouple sheath to the true gas temperature is greatly improved. By appropriate operation, a thermocouple efficiency may be determined, details of the methods being given in appropriate publications [2, 5]. Without the shields, measured temperatures may be in error by as much as about 40°C at a true gas temperature of 540°C, with the error rising to about 260°C at a true gas temperature of 1650°C. Experiments have shown that if the shields are of ceramic—necessary at temperatures above about 540°C—then a minimum of two shields is necessary to achieve satisfactory thermocouple efficiency. Below 540°C, metal shields may be used, but a minimum of four shields is required. The high velocity flow of gases between the shields and over the thermocouple sheath has also given rise to an alternate name for this instrument—High Velocity Thermocouple. It should be noted, however, that many instruments referred to as High Velocity Thermocouples have insufficient shields, and may still be in error.

The venturi pyrometer has been also described in reference 2. This instrument uses two venturi tubes, one measuring the volume of flow of the hot gas, and the other measuring the volume flow of the cold gas, at which point the temperature is also measured. If the flow volume and temperature at the cold temperature are known, the mass of the gas flowing may be determined; this is the same mass that is flowing through the hot venturi. The mass flow and the volume flow rate at the hot venturi can be used to calculate the temperature of the gases flowing through the hot venturi. This is a tedious calculation, but it is accomplished by a small calculator that provides immediate calibrated readout. This instrument is capable of operating over a particularly wide range of temperatures from zero to 2500°C. The calculator responds in a few seconds, and is robust and particularly insensitive to blockage in gases heavily laden with dust. Reference 2 further discusses this instrument.

Both suction and venturi pyrometers have been built in sizes ranging from 1 or 1.3 meters long to 10 or 13 meters long. The larger units have been used in large utility boilers. Suction pyrometers have been made in smaller sizes, only a few inches in length.

9.2.3.3 Gas Sampling. Gas sampling probes are the simplest of all probes. In essence they are tubes, with water cooling where necessary. Some gas sampling probes have a side entry. The sample point can be directed upstream, downstream, or across the stream to determine any possible defects of the direction of sampling; but the sampling direction should not affect the gas analyses, and can be of value if it is desired to sample primarily gas in particle loaded gas streams, by arranging the probe with the aperture pointing downstream. If the sampling aperture is pointed upstream, the same probe can then double as a solid sampling probe if a filter paper carried on a fine wire mesh is inserted as illustrated in Figure 9.2. Most gas sampling probes, however, do not have a side entry. Some may be built with additional water-cooled fingers just inside the sampling orifice so that the gases impinging on the water-cooled finger are more rapidly quenched.

Gas probes are generally made of metal, commonly brass or copper with brazed or soldered joints. Steel tends to rust unless it is stainless, in which case it is more difficult to weld and considerably more expensive. Other designs and materials have been described in the literature, but are usually relevant only to research.

9.2.3.4 Solid Sampling. The most extensive experience of sampling solids from hot gas streams is undoubtedly that gained by the International Flame Research Foundation. The chief characteristic of probes developed by the Flame Foundation is a sintered bronze filter near the tip of the probe to filter out the particles from the gas stream being drawn in. A possible criticism of such designs is that once a layer of particles has built up on the inside of the bronze filter, this may tend to insulate further layers which are still being swept by very hot gases. If further decomposition of the collected

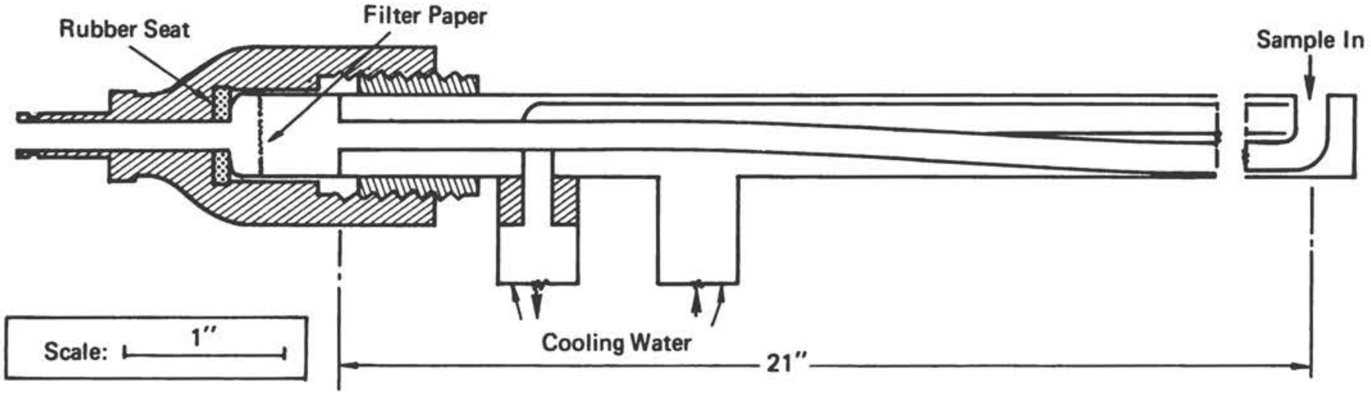


Figure 9. 2 Gas and/or Solid Sampling Probe with Side Entry.

