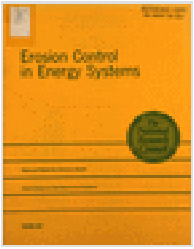

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The conclusions reached led to twelve recommendations aimed at advancing erosion/corrosion technology. These recommendations emphasize long-range planning; development of a fundamental understanding of the erosion/corrosion process; development of erosion/corrosion models and meaningful correlations; development of testing procedures for material response investigations, engineering data and accelerated life tests; and design considerations.

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MATERIALS IN ENERGY SYSTEMS
THROUGH THE REDUCTION OF EROSION

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council

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NOTICE

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Chapter 1

INTRODUCTION

Erosion, corrosion, and erosion/corrosion* interactions are widely recognized as critical problem areas in the operation of energy generation and conversion plants. This report enumerates the range of erosion conditions which are inherent in the various energy systems under development. The following restrictions were imposed on the material presented:

- erosion as used here involves impingement by particulate matter in a fluid medium, including cavitation erosion; and
- since the fluid medium can be either reactive liquids or hot gases containing a variety of corrosive constituents, both wet and dry corrosive attack must be considered in conjunction with particle impingement.

Examination of the range of coupled phenomena associated with energy systems and the development of approaches to overcome outstanding erosion/corrosion problems were the major concerns of the Committee. The areas of consideration were restricted to erosion (when the carrier fluid is nonreactive) and to the effects of erosion/corrosion interactions on materials, but did not include corrosion effects per se.

The National Academy of Sciences had been asked by the Energy Research and Development Administration to convene a Committee to:

- consider erosion problems in energy systems which will be significant in the near term;
- catalog expected problems;

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* The expression "erosion/corrosion," which appears frequently throughout the report, denotes the surface destruction of a material through combined action of the two processes. While the relative contribution to material loss of the two processes is often not apparent, the situations discussed in this report are typically those in which erosion is paramount.

- outline the science of erosion, and the present technology for coping with these phenomena; and
- recommend new approaches for minimizing the impact of erosion in energy systems.

The energy systems considered included coal conversion (gasification, liquefaction, magnetohydrodynamics), high-temperature gas turbines, power recovery systems, solar energy, geothermal energy conversion, wind machines, and slurry piping. Topics such as drill bit development for oil exploration and liquid jet mining procedures were not investigated even though they involve erosion phenomena, because proper consideration of such areas could not be achieved within the time frame and funding level stipulated for the Committee's activities. The current developments in these areas and the timely benefits to be gained would certainly warrant further consideration. Solutions to the erosion problems associated with other energy-related areas such as biomass preparation for utilization in energy systems, oil shale processing, and energy derived from ocean currents are, in some cases, within the near-term state of the art. For others, the progress made in combatting the erosion problems for the systems considered by the Committee will be within the state of the art when such advanced concepts finally reach fruition. Erosion has not been identified as a serious consideration in nuclear power reactors so this area and has not been included explicitly in the Committee's review. The erosion problems associated with the peripheral equipment for conversion of energy from a nuclear source to electricity fall within the range of erosion conditions represented in the Committee's selection.

The primary characteristics of the erosive conditions inherent in the energy system components selected for consideration are identified in Chapter 3. These erosion conditions are categorized at the end of Chapter 3 with respect to temperature and particulate velocities. An assessment is provided regarding the severity of the erosion problem for a specific system or component.

Combatting erosion problems in steam turbines and the redesign of a small gas turbine using ceramic materials to overcome erosion caused by sand ingestion are presented in Chapter 4 as examples of the magnitude of the erosion problem and the interplay between design and materials selection required to reduce the erosion effects to tolerable levels. Since the long-term erosion/corrosion effects in several energy system components will be more severe than these examples, a broadly-based approach to understanding and overcoming erosion/corrosion material degradation processes is certainly warranted. The multidisciplinary nature of the information required is described.

The prevailing state of knowledge pertaining to particulate erosion and corrosion is summarized in Chapters 5 and 6. These comparisons are incomplete but are introduced to provide perspectives on the general character of the work which has been pursued. A significant deficiency is noted both in the type of information required to guide material improvement and also in information to provide data for design considerations. The critical problem areas are related to coupled erosion/corrosion effects which occur in a variety of contexts involving both aqueous and hot corrosion. Chapter 7 is an attempt to provide an overview of the approaches which may be used to begin to attack the erosion-corrosion interaction problem. Negligible information is currently available on erosion/corrosion interactions; however, more information should become available in the next few years, because programs are either underway or are being formulated to better understand the erosion/corrosion interactions.

Chapter 8 describes screening, bench, component and life prediction and verification tests, along with the status of standardization. In addition, the importance and difficulties of accelerated life testing are explored.

Due to the complexity of the erosion/corrosion environments in energy and energy-related systems and the general lack of understanding of material response to the imposed conditions, testing procedures will be an integral part of any investigation whether it be a fundamental mechanism study or an in situ evaluation of a particular component. It is important to recognize early in the evaluation process that appropriate test procedures should be established to insure that:

- the test results are relevant to the conditions under investigation;
- that they are reported in a form and specificity which is useful to other investigators; and
- that the tests be conducted in a manner which will avoid duplication and thereby be cost effective.

There is little doubt that testing at all levels will be an important consideration in the development of near-term and longer-term solutions to the pacing problems. This report presents several significant recommendations and a general testing philosophy which, if assimilated into the program structure before a sizable data base is established, can avoid repetition of the wasted effort which has taken place already in the erosion field. Very little of the tabulated particulate erosion data is valuable for making life predictions. Based on this past experience, it would be advantageous to formulate standardized reporting and test procedures before committing a significant level of funding designated for this problem area over the next decade.

Design considerations for coping with erosion/corrosion degradation of structural components are described in Chapter 9. It goes without saying that the need for construction of advanced energy conversion and generation facilities may outpace material improvements technology. Therefore, it is necessary to develop design alternatives. At present the structural designers must attempt the design of cost effective and efficiently operating systems without very well-established design criteria. The establishment of procedures for rapid communication of results from the materials community is essential. However, it is equally important that the conclusions drawn from any test program be substantiated and that they be translated to the designer in a familiar form. This would suggest that testing facilities be established which can be used to generate handbook data once a material advance has been made. The discussion presented concentrates on problems related to coal gasification; however, the indicated expansion of the usual design considerations to include erosion and coupled erosion/corrosion effects would follow along similar lines in any system involving erosion.

The Appendix summarizes currently funded programs pertaining to erosion/corrosion. The reader can obtain an overview of the magnitude and direction of work currently underway.

The recommendations which resulted from the Committee's deliberations are presented in Chapter 2. The Committee's work was undertaken during a period when several laboratory and pilot plant investigations of the subject area were getting under way and the results of these investigations are beginning to appear. For example, it now is evident that deposition of fine particulates in coal gasification systems and the subsequent build-up of (adverse) layers may be more dominant than the removal of material. The conditions for deposition as opposed to erosion of materials are just beginning to be investigated. Procedures for inhibiting the formation of these layers or for the controlled growth of these build-ups as a protective layer are potential areas for innovation which were not considered in this report. It is anticipated that findings of this nature will be forthcoming in the next few years. Recognition of this fact motivated the Committee to make recommendations more of a procedural nature, rather than specifying certain materials or processes. Recommendations on specific systems would be subject to change much more rapidly than the development of meaningful approaches applicable to a diverse range of erosion/corrosion environments in whatever system they may occur.

The Committee acknowledges that work and actions are under way which are contributing to improvements in the current state of affairs, so the Committee's assessment may only reinforce much of what has already been recognized. In this report, the Committee presented the type of programs required to achieve a modus operandi to minimize erosion problems in significant energy systems independent of whether or not the programs have already been initiated; the Committee elected not to refer to specific on-going technical programs to preclude interpretations of endorsement or criticism of the work in progress.

The most important concern in the Committee's appraisal is how to transfer the results from a multidisciplinary approach, which is required for application in the most severe erosion/corrosion environments, to a useful form for the system and component designer. This is a consideration since a significant amount of basic research is required before the material degradation processes which take place in erosion/corrosion interactions can be understood. This understanding is necessary for materials selection and improvement; therefore, means must be established for utilizing the accomplishments of a materials science program to provide a well-rounded view of the problem area. This same consideration applies to the general field of erosion for less severe environments, where an effective means still has not been developed for translating the available body of knowledge to useful design data.