particles is still possible, this may occur even after collection, sitting in the bronze filter inside the probe tip. Where this possibility exists, and the results may be serious, an alternative is to sweep the total sample right through the probe, and filter out the solids at the cold end of the probe, or outside the probe altogether. Part of this problem is linked to the question of proper sampling rates. It is generally stated that the suction rate should be such that the flow rate inside the mouth of the sampling tube should match the free stream velocity in the flowing gas. This is usually referred to as "isokinetic sampling." This indicates the need either for velocity measurements, using methods described above, or for a null probe design that will automatically indicate when the velocities are properly matched. The effect of a fairly broad probe tip, however, on the upstream flow may sometimes modify the isokinetic requirements. In using solid sampling probes for quantitative purposes, it is therefore generally advisable to make measurements under "standard" conditions using a range of sampling velocities both above and below isokinetic. It is often found that the concentration of solid in the dust stream seems to be suprisingly insensitive to the sampling velocity. However, the point should always be checked.

9.2.4 Sampling Trains

Sampling trains are arrangements to collect solids, condense vapors, and clean the permanent gases for collection and later analyses or for continuous analyses. Pitot tubes require no such arrangements. Pyrometers may require filters and wash bottles to clean gases that may then go through mechanical pumps. This precaution is unnecessary, however, if water, air, or steam ejectors are used for the pyrometers.

The EPA train (see Figure 9.3) uses a Type S pitot tube to determine the velocity so that sampling will be properly isokinetic. The probe is indicated as heated, implying that the stack gases are so cool that condensation may result during transit of the gases from the probe entry to the collection in impingers. The solids are then collected, mainly in the cyclone, with the carry-over stopped by the filter. Condensibles are collected in the impingers, with any carry-over trapped in the spray droplet filter. A vacuum gauge then determines the line pressure; a dry test meter and/or an orifice meter determines the total gas flow through, and the instantaneous flow rate of the gas, respectively. The gas then can be moved to gas sampling bottles, or alternatively can be fed directly to the appropriate on-line analyzers.

In high temperature gas streams where liquid condensibles are unlikely or unimportant, an alternate, simpler system may be used. This is illustrated in Figure 9.4. If the gas temperatures are not enough, the probes used must be either water- or steam-cooled. Steam-cooled probes are used where a condensible (water) is to be measured by direct feed to an appropriate on-line analyzer. If a dry analysis is required, this precaution is unnecessary. If solid samples are to be collected, the necessary filter must be in the probe, either at the tip or at the cool end.

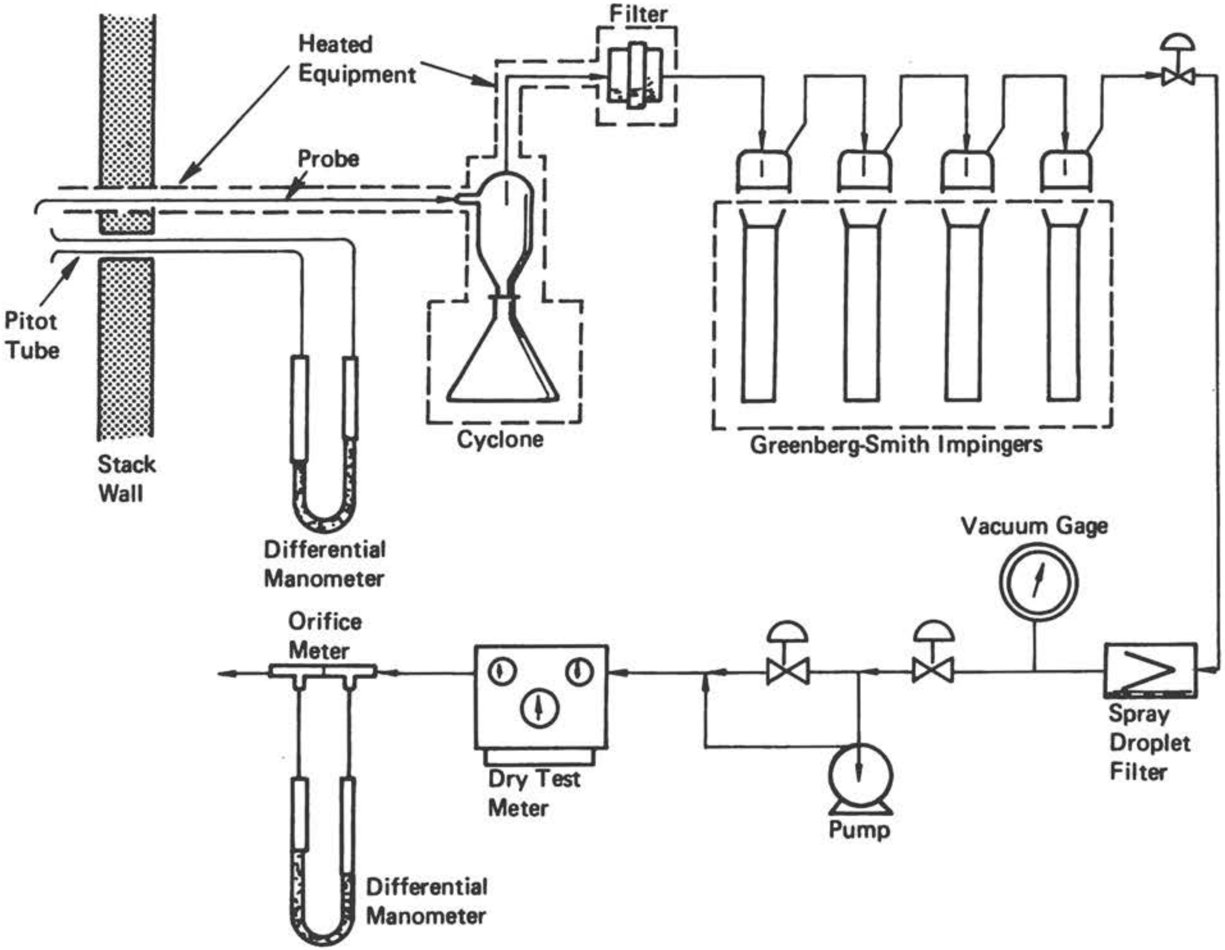


Figure 9.3 EPA Particulate Matter Sampling Train.

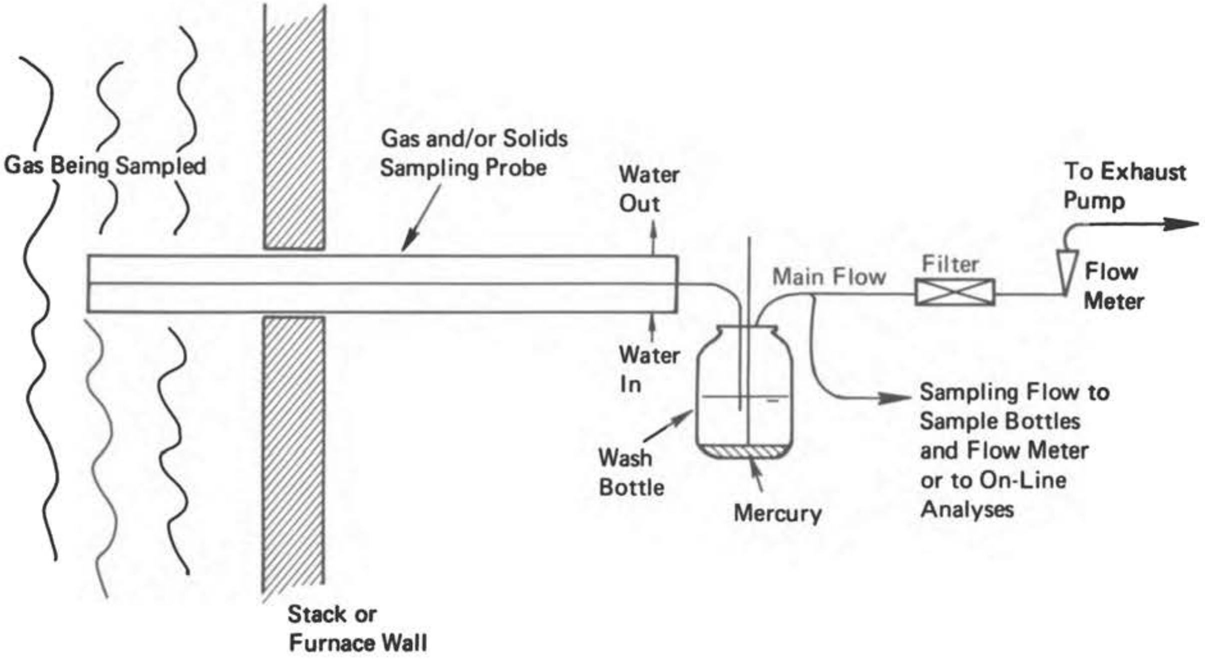


Figure 9.4 Schematic Diagram of Simple Wash Bottle Sampling System.