The Energy Research and Development Administration (ERDA) and the Electric Power Research Institute (EPRI) are in a unique position as primary funding sources to provide the means for significant advances in erosion/corrosion technology to meet the developmental objectives associated with energy systems. This research would have a valuable spin-off in other applications involving erosion and corrosion. The resulting contribution to conservation of materials, especially critical material resources, is obvious. A realization of the magnitude of the problems and what must be done to provide effective solutions, establishment of phased priorities, coordination of diverse activities, generation of results on a timely and integrated basis, and the need for assimilation of results from many fields into a design data base cannot be overemphasized.

In reviewing the state of the art in erosion and corrosion technology, the number of unanswered questions which could be raised far outnumbered those which the Committee could consider in some depth. It became apparent that the development of a design data base for the spectrum of erosion/corrosion problems likely to be encountered in energy systems is a critical issue. The bulk of the available erosion test data applicable to temperatures below 390°F (200°C) still has not been properly developed for design purposes. There is a sparsity of erosion data at temperatures above 390°F (200°C) and there are virtually no data available on erosion/corrosion effects for any temperature regime. After reviewing the available information and assessing the complexity of many of the potential erosion/corrosion interactions and operational life-times required, the Committee concluded that engineering a structure for long-term exposures to hostile environments requires a multi-disciplinary approach.

A general strategy is outlined in the recommendations which follow to generate the requisite information on a timely basis in an organized and cost effective manner. Due to the complexity of the possible erosion/corrosion interactions, basic research approaches are required to gain understanding of the dominant mechanisms of material degradation so that either alternative materials can be selected, or directions for improvements in existing materials can be indicated; a comprehensive test program and establishment of testing procedures are necessary to supply meaningful data on material behavior. Testing is also needed for component life predictions; effective means must be devised for compiling the information obtained in the various phases of the overall program into a useful form for designers; and communication of problems in operating systems and potential solutions evolving at many levels of investigation must be established between groups of individuals with diverse backgrounds and viewpoints.

This report will have served a very useful purpose if it can stimulate:

- the creation of carefully developed multi-disciplinary approaches to erosion/corrosion problems wherever they occur;
- the development of meaningful test procedures and usable data; and
- the rapid transfer of the results from basic materials science programs to erosion/corrosion design criteria.

Chapter 2

CONCLUSIONS AND RECOMMENDATIONS

The useful operating life of many components in advanced energy systems will be restricted by the erosion/corrosion conditions associated with the desire for higher efficiencies of energy conversion. The design decisions which must be made to have an energy conversion plant operate for more than 20,000 hours without a major and costly shutdown due to the failure of a critical component are not possible at the present time. Obviously progress will be made, but can the means by which the near-term objectives be met be made more efficient? It should also be kept in mind that successfully meeting one operating objective leads to the desire to establish more lofty objectives. Thus, while compromises in operating conditions and in the desired efficiencies must be made for the near-term, the desire to push back these restrictions will arise in the long run. It is certain that erosion/corrosion related failures will be inherent in the development of most of the near- to long-term energy systems.

The Committee's deliberation covered many specific aspects of erosion phenomena in energy systems; however, the recurring issues which emerged were:

- the general sparcity of available design information;
- the lack of understanding of long-term erosion/corrosion processes in materials; and
- the inability to identify the material properties which would lead to improved resistance to erosion/corrosion attack.

Note: In the following paragraphs, higher priority recommendations are printed in capital letters.

A. LONG-RANGE PROGRAM STRATEGY

Conclusion

Problems related to erosion or corrosion and to a coupled effect, such as particulate erosion of helicopter rotor blades, erosion-ablation coupling for re-entry vehicles, and rain erosion degradation of electromagnetic window materials, have demonstrated that the magnitude of the problem is usually more severe than anticipated in the preliminary design phase. Erosion aspects ultimately become a primary limitation on the desired operation of the system. This prior experience should provide motivation for anticipating the need for an erosion/corrosion design base which is required now and will continue to be required over the next few decades.

Recommendation

LONG-RANGE CONSIDERATION OF EROSION/CORROSION PROBLEMS AND THEIR IMPLICATIONS SHOULD BE ADOPTED BY AGENCIES CONCERNED WITH MAJOR ENERGY SYSTEMS. A COMPREHENSIVE STRATEGY FOR UTILIZING THE RESULTS FROM BROADLY BASED APPROACHES SHOULD BE ESTABLISHED NOW.

B. UNDERSTANDING MATERIAL RESPONSE IN EROSIVE ENVIRONMENTS

Conclusion I

An understanding of erosion/corrosion processes is important since it provides a rational basis for material improvement, provides the physical basis for modeling studies, and provides a unifying basis for stipulating when different materials are likely to display similar behavior. Characterization of erosion/corrosion phenomena in metals, ceramics, composites and coatings requires an interdisciplinary, broadly based, coordinated effort to effectively keep the potential contribution from the materials science community abreast of the design requirements.

An all-encompassing program of this nature on erosion/corrosion appears timely. It is not advisable that the entire program be confined to a single laboratory, since insufficient expertise exists at any one institution. Progress relies on the involvement of individuals with the appropriate expertise. The motivation for new ideas and rapid advancement of worthwhile observations is greatest in a competitive environment. Serious consideration should be given to industrial laboratories for the primary coordination function, since there may be a greater consciousness among industrial research managers of the need for solving problems, for reporting research accomplishments on a regular basis, and for interfacing more effectively with the application areas. The following general subject areas are representative of the expertise required: materials, including metals, ceramics, composites, and coatings; fluid dynamics; numerical analysis; projectile impact phenomena; dynamic properties of materials testing; elevated temperature evaluations of materials, deformation and fracture mechanics; statistical analysis; corrosion (various aspects); surface analysis; microscopy (electron and optical); phase equilibria; and thermodynamics.

An undertaking of this nature could rapidly become overwhelming. Task groups should be organized for short durations to study various aspects of the proposed program in more depth than presented here. For example, on a near-term basis, conditions can be identified for which the procedures to control erosion/corrosion interactions are apparent. First of all, there are combinations of particle sizes, velocities, and temperature for which the erosive component is so severe that it can only be decreased through design to avoid particulate impact or by particulate removal from the gas stream. In the case of metallic alloys, particle sizes greater than 20 μm at gas velocities above 100 fps (30 mps) represent conditions which are highly erosive at 1600°C (870°C) regardless of the corrosive conditions. Secondly, when the erosive conditions are sufficient to provide metal removal in alloy systems, a corrosive process that results in the development of a dense, adherent reaction product on the surface may decrease the erosion rate. Finally, in cases where the corrosion reactions enhance the effectiveness of the erosive media to remove material, steps taken to change the nature of the corrosion process are a meaningful way to combat the erosion/corrosion interactions.

Recommendation I

THERE IS A HIGH PRIORITY FOR GETTING AN EROSION/CORROSION STUDY UNDER WAY AS SOON AS POSSIBLE. A COORDINATED BASIC RESEARCH PROGRAM IS NEEDED TO UNDERSTAND AND CHARACTERIZE EROSION/CORROSION INTERACTIONS IN A VARIETY OF MATERIAL CLASSES. THE APPROPRIATE AND BEST EXPERTISE FROM MANY ORGANIZATIONS SHOULD BE UTILIZED.

Conclusion II

Computer analyses will be helpful in modeling the eorsion/corrosion interaction in mechanism studies. Materials-oriented investigations will provide the physical basis for the events leading to material removal. Computer programs can be developed at different levels of sophistication to model the material removal process.

Sensitivity analysis, which can be compared with experimental results, will permit the determination of the effect that changes in material properties or the corrosion rates will have on material degradation. This effort should be undertaken in conjunction with materials-based programs and should have a modest level of support.

Conclusion III

Modeling studies are required to characterize the erosive environments. Computer analyses are required to characterize the flow of particle-laden fluids in order to estimate the influence of particle concentration effects (such as the particle-particle interactions within a boundary layer, the flow conditions for particle shielding of the surface, and the statistics of the actual particle impact angles due to these effects) on the number of successful particle collisions, the influence of the flow geometry, and the distortion of soft or liquid particles prior to impact. Continuum and discrete models for particulate flow are available, but will have to be re-derived for intermediate- to high-particle concentrations in both liquids and gases. The governing equations will have to be incorporated into computer codes in order to investigate realistic flow conditions and geometries. This is an important aspect of computer modeling and should be well-supported in the near term.