Under normal conditions, condensation usually occurs inside the sampling probe, and for that reason the probe is generally inclined slightly to aid the drawing of the condensate out of the probe in the direction of the gas flow. If condensation does occur, it is desirable to have a solid sampling filter at the tip rather than at the cold end. If a solid sampling filter is required at the cold end, steam cooling may be necessary. The gases leaving the probe are then drawn through a simple wash bottle. The line leaving the probe dips under the surface of water and wash bottle so the gases will bubble through. Certain of the gases will then be quite readily absorbed in the water, such as CO_2 or SO_2, but the concentration usually reaches saturation quickly with no further change. If the gases are readily absorbed by water but are at such low concentrations that the water does not saturate (e.g., NO_2) this method cannot be used and the EPA train or some variant is necessary.

The gas is drawn out of the bottle from the top. It is often advisable to have an additional tube which runs from the atmosphere down to near the bottom of the bottle, just penetrating the surface of the mercury layer in the bottom. The tube acts as a short circuit if the probe is blocked. The pump draws air from the outside, thus preventing the release of a high vacuum.

9.2.5 Readout and Analysis

The methods of readout and/or analysis for the different measurements summarized above are varied and complex even for any one single measurement. The following sections discuss the most common methods.

9.2.5.1 Velocity. Readout for a pitot velocity probe is, as we have seen, a manometer of one form or another; a simple U-tube or a much less time-responsive, but sensitive draft gauge. If the manometer is too sensitive, then accurate reading of the pressure difference becomes impossible, and some form of continuous recording of the pressure variation has to be made and averaged.

9.2.5.2 Temperature. For pyrometers using thermocouples, the readout is a millivoltmeter or a milliammeter; most commonly used are recording potentiometers. These can be calibrated in millivolts, or directly in temperature, so long as the scale is matched to the thermocouple materials being used. For recording many points, such as the temperatures of a furnace or incinerator wall, a multipoint recording potentiometer is used. With the venturi pyrometer, the venturi measurements pass through a special computer which calculates a response indicated directly as temperature by an appropriate instrument. In this instance, the computer and readout have to be specifically matched to the venturi pyrometer.

9.2.5.3 Gas Analysis. Gas analysis presents a substantially more complex problem. The method of analysis and readout is determined to some extent by the instruments currently available. These offer a choice between batch or continuous, on-line analysis; between a chemical, wet method, and a physical method; between analysis of the group of gases in the sample by the same instrument, as in chromatography, or separate analysis of each gas by instruments such as the non-dispersive infrared analyzer (NDIR). Some gases present in trace quantities, such as NO_2, may be highly soluble in condensate in cooling gases. In such instances, the fully water-cooled probe is inappropriate, and, even more, the water wash bottle. A steam-cooled probe with heated lines to the analyzer is then necessary. These lines and the probe can present problems if particulates and other interfering constituents have to be removed before the sample enters the analyzer. All these factors must be considered in the design of a gas analysis train and matched analyzer and readout equipment.

Wet chemical methods on batch samples were the first means of analyzing any particular gas. More recently, physical methods have been adopted, but using batch analysis in many cases. However, there are now continuous physical analyzers, and batch methods have been adopted for continuous processing. This transition from one method to another can be seen in the development of continuous on-line analyzers for pollutant emissions at low concentrations. Wet methods, however, should not be disregarded.

The best known of the chemical wet methods for gas analysis is probably the Orsat. The best known form is a three-bottle system with solutions for adsorbing oxygen, carbon dioxide, and carbon monoxide. When the individual gases are adsorbed, there is a corresponding reduction of volume which can be measured directly. Although the Orsat contains only three bottles in most constructions, other analyzers designed on the same basis are capable of analyzing more complex mixtures of hydrocarbons. In some instances, the analyzers include means for oxidizing some of the combustibles and determining the combustibles by the added volume of water and carbon dioxide. Industrial analyzers, which operate on batch samples, but automatically to provide a more or less continuous readout, have been available for many decades, mainly for oxidizing CO_2, but with appropriate adaptions can also analyze CO and hydrogen together. More specialized wet methods of analysis require absorption of the specific gas in an appropriate solution followed by titration. These wet methods are now being largely superseded by more direct physical methods, but they are still in significant use.

Analyzers based on physical properties fall into two groups: (1) analyzers that only analyze a single gas at a time; and (2) instruments that analyze all or most of the gases in a given sample, with a successive readout of the components. The first group is more amenable to continuous, one-line analysis. The second group is most easily used with single batches, but by appropriate automatic sampling has been adapted to continuous analysis.

The multiple component analyzers include: (1) chromatography; (2) dispersive spectrometry; and (3) mass spectrometry. In chromatography, the gas sample to be analyzed is injected into a carrier gas, frequently hydrogen or neon. The carrier gas carries it through a separation column, with columns operating either by absorption or by partition. In absorption, the gas is absorbed on a solid obeying Henry's law. In partition, gas is absorbed with partition following Nernst's law.

Various solid materials have been found to be effective in columns. Data on different materials are best obtained from catalog sources. The function of the column is to separate the components, which enter together, but leave in sequence. At the end of the column is a detector that responds to the concentration of the appropriate component leaving the column in the carrier. Since the detector response also depends on the nature of the gas emerging, the instrument must be calibrated for each individual gas. The simplest detector is a thermocouple in a flame which, therefore, requires a combustible carrier gas (generally hydrogen). As the analyzed constituents pass through, the flame height changes, and the thermocouple responds accordingly. The two most common detectors, however, are the flame ionization detector (FID) and the thermal-conductivity detector. The FID also requires hydrogen as a carrier gas as well as a flame of hydrogen. Ions are formed in the flame and if a potential is applied between a potential ring and the burner, a current proportional to the constituent concentration (and also to the rate of flow) can be measured. In the thermal conductivity detector, the out-of-balance voltage in a bridge circuit can be measured and recorded as a function of the constituent concentration [2]. In dispersive analysis, use is made of the principle that individual gases will absorb specific light frequencies. If the gas sample is scanned with a progressively changing sequence of wave lengths, and the transmission is measured, the plot of percent transmittance against frequency will give a plot showing strong absorption at particular frequencies represented by the individual gases. The extent of absorption is also proportional to their concentration. The mass spectrometer can also be regarded as a type of dispersion instrument, or a separation instrument (in the case of the time-of-flight spectrometer). The readout in this instance is an intensity value at a particular mass number that then has to be identified with a particular gas.

Of the single gas continuous analyzers, the non-dispersive infrared analyzer (NDIR) is the most widely used. This is like a dispersive analyzer except that it is operating at a single wave length, designed for use with a single gas. The advantage of the individual analyzer as compared with the multiple gas analyzer is that if the instrument breaks down, only one reading is lost, whereas with the multiple gas analyzer if the instrument breaks down, all readings are lost and the experiments must be terminated. Very much less common is non-dispersive analysis in the ultra-violet region (NDUV). One other continuous analyzer that is now becoming quite common is for analysis of nitric oxide, and it depends on the phenomenon of chemiluminescence. Nitric oxide reacts with ozone to form NO_2 with release of light, and the emission is proportional to the percentage of nitric oxide if ozone is in excess. This is currently regarded as the most reliable of all the NO_x analyzers.

Other special function analyzers also exist. Instrument handbooks are best consulted for details.

9.2.5.4 Solids and Smoke. Solids collected in solid sampling probes are analyzed by a variety of standard methods depending on the nature of the solid and the objective of the experiment. The solids can be organic, or inorganic, or both. If the organic component is of interest, this will be analyzed first for combustible and ash, and then for its elements (C, H, O, N, and S). Volatile matter may also be of interest: X-ray analysis to determine crystal structure may also be carried out. The inorganic constituents may also be appropriately analyzed. Clearly, the type of analysis to be carried out depends on the nature of the material being fired and the interest in the product material. A prime factor in particulate behavior is the concentration of particulate matter in the gas stream. To determine this, the particulate matter must be collected quantitatively, and the volume of gases pulled through the probe, from which it is assumed the particles have been separated out, must also be measured. As an adjunct or alternative to this quantitative measurement, some form of light obscuration meter is frequently used in the stack. This consists of a light source to provide a beam through the stack with an appropriate sensor on the far side. This is commonly calibrated arbitrarily in terms of Ringlemann grids. The readout consists of percentage obscuration. The instrument is of greatest value if it can be correlated with direct concentration measurements using solid sampling probes. An alternative to the light obscuration meter, but serving essentially the same purpose, is a sampling device that pulls gases through a filter paper; material collected on the filter paper is weighed, or the density of the strain is determined by some densitometer method.

9.2.6 Some General Aspects of Analysis.

A number of components of interest in measuring incinerator performance are listed in Table 9.1. These are divided into four groups. Each constituent in each group is followed by a representative range in which that component can be expected to be found if the incinerator is either working satisfactorily (yielding a low value) or unsatisfactorily (yielding a high value). In high temperature incineration, no combustibles should be present in the exhaust gas. Their presence most likely indicates the existence of by-pass in the mixing pattern; or too short residence time due to overfiring or over cooling of the flame due to the addition of too much inert. Unburned hydrocarbons should thus be analyzed as a good index of the performance of the incinerator. Table 9.1 includes a number of constituents not specifically mentioned in the discussion above. In particular, methods for determination of oxygenates and other components may need special consideration. Table 9.2 lists methods for a number of specific components of interest. Special methods for analysis of SO_2 and NO_x, are listed in Tables 9.3 and 9.4.