Conclusion IV

Computer modeling of critical system components should be undertaken to establish the sensitivity of these components to damage through bombardment by various particle distributions. Both the size of the component and its design can be varied to establish quantitatively the component life/particle concentration data required by the component and system designer. Turbines, fans, slurry pumps, valves, tapered constrictions, tees and elbows are some of the components for which these studies should be undertaken. These calculations are essential for design decisions but are equally important in relation to the construction and utilization of erosion/corrosion test facilities.

It should be recognized that the number of parameters involved in the compilation of engineering data on erosion/corrosion effects on a single material is considerable. Typical parameters independent of those defining the response of the target material are the particle size, particle shape, particle material properties, impact velocity, angle of attack, temperature, nature of the corrosive environment, and length of exposure to the corrosive environment. Several of these parameters are more complex than simply stating a single representative quantity, such as, the temperature variation of the particle properties and the characterization of the corrosive environment which may include several different corrosive agents. The complete description of the erosion/corrosion response of a single material would thus involve an elaborate and intractable testing program.

Computer models can be used to extend limited and more costly experimental results to a wider range of conditions. This approach can be successful if at least first generation models are developed early and the test conditions are carefully selected to supply the needed data and to check the extrapolation. The significance of this function gives it a high priority and it should be well-funded; however, the programs undertaken should be coordinated with the other areas described here as well as with existing and future test facilities.

Recommendation II

Computer modeling studies should be initiated in the following areas:

- description of the material's response to particle collisions including the events leading to material removal;
- characterization of the erosive environment related to a particular system component; and
- ESTIMATION FOR PRELIMINARY DESIGN PURPOSES OF MATERIAL REMOVAL RATES AS A FUNCTION OF THE OPERATING AND ENVIRONMENTAL PARAMETERS.

C. MATERIALS DEVELOPMENT

Conclusion

The problems of component erosion/corrosion in power generation systems will continue to increase as system temperatures are raised and as more high-impurity content fuels are burned. Metallic alloys, ceramics, composites and coatings must be tailored to resist the specific environments in particular systems and components. It is our assessment that at the present time there are no materials of proven durability (in terms of component replacement or refurbishment costs) for constructing many of the critical components in large plants already in the planning phase. However, development of even simple alloy modifications can take five years to reach production readiness, a new alloy can take ten years. The time scales for new material concepts are difficult to specify.

Significant improvements in erosion/corrosion resistance and cost reductions can be achieved through better understanding and control of compositional specifications in materials. For example, better definition of a metallic alloy's structure and form is required in relation to the manufacturing process and intended application. Obviously, compositional variations directed toward improved erosion/corrosion resistance must be balanced against modification of the significant thermostructural properties which may be related to these compositional variations.

Recommendation I

Some work should be supported on a near-term basis for optimization of the erosion/corrosion properties of currently available classes of materials.

Recommendation II

Some energy systems contemplated, such as coal gasification plants, will require enormous quantities of materials. Therefore, for reasons of availability and cost, studies should be initiated to determine the feasibility of substituting lower cost, more readily available alloying elements for costly, difficult to obtain strategic elements (e.g., chromium) in erosion/corrosion resistant materials.

Recommendation III

MANY COMPONENTS FOR ADVANCED SYSTEMS WILL BE MADE FROM CERAMICS RATHER THAN METALS. THE TECHNOLOGY FOR DESIGNING, FABRICATING, AND INSPECTING CERAMICS IS MUCH LESS WELL-DEVELOPED THAN FOR METALS. HENCE, A MAJOR EFFORT IS NEEDED IN THIS AREA.

D. TESTING

Conclusion

A broad range of erosion and erosion/corrosion testing will be required. Experience in solid particle erosion testing shows that a minimal amount of useful design data has been generated over the last twenty years. Due to the complex nature of the erosion/corrosion interactions and the long-term nature of the research required for modeling and understanding the complete phenomena, it is not surprising that an accepted screening test has not been developed for comparison and selection of materials. Past experience in development of rain erosion resistant materials for aircraft radomes has been based upon empirical tests utilizing rotating arm facilities which have become accepted as a standard method for ranking materials. One of the key features of this technique is that it provides excellent simulation of the environment with multiple impingement of calibrated rain drops at carefully controlled velocities.

This same philosophy could be adopted for development of an accepted test methodology for screening materials for solid particle erosion/corrosion-elevated temperature conditions, since reliance upon very simple laboratory techniques or single impact tests (useful for mechanisms studies) have been unsuccessful in the past for translating results to the complex operating environments.

No matter what form of testing is employed it is essential that the erosive enviroment is accurately characterized. The particle size distribution, impact velocity, angle of attack, and other test parameters can be determined experimentally supplemented by computer analyses of particulate-laden flows. If the data is to be used for design purposes it is important that the actual test conditions correspond to the conditions the investigator specifies in reporting the test data. Consideration must be given to the statistical nature of the process; reasonably accurate characterization of the size, shape, and material properties of the particulate; monitoring of gas compositions; and the flow conditions in the vicinity of the target. Proper characterization of the test environment has generally been overlooked in solid particle erosion testing.

Well-planned tests should be conducted to confirm the predictions from laboratory erosion/corrosion data in conjunction with computer modeling studies. Instrumentation should be designed to provide nearly continuous measurements of the characteristics of the fluid and particle enviroment and it appears possible to simultaneously monitor erosion/corrosion rates. Limited testing under very well-instrumented conditions would certainly provide confidence as well as point up deficiencies in the various approaches developed under the general program strategy.

Recommendation I

Procedures for laboratory, screening, and pilot plant testing should be established now. The other recommendations in this report will be difficult and inefficient to implement unless this is done.

Recommendation II

A MAJOR INITIATIVE MUST BE UNDERTAKEN IN THE AREA OF ACCELERATED LIFE TESTING. THE EFFORT MUST FOCUS ON HOW TO MEANINGFULLY ACCELERATE THE COUPLED EROSION/CORROSION EFFECTS, OR IF THEY ARE NOT SEPARABLE, THE MOST DOMINANT FEATURE OF THE PROCESS (SCALE REMOVAL, SCALE FORMATION, PARTICULATE IMPINGEMENT, ETC.)

All testing cannot be in the accelerated mode; accelerated tests will have to be carefully verified so as to assure that the corrosion/erosion phenomena involved by the accelerated techniques are not modified to the point that they no longer pertain to the actual conditions of interest.

Recommendation III

The American Society for Testing and Materials G2 Committee on Erosion and Wear is actively engaged in formalizing the reporting procedures for solid particle erosion testing and in establishing an erosion testing methodology. This group could also play an active role as the focal point for much of the required erosion/corrosion testing methodology described here.

E. DESIGN PROCEDURES

Conclusion

The compilation of a design data manual covering principles and practices related to erosion and corrosion in energy conversion plants should be carried out on a continuing basis. This manual, or series of manuals, would serve to collect, analyze, and condense the information obtained from diverse sources into a form useful to designers.

A collection of engineering data useful for the design of components should be assembled. Test data should be taken so that it can be used with computer modeling studies which predict the particle impact angles and velocities, number and distribution of particle sizes passing through a component. Data must be available for materials in the state in which they will be when subjected to the operating environment of the system. The behavior of engineering materials in the actual environments in operating equipment must be defined and the analysis of material degradation for commercial materials should be further developed. An effort should be made to avoid extensive studies of erosion situations that are too oversimplified.

Recommendation

Careful consideration should be given to the preparation of design manuals for erosion/corrosion effects and the type of information required should be reflected in the overall program strategy.

F. FAILURE ANALYSIS DATA CENTER

Conclusion

The failures due to erosion/corrosion effects occurring under operational conditions are the final assessment of how well the information generated in all of the suggested phases of the program strategy outlined here is assimilated into the actual design. It is anticipated that failures will not be completely eliminated. However, the careful analysis of the failures occurring in pilot plants can be used effectively to avoid occurrences of the same failure in scaled-up versions of the system. It is necessary that an accurate appraisal is made of the cause of the failure and that this information is brought to the attention of both the materials and engineering community so that the emphasis in the on-going programs can be directed toward actual problems and not simply anticipated problems of academic interest.