TABLE 9.1 Components of Interest for Measuring Afterburner Performance

Components	Concentration Range, ppm
Hydrocarbons:	
Total	10 to 20,000
Non-Methane	10 to 20,000
Paraffins	10 to 20,000
Olefins	10 to 20,000
Aromatics	10 to 20,000
Oxygenated Organics:	
Carbon Dioxide	0.5 to 10%[a]
Carbon Monoxide	10 to 20,000
Acids	1 to 500
Aldehydes	1 to 1000
Particulates:	
Combustible	0.01 to 10 grains/cu ft
Non-Combustible	0.01 to 10 grains/cu ft
Visible Emissions	0.01 to 10 grains/cu ft
Other Components:	
Sulfur Dioxide (SO_2)	5 to 20,000
Sulfur Trioxide (SO_3)	5 to 1000
H_2S, Mercaptans	1 to 10,000
Halogens	5 to 10,000
Nitrous Oxide (NO_x)	5 to 5000
Water	0.1 to 10%[a]
Oxygen	0.1 to 20%[a]

[a] Not a pollutant, but determination may be needed for control.

Source: Reference 6

9.3 Testing Structural Materials

9.3.1 Introduction

Testing of structural materials for incinerators deserves special attention owing to the already well-known accelerative effects of complex environments together with cyclic process. Available data from steady-state testing or from environmental components including only a single species are useless and possibly misleading. These simple tests are useful as a design guide but must be treated with care since the service conditions may be similar to the test conditions but may not include synergistic effects. A classic example would be the resistance of gold to corrosion by either nitric or hydrochloric acid. Either acid by itself does not attack gold, but a mixture—aqua regia—is extremely corrosive. Meaningful data can only be obtained by testing under conditions which truly duplicate the operating environment. The evaluation of materials for incinerator construction presents a number of constraints. Testing must be done on a real-time basis; accelerated tests would be either of limited value or possibly misleading. A continuous heating test, for example, would ignore thermal cycling effects and corrosion by hygroscopic deposits while the incinerator is cooling or inactive. The variations in concentration of the corrosive deposits and solutions would be difficult to duplicate in an accelerated test.

As more information is developed, it may be possible to develop an accelerated test, but this conclusion should be reached with care. The model waste used during testing should be either salt-water flushed sewage with normal wastes of human origin or a seawater slurry of organic and inorganic materials encountered in normal operation. Incinerator pyrometric equipment should be the same as that used in operational incinerators so that the apparent observed temperatures during testing will be the same as those observed under actual service conditions. Additional pyrometric equipment to determine true test temperatures will be needed to establish the relationship between actual and apparent temperatures.

Test samples should not be limited to small, flat plates or coupons but should include specimens for the evaluation of crevice corrosion and stress corrosion cracking. Test cycles should duplicate operational conditions to permit evaluation of such factors as delayed fracture and thermal cycling effects. Thermal cycling tests should duplicate operational heat-up and cool-down rates.

TABLE 9.2 Methods for Determination of Oxygenates and Other Components.

Compound Determined	Method	Lower Limit, ppb	Absorptivity (L/mol cm)
Aldehydes	Methylbenzothiazolone Hydrazone Spectrophotometric (650 nm)	20	50,000
Aldehydes and Ketones	Dinitrophenylhydrazine Spectrophotometric	40	27,000
Acrolein	4-Hexylresorcinol Spectrophotometric (605 nm)	20	17,000
Formaldehyde	Chromotropic Acid Spectrophotometric (570 nm)	20	19,000
Carboxylic Acids	Absorption-titration	--	------
Esters	Hydroxamic Acid Spectrophotometric (530 nm)	100	1,100
Carbon Monoxide	Non-dispersive infra-red (NDIR)	1000	------
Carbon Dioxide	NDIR	2000	------
	Orsat.	0-5%	------

Source: Taken from various references but summarized in reference 4.

TABLE 9.3 Methods for the Analysis of SO_2.

Method	Principle	Instrumentation	Applicability	Limitations
Hydrogen Peroxide Titration Method (EPA Method 3)	$SO_2 + H_2O_2 \rightarrow H_2SO_4$ Titration with base or Ba^{++}	Laboratory Equipment: Absorber and titration units	Range: 0.01 to 100 ppm	Requires reagent additions
Hydrogen Peroxide Conductometric Method	$SO_2 + H_2O_2 \rightarrow H_2SO_4$ Measure Conductivity	Monitors: Leeds and Northrup, AEROSCAN Westhoff U3S ULTRAGAS ANALYZER Instruments Development, IDC 902-1 Scientific Instruments, SI-67	Range: 0.01 to 5 ppm	Inteference by salt aerosols and acidic and basic gases which may be eliminated by filters.
Electrolytic (Coulometric) Method	$SO_2 + Br_2 + H_2O \rightarrow 2HBr + H_2SO_4$ $SO_2 + I_2 + H_2O \rightarrow 2HI + H_2SO_4$ Br_2 and I_2 generated electrolytically.	Monitors: Consolidated, TITRILOG Beckman Instruments, Model 906 Barton 286 SULFUR TITRATOR Phillips Instruments, Model PW 700 Atlas Electric Devices, Model 1200	Range: 0.01 to 5 ppm Monitors simple to operate and reliable for unattended service.	Interference by oxidizing materials, aldehydes, olefins, and hydrogen sulfide. (Some interference can be eliminated by filters.)
WEST-GAEKE Colorimetric Method ASTM D 2914	Formation of dyestuff by reaction with bleached pararosaniline.	Laboratory Equipment: Spectrophotometer	Range: 0.01 to 5 ppm	Procedure cumbersome. Continuous analyzer needs close attention
		Monitors: Atlas Electric Devices, Model 1500 Technicon Corp., AUTO ANALYZER	Most nearly specific method for SO_2	
Electrochemical Sensor	Oxidation in a membrane-covered cell.	Monitors: Dynasciences, SS-330 Envirometrics, NS-200 Theta Sensors, LS-800-AS	Range: 0 to 5000 ppm Simple to operate	NO and NO_2 interfere slightly.