A system should be established for having on-site experts who can evaluate the seriousness of the situation, make judgments as to the appropriate corrective measures, determine whether the failure is an isolated event or involves a fundamental issue, and can obtain the data necessary for further analysis of the failure. The on-site inspection capability supplemented by reasonable monitoring of operating conditions in critical areas of the system using diagnostic instrumentation would greatly enhance the value of the failure analysis tabulations.

The rapid communication of both operating experiences which resulted in erosion/corrosion failures to the erosion/corrosion community and the translation of new developments in materials to design criteria would certainly be desirable. To accomplish this it is necessary to bring together the best talent to meet the challenges in this complex area. At timely intervals, workshops should be organized to exchange and clarify information or to develop an approach for particular problems on a broader basis than has been done in the past. Of course, meetings on topics of a more specific nature would continue.

Recommendation

Collection, classification, dissemination of failure analyses for failed components in operating systems (pilot plants, prototype demonstration units, and on-line units) should be supported.

G. EROSION/CORROSION ADVISORY PANEL

Conclusion

Several positive steps have been made with regard to establishment of cooperative effort between plant designers and operators, research engineers, and material scientists. The recently constituted Committee T12A of the National Association of Corrosion Engineers is providing a forum for interchanges on the problems in coal gasification systems. Several workshops sponsored by ERDA and other organizations have focused on the materials aspects of erosion/corrosion in coal gasification and the establishment of a design/materials interface. The G2 Committee of the American Society for Testing and Materials is reviewing erosion testing procedures. In addition, sessions on erosion are becoming popular at professional society meetings. These functions should be supported; however, realizing that erosion/corrosion will be a prevalent problem area for some time, it would be advisable to organize an integrated approach on a more formal basis. It is timely to do so before a sizable body of data is generated.

An advisory panel should be formed to span the basic and practical aspects of erosion and corrosion, computer modeling, commercial material production procedures, plant design, and plant operation. Since the panel members would be actively engaged in erosion/corrosion related problems, they would be able to represent the needs and accomplishments within their respective areas. The panel would be the nucleus for the creation of interchanges among a greater number of individuals. They would be concerned with the proper balance in an integrated program of research which would be responsive to engineering requirements. The panel would also encourage the distribution and updating of erosion/corrosion design data. Essentially the panel's function would be to step back periodically from the day-to-day developments and assess near- to long-term situations in a broader context than is generally possible.

Recommendation

A permanent technical advisory panel concerned with erosion/corrosion related activities should be established by ERDA.

The above conclusions have been stated in general terms; supporting details and specific data are in the chapters which follow.

Chapter 3

EROSION CONDITIONS IN ENERGY SYSTEMS

The main features of various energy systems are described with respect to their potential for erosion damage. An assessment of the range of erosion conditions which must be investigated are presented in this chapter based on these descriptions. It was the consensus of the Committee that the erosion problems associated with solar energy conversion and wind machines were within the prevailing state of the art and do not require extensive developmental programs to overcome the problems which may arise. On the other hand, long-term operation of MHD systems presents erosion problems of such a magnitude that considerable emphasis must be placed on materials development and design considerations. Although the most extensive discussions pertain to coal conversion systems, the range of erosion problems, the approaches suggested for their resolution, and the particular environmental conditions are generally applicable to the erosion problems which are of primary concern for other systems as well. An effort is made here to display the commonality of erosive conditions for several energy systems and to point out the relative distribution of conditions which should be investigated within the complete range of variables: temperature, particle velocity, particle type, and corrosive environment.

A. COAL CONVERSION

Considerable practical experience is being gained from the operation of pilot plants with regard to the magnitude and source of the erosion problems which subsequently may be encountered in the operation of demonstration plants. Several types of coal gasification and liquefaction processes are under development. The overall features of these systems are described in References 1-3. For the discussion of coal gasification systems, the prevailing erosive environments are summarized in Table 3-1 in terms of representative gas compositions, the operating temperatures, and pressures in the gasifiers. The operating variables associated with coal liquefaction systems are summarized in Table 3-2. These summaries are intended only to provide some perspective on the nature of the erosive environments which may be encountered. In Chapters 4 to 6, this

TABLE 3-1 Gasification Process Conditions

Gasification Process (Location)	Product Gas Analysis (Design Values)									Gasifier Conditions	
	Percent H_2O	Percent H_2	Percent CH_4	Percent H_2S	Percent CO	Percent CO_2	Percent N_2	Percent C_2H_6	Percent Other	**Temperature °F (°C)**	**Pressure psig (MPa)**
BI-GAS (Homer City, Pa.)	48.0	12.7	8.1	0.7	22.9	7.3	0.3	-	-	1700-2700 (920-1480)	1000 (6.89)
CO_2 ACCEPTOR (Rapid City, S. D.)	17.1	44.6	17.3	0.03	14.1	5.5	0.2	0.37	NH_3 0.8	1500 (810)	150-300 (1.03-2.07)
HYDRANE (Morgantown, W. Va.)	-	22.9	73.2	-	3.9	-	-	-	-	1700 (920)	1000 (6.89)
HYGAS (Chicago, Ill.)	24.4	22.8	14.1	0.9	18.0	18.5	-	0.5	-	1500 (810)	1000 (6.89)
KOPPERS TOTZEK (Commercial)	9.6	33.1	-	0.3	50.4	5.6	1.0	-	-	1700-2700 (920-1480)	15 (0.0103)
LURGI (Commercial)	50.2	20.1	4.7	0.6	9.2	14.7	-	0.5	-	700-1100 (370-590)	450 (3.1)
SYNTHANE (Bruceton, Pa.)	37.1	17.5	15.4	0.3	10.5	18.2	0.5	0.5	-	1500-1800 (810-980)	500-1000 (3.55-6.89)
WINKLER (Commercial)	23.1	32.2	2.4	2500 ppm	25.7	15.8	0.8	400 ppm	COS	1500-1850 (810-1010)	15 (0.0103)

NOTE: Adapted from "Clean Fuels from Coal Symposium II Papers," sponsored by the Institute of Gas Technology, IIT Center, Chicago, Illinois, June 23-27, 1975, p. 904.

TABLE 3-2 Liquefaction Process Characteristics

Process (Location)	Process Type	Coal Type	Temperature °F (°C)	Pressure psig (MPa)	Liquid Product
SOLVENT REFINED (SRC) (Pittsburgh & Midway Coal Mining Co., Merriam, Kansas	Hydrocracking of slurry mixed with hydrogen	High sulfur, high ash	850 (455)	1500 (10.3)	low sulfur, low ash solvent refined coal M. P. = 350°F (175°C)
SYNTHOIL (Pittsburgh Energy Research Center, Pa.)	Hydrodesulfurization Fixed-bed catalytic reactor	High sulfur	840 (450)	3000 (20.6)	Low sulfur, low ash fuel oil
H COAL PROCESS (Hydrocarbon Research, Inc., Trenton, N. J.)	Catalytic hydroliquefaction, ebullient bed reactor	High sulfur	850 (455)	3000 (20.6)	Low sulfur, low ash, heavy and light distillates and boiler fuel oil
CRESAP (Fluor Engineers, Los Angeles, Calif.)	Hydrogen cracking of extracted coal	High sulfur	850 (455)	3700 (25.5)	Fuel oil
DIRECT HYDROGENATION (Rocketdyne, Canoga Park, Calif.)	Direct rapid mixing of heated hydrogen and pulverized coal		1800 (982)	970 (6.7)	Heavy oil

information is coupled with the current understanding of erosion and erosion/corrosion phenomena and provides a foundation for developing a rational basis for coping with the anticipated problem areas.

A system for gathering, evaluating, and disseminating information about operating experiences and component failure experiences in coal conversion pilot plants has been put into operation by ERDA and the National Bureau of Standards (NBS). The objectives of this program are to assist plant operating personnel in preventing plant shutdowns and in extending the useful life and reliability of plant components. The program has been developed to obtain information on the reliability of materials and components in coal conversion pilot plants. It consists of a system to report all significant operating incidents and component failures to NBS so that material and component reliability data can be evaluated and disseminated to coal conversion plant operating personnel and others.