Source: Reference 6

TABLE 9.4 Methods for NO_x Analysis.

Method	Principle	Instrumentation	Applicability	Limitations
Phenol disulfonic acid method ASTM D 1608 (EPA Method 4)	$NO_x \xrightarrow[H_2SO_4]{H_2O_2} HNO_3$ Phenol disulfonic acid nitrated to produce yellow color	Laboratory spectrophotometer at 400 mμ	Range: 5 to 1000 ppm for all nitrogen oxides except N_2O	Not sensitive below 5 ppm
Sulfanilic Acid Method (Saltzman) ASTM D 2012 SAE J177	NO_2 converts sulfanilic acid to diazonium salt. Salt couples with amine to produce deep violet color	Laboratory spectrophotometer at 550 mμ. Continuous Analyzers Beckman Acralyzer Technicon AUTO ANALYZER	Range: 0.01 to 4000 ppm. Specific for NO_2 NO determined by prior oxidation. Useful air and exhaust analysis. Faster than disulfonic acid method.	Equipment somewhat more complex than for phenol disulfonic acid method.
Ultraviolet Absorption Method	NO_2 has maximum at 400 mμ with absorptivity = 170 liters/mole cm. NO is transparent above 230 mμ	Continuous Analyzers: Beckman NDUV Model 255 plus oxidation system.	Range: 10 to 6000 ppm. Determines NO_2 directly. NO determined by prior oxidation.	NO is a reactive gas and can be partially lost unless precautions are taken.
Infrared Absorption Method	NO has band at 5.4 μ with absorptivity = 2 liters/mole cm	Continuous Analyzers: Beckman NDIR Model 315A Mine Safety Appliance Model LIRA 200	Range: 10 to 4000 ppm Determines NO directly	Water vapor interferes and must either be constant, or preferably removed.
Electrochemical Sensor	$NO+NO_2$ permeate membrane on sensor and are electrochemically oxidized. Resulting current is proportional to NO_x concentration.	Continuous Analyzers: Dynasciences NX-110 and NX-130 Envirometrics Model N-122 Theta Sensors Model LS-800-ANX	Range: 2 to 10,000 ppm Models available for NO_x or NO_2	SO_2 interferes but can be eliminated or compensated for.
Chemiluminescence	The light resulting from the reaction of NO with ozone is measured with a photomultiplier. NO_2 must be converted to NO to be measured.	Continuous Analyzers: Thermo-Electron Corp. Bendix, Environmental Science Div. REM, Inc., Model 642	Range: 0.01 to 10,000 ppm	No known interference.

Source: Reference 4

The above emphasis is on testing the total environment, but in real-time reflects the uncertainty in interaction effects. The testing may either not be severe enough, or it may be too severe and would unnecessarily disqualify a good material.

9.3.2 Test Apparatus

Materials should be tested both in operational prototype equipment and in laboratory test chambers in which specific environmental factors can be controlled and evaluated. Measuring gas composition and temperatures is most important. Any prototype testing apparatus in which such testing is performed can itself be evaluated, and attention to such a possibility should be given in the material design.

9.3.3 Past and Future Laboratory Testing

Results to date from testing which was conducted in support of shipboard incinerators are based on the assumption that the inner liner of the incinerator will be subjected to a 760°C operational temperature. In these burner rig tests, byproducts of incinerated urine impinged on test coupons producing an extremely harsh environment in which molten salts were in continuing contact with the metal surfaces [6]. On the basis of these tests, it was deduced that the following several alloys showed promise as inner liners of incinerators: Inconel 690, Inconel 671, Haynes 150, 310SS, 446SS, 309SS, RA-333, and Haynes 188 [7]. Burner rig tests have proven useful in establishing relative order of merit of candidate materials.

Testing of several prototype incinerators produced one surprising result. One incinerator with a 309 stainless steel inner liner performed very well. This design used an air-cooled inner liner; the temperature of the inner liner was probably about 650°C. At this temperature, the corrosion rate due to molten salts is greatly reduced because the corrosive reactions must occur in the liquid rather than the solid phases. During incineration, this inner liner remained black, indicating a wall temperature below 650°C. Any salts deposited on the wall appeared to be present as solids, eliminating molten salt attack.

While the laboratory studies to date have given an insight into corrosion mechanisms, the range of temperature effects studied is too limited to encompass the existing designs. The laboratory material testing programs should be extended to encompass the full range of design parameters proposed by competing contractors.

Laboratory experiments should encompass high temperature exposure, low temperature corrosion, and cyclic heating conditions. The high temperature phase of testing should include, but not necessarily be restricted to:

1. Immersion in a fused salt mixture such as Na_2SO_4-K_2SO_4-NaCl:
   - cyclic versus constant immersion;
   - exposure to combustion gases; and
   - effects of stressed U-bends, welds, lap joints.

2. Partial immersion in salt mixtures to provide an interface between deposits and combustion products with same variables as above.

3. Coating of surface with salt mixture during exposure to products of combustion over a range of operating temperatures.

4. Impingement of burnable residue directly on the metal surface at elevated temperatures.

These tests are, at best, semi-quantitative. They are useful in assessing relative merit of candidate materials under conditions similar to those encountered in operational incinerators.

The low temperature phase of testing should include cyclic exposure above and below the dew point of combustion gases in contact with acidic deposits. Both short-term (8 hour) and long-term (7 day) exposure to high humidity at ambient temperature would be evaluated to simulate daily shutdown and longer term inactivity of the incinerator.

As described in Chapters 5.0 and 6.0, extensive municipal incinerator experience has shown that the addition of small amounts of inert materials such as clay, limestone, and other refractory materials improves corrosion resistance of materials of construction. On the other hand, small amounts of metals such as lead, zinc, and vanadium accelerate the hot corrosion processes. Both effects should be studied in the laboratory and evaluated on specimens in the test incinerators.

9.3.4 Evaluation Techniques

Techniques which should be used to evaluate test coupons are:

1. Visual inspection at the end of each test cycle;

2. Weight change determination;

3. Chemical and X-ray analysis of corrosion products and deposits;

4. Nondestructive testing: dye-penetrant, radiography, microprobe analysis; and

5. Metallography: light microscope, scanning electron microscopy.

9.3.5 Performance Projection

There are no simple rate laws which govern the damage accumulated by these complex attack processes. Care should be taken to note that complex cyclic processes sometimes produce abrupt accelerations when critical conditions, (e.g., of oxide rupture) are reached

9.3.6. Future Studies

Depending on the materials which are shown to be promising in preliminary screening tests, various testing procedures following previous sections should be utilized. Depending upon whether the material is ceramic or metal, emphasis would be placed differently, e.g., thermal shock is a major issue with ceramics whereas low temperature chloride stress-corrosion cracking is a concern with many metals.

Special attention should be directed to the status of the alloy, Inconel 671 which appears to be the most promising metallic material. In order to provide a final qualification, the following tests should be undertaken:

- The temperature range of testing should be expanded; additional tests should be run at 650°C and 870°C.
- The effect of thermal excursions to 980°C should be determined.
- Fabrication and repair techniques for Inconel 671 should be established.
- The effects of long term aging on properties of the RS-122 weld metal should be determined.
- Additional tests delineating the effects of thermal cycling should be conducted.
- The effect of protective coatings (MCrAlY) should be determined.
- The effect of additives (corrosion inhibitors) should be determined.

- Additional work is necessary to determine ash compositions and melting points as well as interactions which may occur at high, low, and ambient temperatures.
- Prototype operation of an Inconel 671 liner under actual operating conditions should be conducted as soon as possible.

Candidate ceramic materials should be similarly evaluated.

REFERENCES

1. Federal Register, Vol. 36, No. 247, pp. 24876-95, (1971).

2. Chedaille and Braud, Measurements in Flames, Crane, Russak and Company, (1972).

3. Environmental Engineers Handbook, Vol. 2, B. G. Liptak, editor, Chilton Book Co., Radnor, PA, (1974).

4. Rolke, Hawthorne, Garbett, Slater, Phillips, and Towel, "Afterburner Systems Study," S-14121, Report to EPA (Office of Air Programs), Shell Development Co., Emeryville, CA, (1971).

5. Land and Barber, Iron and Steel Inst., Vol. 184, p. 289, (1956); Trans. Soc. Instr. Tech., Vol. 6, No. 3, (Sept. 1974).

6. Von Doering and Bergman, "Construction and Operation of a Hot Corrosion Test Facility," ASTM Materials Research and Standards, (Sept. 1969).

7. Wacker, G., Private communication, Naval Ship Research and Development Center, (1975).