All reports of operating discrepancies and component failures received from the coal conversion plants are reviewed and evaluated at the Failure Prevention Information Center for completeness and accuracy. A detailed technical summary is prepared from the information about each incident and these records are classified according to process, material, failure mode, subsystem category, and information source. This information is analyzed to identify significant problem areas, to determine corrective actions to solve component problems, and to conduct failure mode analyses for coal conversion plants. Centralized coordination of the failure prevention activities ensures that adequate and accurate diagnostic failure analysis is conducted and will enable the identification of significant and recurring problem areas common to many coal conversion pilot plants. This provides a means for sharing and exchanging information between pilot plants about component failure problems and successful corrective measures to prevent future problems. Table 3-3 and 3-4 indicate the failure information available at the Center as of March 24, 1977. The high number (16 percent of the total) of erosion-related failures establishes the fact that erosion is becoming a serious design consideration. Erosion and corrosion are responsible for 49 percent of all failures, according to the information available at the Center. The erosion failures are further elaborated upon in Table 3-4 and show that piping, pumps and valves account for the bulk of the erosion failures.

TABLE 3-3 Failure Mode Analysis

Failure Mode	No. of Items	
Corrosion	129	
Carburization		12
Metal Dusting		5
Oxidation		8
Pitting		12
Sulfidation		30
Creep	4	
Design	42	
Equipment Malfunction	36	
Overheating		30
Overstressing		2
Erosion	64	
Fabrication	14	
Welding		10
Fatigue	10	
Quality Control	18	
SCC	6	
SCC-CL	31	
Thermal Cycling	3	
Thermal Shock	2	
Thermal Stress	5	
Unknown	31	
	395	TOTAL

NOTE: Data from NBS/ERDA Failure Prevention Information Center
March 24. 1977

TABLE 3-4 Failures by Components

Component	Erosion No. of Items*	Corrosion No. of Items	All No. of Items
Auxiliary Process Equipment	6	7	43
Instrumentation	0	1	7
Material Evaluation	9	32	42
Piping	24	67	163
Bellows	3	9	32
Thermowells	4	12	15
Pressure Vessel	3	8	23
Gasifier	1	2	5
Regenerator	1	2	5
Boiler	0	3	4
Pumps	19	5	27
Rotating Equipment	0	0	6
Thermocouple	2	18	22
Unknown	0	0	0
Valves	21	10	38
TOTAL	84	148	371

* Total items do not compare with Table 3-3 as a result of multiple item reports.

NOTE: Data from NBS/ERDA Failure Prevention Information Center March 24, 1977

1. Coal Gasification Systems

Erosion of coal gasification units has been mentioned in a number of publications(3-5), but relatively little has been said about the details of the erosion conditions which are apt to arise. An attempt is made here to consider in more specific terms the nature of the erosion conditions, to classify the range of environments in a manner which removes the dependence of our assessments on a particular system, and to discuss the erosion problems associated with defined operating regimes.

A schematic diagram of a typical coal gasification process is shown in Figure 3-1. Details on the types of components and equipment involved at various steps in the process are listed in Figure 3-2. The methods used and problems experienced in coal preparation and handling are somewhat similar to those experienced by current solids-handling processes. However, the scale of operation intended in gasification production is larger. Other process areas such as the gasifier, the ash handling area and the quench areas are fairly unique. The anticipated problems are discussed in detail in the following sections.

a. Gasifier Vessels.(6) Gasifiers fall into four general categories: (1) fixed bed, (2) fluidized bed, (3) entrained process, and (4) molten bath systems.

The fixed-bed design is an old and reliable method whereby coal is supported on a grate and maintained at a fixed depth. Air or oxygen-steam mixtures flow through the grate from the bottom. The fuel bed is characterized by zones, including an ash zone at the grate surface, an oxidizing zone, a reducing zone, and a preheat zone. The Lurgi gasifier is one of the best known fixed-bed gasifiers.

In the fluidized bed, pulverized coal is levitated on a rising column of gas; the combustion process takes place with high particle mobility, high heat transfer, and high gasification rates. A high steady-state ash content is required to attain complete carbon conversion. The HYGAS process uses a fluidized bed gasifier.

In the entrained process, pulverized coal is carried into the reaction chamber by the reacting gas. The particles are separate and discrete as they react in the gasifier. About 50 percent of the ash leaves as slag, quenched and granulated, and the rest leaves as fly ash with the product gas stream. The Koppers-Totzek process uses the entrained coal system.

In the molten bath system, molten iron and slag or molten salt are contained in a gasifier and coal/limestone is injected into the bath while air or oxygen is injected with a separate lance. The resulting reaction produces a

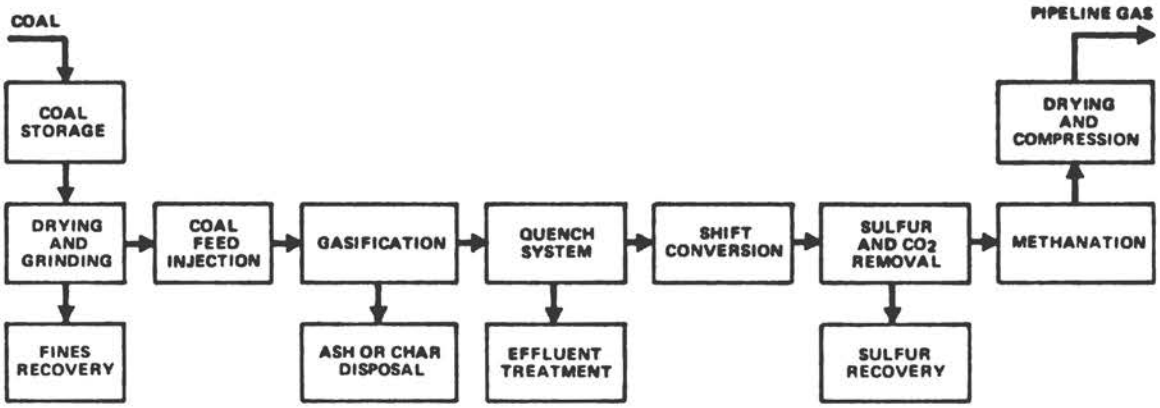


FIGURE 3-1 Coal Gasification Operations

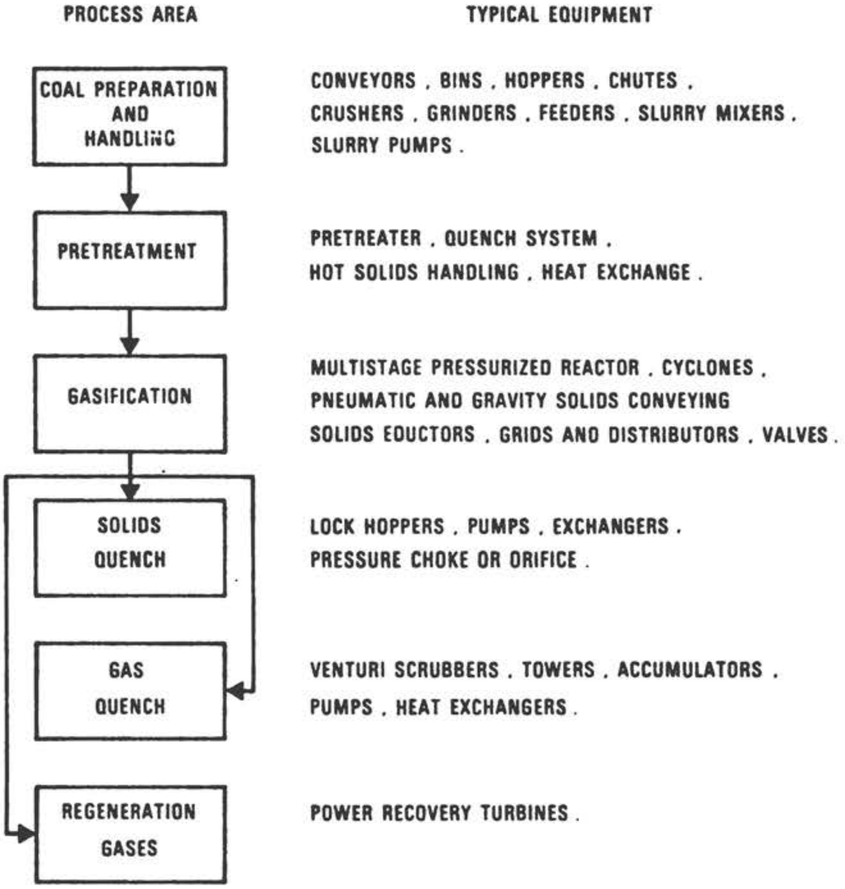


FIGURE 3-2 Equipment Used in Coal Gasification

sulfur and ash free, low BTU gas. The Atomics International molten salt process is an example of a molten bed gasifier.

The internals of most gasifiers are limited to a refractory lining and various inlet and outlet parts. The fixed-bed gasifiers also contain a grate (with moving parts) and a rotating coal distributor. Mechanical wear is the most prevalent failure mode for these parts of the fixed bed gasifier. Considerable experience has been gained on the severity of the wear of mechanical parts in the Lurgi gasifier. The design of new plants takes this experience into consideration.

In advanced gasification concepts (as listed in Table 3-1) operational experience is limited to pilot plant operation with operation periods of not more than 200 hours. This is insufficient experience to uncover erosion problems which may be serious enough in full-scale commercial operation to cause shutdown of the system. At the present time, potential erosion problems in the gasifiers for advanced gasification systems are essentially a matter of conjecture. For those systems in which pulverized coal is injected into the gasifier (BI-GAS, Koppers-Totzek), there is a distinct possibility that nozzle or restrictor erosion will be a serious problem and that impingement on a refractory lining can result in localized erosion-penetration of the lining requiring shutdown and lining repair or replacement.

In the agglomerated-ash concept, transfer lines between the combuster and the gasifier must handle 20 kg (44 lbs.) of hot ash per kilogram of coal gasified. High temperature erosion problems can be expected in these transfer lines.

Injection systems for introducing a gas-coal mixture into molten salt or iron bath are possible sources for erosion problems. The high temperature, corrosive environment presents potential erosion/corrosion problems which have not yet been encountered.

b. Lockhoppers. Important steps in the coal conversion process include the introduction of reactants and the discharge of materials after reaction in the gasifier. The most widely-used system to accomplish these functions is the lockhopper. (Figure 3-3 depicts a simple lockhopper system.) Solids such as coal, char, or other materials are transported to the top of the system and fed through the first valve into the loading hopper. The valve is closed and the loading hopper is then pressurized. The second valve is opened and the solids fall into the reactor. The second valve is then closed and the loadhopper depressurized. The process is repeated as necessary. The

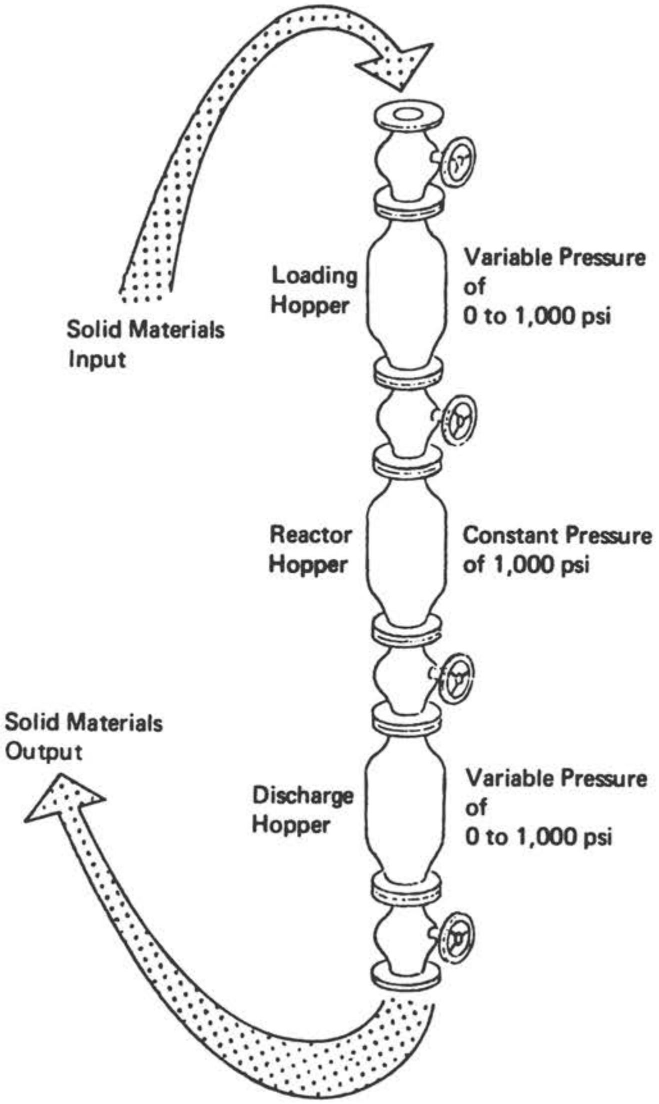


FIGURE 3-3 Simple Lockhopper System

discharging of spent materials follows a similar schedule in reverse order.

The major problem with lockhopper valves is failure to seal. These failures can be traced to various mechanisms. The most damaging mechanism is erosion. In some cases, critical sealing components become eroded due to impingement of solids passing through these components when the valve is open. Further, erosion can result from leakage across the sealing elements when the valve has been closed and a pressure differential created. Another failure mechanism is component wear and abrasion. This involves direct contact between the valve components. Abrasion is the result of migration and deposition of process particulate matter on the critical bearing and sealing surfaces of the valve. Unfortunately, there is a lack of well-documented information pertinent to the failure of lockhopper valves.

c. Pumps. The transfer of liquid-solid slurries or gas-particle mixtures through various sectors of gasification systems at different pressures is dependent on the operation of pumps and compressors. A slurry could, in one example, consist of 50 percent coal particle solids in light oil at temperatures up to 150°F (66°C). Delivery pressure could be 1,000 psi (7 MPa) (HYGAS process). Both centrifugal and reciprocating pump designs are being used. Typically the pump portions wetted by the slurry mixture are coated with a hard metal overlay to increase their erosion resistance. Failures in adequacy of the overlay and in overlay adherence to the cast or wrought component have been reported. The base metal erosion resistance is usually very low and failure follows quickly after loss of the overlay protection. Pilot plant operation in one case required improved weld overlay materials and pump velocity derating after serious erosion problems had been experienced(7).

Information on pump service life in these applications is becoming available. Experience with char slurry pumps (SYNTHANE process) having Ni-Hard casings and 28 percent chromium-iron impellers indicates in-service lives of from 600 to 1,200 hours. In another example(8) a slurry pump developed an erosion failure after 13 days operation due to a perforation in the steel casing caused by an eddy in the slurry flow at that location. The pump operating temperature was 750°F (400°C) and the flow 60 gpm (203 lpm). About 1/4 inch (6.4 mm) of steel was eroded away in service. Geometric irregularities in the pump caused erosion in several other locations. The pump was repaired using a hard metal facing approach. Concern over the design of the original pump was also expressed. Problems reported involve pumps used at relatively low solids concentrations.

Cast steel circulation centrifugal pumps in the SYNTHANE gas quench system have experienced erosion/corrosion problems resulting from acidic environments and coal/ash particulates. Overlaying critical regions with more corrosion resistant stainless steel was effective in extending the part life in this instance.

Other pump designs are used in various pilot systems. A nine-stage auger pump (steel rotor, viton stator) failed in slurry operation in a solid-liquid separation unit in one system(9). Erosion of the rotor caused clearance enlargement and loss of discharge pressure. In another screw-type pump application involving diatomacious slurry feeding at 700°F (370°C), excessive erosion and wear were experienced on the shafts, the pump bodies, and the shaft seals(10). Pump shaft seal problems have been identified in other applications. At the Fort Lewis, Washington plant, which utilizes the solvent-refined coal process, some 30 pumps having rotating carbon washer seals and Teflon parts experienced failures. It was necessary to change materials (tungsten carbide washers, asbestos-containing parts) and to lower particulate concentrations (using 5 micrometer filters and cyclone separators) in order to achieve satisfactory performance.

d. Valves. Shut-off and pressure letdown operations at valves of various designs (ball, butterfly, etc.) are required at many stages in coal conversion systems. Erosion in valves leads in most cases to gradual deterioration, principally loss of seal within the system. Hence, failures are not usually spectacular but satisfactory erosion resistance of valves in such applications is clearly desired. Improved design, as well as the use of more erosion-resistant materials, is indicated. Operations such as pressure reduction are clearly more suitable for an orifice or choke approach design rather than the use of conventional valve components.

Reciprocating pump problems may on occasion involve check valves in the pump (HYGAS experience). Metal-elastomer designs may not withstand the erosion and temperature conditions that are present. Hard-facing alloys may need to be incorporated into the valve seal designs. Gate valve failures have been reported to result from erosion. In one instance, dolomite particulates moving at 55 to 100 fps (16-33 ms^{-1}) at 1450°F (788°C) caused severe erosion in a gate valve liner, probably as a result of misalignment. Ball valve designs used in lockhoppers at ERDA's Morgantown facility have suffered from erosion problems. Leaks developed that prevented adequate sealing at the valves (probably due to erosion and contamination build-up on the valve surface). Valve seat replacement materials that led to more acceptable experience included hard, proprietary alloys as well as 25 percent Cr-white iron materials.

Pressure letdown at valves may cause severe erosion problems. Originally the hot, product gas line at Morgantown contained butterfly valves faced with wear resistance metals. However, service at 1300°F (700°C) in some cases reached only 30 hours. A design change that substituted tungsten carbide fixed orifices for the letdown feature of the valve produced much more acceptable service. It appears that design as well as proper material selection is crucial in such applications.

e. Cyclones. Particle removal from the off-gas is a necessary feature of all gasifiers, hence, the erosion effects on cyclone separators are of concern. Proper design, including lining with replaceable, hard metal liners, can significantly extend component life. Outlet nozzles are often designed to be replaceable and wear-plate inserts are recommended where possible. Piping and joints near cyclones also benefit from proper design for extended erosion-resistant life. Misalignment of only a few degrees at joints can drastically increase erosion rates. The use of internal weld-rings or other protrusions can cause turbulent flow and high, local erosion. Pipe liners or inserts that disturb the smooth gas flow conditions can also lead to serious erosion problems.

f. Piping Alignment and Joining. The external piping connecting the various stages in the gasification section of each plant is subject to the same considerations as the gasifier reactors. In addition, there are special considerations relating to erosion and expansion. In general, an outer steel pipe will be used as the pressure container. This will be internally insulated to optimize the design temperature. The steel selected must have strength and ductility and resistance to hydrogen attack. If condensation is expected at the wall, it will require corrosion protection. Early hydrogen piping systems employed water jackets, but unjacketed lines have been used successfully. In general, piping designs used in ammonia plants or in hydrogen units are the minimum requirement for gasification service.

2. Coal Liquefaction Systems.

a. General features. A number of liquefaction systems are under development at present. They are not as diverse as the various gasification systems and generally use the principle of hydrogen cracking at high pressure.

The operational conditions for several systems are summarized in Table 3-2. Process streams of liquefaction systems and operations which do not contain solid coal particles are similar to petroleum process streams. Operating temperatures, however, are generally much lower than in gasification systems and fluid flow within the reactors is not in a velocity range where erosion would be of concern. Much of the coal handling, crushing and transport to liquefaction systems are analogous to those for the coal gasification systems already discussed in this chapter. Introduction of the coal into most liquefaction systems, except for direct hydrogenation processes, involves a slurry mixture of crushed coal and solvent or liquid product.

Depending upon the particular plant and portion of the system, pressures can range upward from 1500 psi (10.5 MPa) (see Table 3-2). Temperatures also vary with process from about 850°F (455°C) to 1800°F (960°C) (see Table 3-2). Solvents and liquid products often laden with coal or wastes complicate the operation of these systems.

b. Problem Areas in Liquefaction Systems

Agitation Equipment. Agitation equipment to maintain the fluid hydrocarbon-coal slurries at high temperatures and relatively high velocities have proven to be particularly troublesome from a mechanical point. Shafts and vanes become worn and eroded from abrasion by the suspended particles, resulting in excessive vibration.

Pumps. Packings in slurry pumps have been a center of difficulty because of the abrasive nature of the coal slurry in the hydrocabon solvents operating frequently above 600°F (316°C).

Another problem area has been pump housings. Cast irons cannot be used in conjuction with the flammable solvents (API Standards 610); therefore, abrasive-resistant materials for housings have to be found or developed.

Valves. Valves in liquefaction plants are particularly troublesome because of solvents, tars, particle concentrations, high temperatures and high differential pressures which result in high velocities. Tars collect on valve facings causing degradation and corrosion which permit accelerated erosive attack.

Aside from serious valve erosion problems, the most severe problems encountered in coal liquefaction involve corrosion. Large quantities of acidic solutions are produced in the liquefaction process. Pumps, fillers, condensers and piping handling these sour waters are major problems. Austenitic stainless steel components have been reported failing in one to two weeks.

B. POWER GENERATION

There are a number of power generation systems which can be expected to exhibit significant erosion/corrosion problems. Some of these systems will burn coal directly (conventional steam, pressurized fluidized bed (PFB), magnetohydrodynamic generators (MHD), the helical expander, etc.). Others will burn high impurity content, less costly grades of petroleum fuels (residual oil) or coal-derived liquids.

1. Steam Systems

There are two potential erosion/corrosion problem areas in steam power systems: heat exchanger tubes, and the steam turbine itself.

a. Heat Exchanger Tubes. Steam heat exchanger surfaces can be of three kinds: boiling tubes, which form the boiler walls; superheater tubes, which are usually in the combustion chamber; and reheater tubes, which are located above the combustion chamber. It is convenient to consider the attack of surfaces exposed to the fireside and the water/steam side of these heat exchanger tubes separately.

(1) Fireside. The environments developed on the fireside of heat exchanger tubes depend upon the combustion process. In conventional steam boilers, there will be a combustor where pulverized coal (or oil) is burned directly. In PFB systems, pulverized coal mixed with crushed limestone or dolomite for sulfur control is burned in a continuously moving or fluidized bed. In direct fired boilers, high-temperature combustion releases fuel-bound impurities such as sulfur compounds, halogen salts, and other non-combustibles. These oxidize, combine, and condense on the boiler tubes, often as liquid slags which cause hot corrosion.

The gas velocity to maintain fluidization in the PFB is in the range of 2 to 10 fps (0.6 to 3 ms^{-1}). The particle velocities in the bed are probably within this same range. Gas velocities may be higher between the heat exchanger tubes and local particle velocities may be higher in regions of bubble collapse. Model studies suggest that local particle velocities do not exceed the fluidizing velocity by more than a factor of two. The nature of the ash in the combustor depends upon the bed temperature. At temperatures of 1470°F (800°C) to 1650°F (900°C) the ash is fine and soft and the principal erosive species is the acceptor or possibly mineral fragments from the coal. At higher temperatures, up to 2010°F (1100°C) as may be experienced in carbon burn-up cells, there may be fusion of the ash to produce a harder erosive ash species. At the present time it does not appear as though erosion of heat exchanger tubes in the bed is a problem.

The gas composition in the bed is always oxygen-rich, although the oxygen potential can vary with position and with time. The deposition of ash or char could lead to corrosion of the tubes. Particulate erosion could become more significant by removing the corrosion products.

Fine particles will be carried into the freeboard above the bed by the ascending gas. Gas velocities in the freeboard will be higher than in the bed and will be in the range of from 30 to 100 fps (9 to 31 ms^{-1}). The ash particles should be soft and friable so that if erosion takes place, it would be due to the elutriated limestone or dolomite and rock particle inclusions in the coal. The gas composition in the freeboard would be slightly less oxidizing than in the bed since some combustion occurs in the freeboard. As a result of this combustion, the temperature of the freeboard is usually greater than that of the bed. As in the case of tubing in the bed, corrosion may be a problem in the freeboard and this could be aggravated by erosion.

In both the bed and the freeboard, deposition of ash principally as sulfates of sodium and potassium may occur. Such deposits will cause hot corrosion attack of the tubing.

(2) Water-Steam Side. Corrosion of feed-water pipework, pumps, and heater tubes, sometimes serious in its local effects, can result in the transfer of material to the boiler water which could initiate corrosion of the internal boiler surfaces. Accelerated oxidation of the metal at steam-generating tube surfaces, usually in positions of high heat-transfer rate, can cause failures. This is a very serious problem in that the corrosion might be initiated by several factors and its incidence is unpredictable at present; "rusting," caused by access of oxygen dissolved in the water during idle periods, is one of the probable contributory causes. Other serious "on-load" water-side corrosion phenomena are stress corrosion of expanded tube-ends, and "caustic cracking" of steel in fissures where alkaline boiler salts can concentrate.

Significant corrosion of metal in contact with superheated steam occurs only when entrainment of boiler water, with its dissolved salts, has taken place. It is probable that at supercritical pressures some salts are appreciably volatile, but no corrosion from this cause has been experienced. Corrosion-fatigue cracking of superheated steam piping and manifolds has been initiated by the impingement of water, condensed on "cold," unlagged surfaces, in a stagnant steam space above the site of corrosion.

b. Steam Turbines. Concern for liquid impingement erosion arises in connection with steam turbines. The last turbine stages operate in the moist vapor region; some of the small condensation droplets are deposited onto the stationary blades where they can coalesce and then be spun off in the form of larger droplets. These accelerate only slowly and, therefore, do not follow the streamlines of the main steam flow through the rotating blades. Instead, these slow-moving droplets are hit by the rotating blades at a relative speed which can be almost equal to the peripheral speed of the rotating blades themselves(11,12). Direct observation of these events has been accomplished(13). Steam turbine blade erosion first became a concern in the 1920s, and some of the early research into liquid impingement damage are still enlightening(14,15). As a result of increasing turbine rotor diameters and, correspondingly, blade tip velocities, the erosion problem has generally increased over the years. In spite of improvements in turbine blade materials, most manufacturers find it necessary to use protective measures such as Stellite® Alloy 6B strips or flame-hardened regions in those blades most susceptible to erosion.

With the high [up to 2000 fps (610 ms^{-1})] blade tip velocities in new designs and the increased moisture levels generated in current nuclear power plants (where the steam entering the turbine is not superheated), control of erosion damage is no longer possible through improved materials alone. Moisture removal techniques and control of the moisture dynamics within the turbine must be included so that damaging impacts with large slowly moving droplets will not occur. A better understanding of the turbine erosion problem resulted from comprehensive studies sponsored by NASA(16-19).

While low-pressure blade erosion by moisture has been a fact of life in turbine experience for many decades, the problem of high and intermediate pressure stage erosion by solid particles first emerged in the early 1960s, when service inspections were made on relatively new high-pressure, high-temperature fossil-fuel machines.

Specifically, the problem occurs in the control stage and/or in the first intermediate pressure stages following reheat. It takes the form of thinning or scalloping of nozzle trailing edges, of wear on the nose and grooving of the pressure surface of rotating blades, of cutting away of the shroud and tenon rivets and sometimes of other areas. It has required replacement or repair of many blade rows and is considered a major service problem by many utilities.

Investigations both in this country and in the USSR have concluded that the damage is produced by hard oxide particles carried over from the boiler where they originate from scale formation in the superheater and/or reheater tubes. These studies are described in a number of references(20-27).

The general conclusion is that scale is formed in superheater and/or reheater tubes of pearlitic (i.e., low alloy) steels, subjected to excessively high temperature, [over 1090°F (585°C)]. The problem is worsened by increased flow velocities during part-load operation. Some of the suggested remedies are:

- using austenitic or other scale-resistant materials for superheater and reheater tubes;
- rigorously limiting internal wall temperatures of tubes to acceptable levels for controlling scale formation;
- chemically cleaning the tubes periodically to remove scale;
- using variable-pressure (full-admission) mode of turbine start-up to limit steam flow velocities (and hence particle impact velocities) in the control stage; and
- using more erosion-resistant blade materials.

Some studies directly related to this problem include the ASME-sponsored high-temperature scaling tests on superheater tube materials reported by Eberle and Anderson(24), a mathematical analysis of the motion of particles within blade passages by Shkolnik and Ushakov(25), a relatively optimistic report on the practicability of chemical cleaning of tubes and pipes by Lux(26) and changing the start-up procedures by Reinhard(27).

The solid particle erosion problem in steam turbines must be viewed and solved on a systems basis, with the emphasis on eliminating the cause -- the scale particles.

2. Gas Turbines

Gas turbines are used for generating electric power and for propulsion systems. In the area of power generation, the turbine can either serve as the topping portion of a combined cycle system, as a direct drive for a convertor, or as a power recovery component of a pressurized fluidized bed or other system. Such gas turbines are expected to be life limited primarily by the combined effects of corrosion and erosion produced by fuel/air contaminants and impurities. These effects result from high velocity particles impinging on the airfoils of the turbine as well as combustion product corrosion. The exact mechanisms of corrosion/erosion interactions are poorly understood but the effects are known to be serious. Many industrial turbines are designed for lives in excess of 20,000 hours but corrosion/erosion damage can reduce these lives to times as short as 1000 hours.

There are two major sources of the erosive particles: the air and the fuel. Dust particles entering with the combustion air can result in direct erosion of turbine components. Incomplete combustion of the fuels can form hard carbon deposits in the combustor which break off sporadically to produce turbine airfoil erosion. Similarly, oxidation of fuel/air impurities can result in hard oxide particle formation in the combustor. Also, decreasing gas temperatures and pressures, as energy is extracted by each turbine stage, can result in condensation of specific salts at predictable locations in the turbine. Significant condensation can lead to rapid losses in turbine efficiency due to gas path blockage and aerodynamically adverse buildups on critical airfoil surfaces. The breaking loose of such massive deposits can be a further source of turbine erosion. And finally, the accompanying hot corrosion attack of turbine airfoils surfaces in such "dirty" combustion gases can enhance erosive loss. Corrosion can even cause varying-sized metallic fragments to be totally undercut and lost to the gas stream so they can also contribute to particle impact damage.

Erosion alters optimal airfoil contours and so lowers engine aerodynamic efficiency. Erosion can locally reduce the load bearing cross section of an airfoil so that gas bending and rotational stresses can exceed design limits and produce early fatigue or creep rupture failures.

There is wide industrial experience with erosion/ corrosion damage. In the petrochemical industry, turbines serve to recover energy from the process gases as well as to generate compressed air. Similar applications have been found in blast furnace operations. And, on oil and gas pipelines, especially in desert regions, gas turbines providing power for remote pumping stations can suffer corrosive and erosive degradation.

Simple cycle gas turbines are presently used to provide peaking power for electric utilities. Combined cycle systems (gas turbines topping steam boilers) offer attractive conversion efficiencies (approaching 40 percent or more from coal pile to bus bar) for intermediate and base-load utility service. Such turbines currently operate on a variety of relatively "clean" distillate fuels and thus seldom experience serious erosion. If these turbines could be modified to resist erosion and corrosion caused by burning residual oils and from coal-derived liquids which have much higher ash and impurity levels, this country's energy options would be greatly expanded.

In PFB systems, the coal is combusted at relatively low temperatures [1600-1800°F (870-980°C)] which are below normal ash fusion temperaures. Thus, the amount of hard ash particles going through the turbine, even without hot gas clean-up, can be expected to be small. However, char and bed particulate matter carry-over are potential sources for turbine erosion. This type of attack may also be expected in turbines operating in combination with coal gasification systems.

Thus, consideration of the erosion problem in turbines must deal with the combustion air and fuel impurities; the turbine operating temperatures, pressures and velocities; the turbine airfoil alloys; the size and criticality of airfoil radii and contours; and the required turbine cost effective life, as well as the implications of an erosion producted outage.

a. Erosion: The Source and The Problem. The first source of potential erosion-producing particles comes from the atmosphere -- the turbine intake air which can carry a variety of dust particles. Representative concentration of dusts in the air and dust particle size ranges by source are presented in Ref. 28. Here Nordberg shows residential environments to contain particle concentrations of 0.001-0.003 mg/ft^3; industrial environments of 0.003-0.055 mg/ft^3; agricultural environments from 0.05-0.5 mg/ft^3; and very dusty military and road construction environments to range from about 0.5-10 mg/ft^3. The ranges of mean particle diameters of such dust were also presented. Atmospheric dusts were shown having 1.0-20 μm mean particle diameters; fine sand from 20-200 μm; pulverized coal from 30 to 500 μm; and coarse sand from 200-1000 μm (25.4 μm/0.001 in.). Such airborne dusts are amenable to removal by low-temperature inertial cyclone type separators [80-90 percent efficient for fine (50 percent < 8 μm) and coarse dusts (50 percent < 20 μm)]. Cyclones can be combined with secondary impingement filters to reach 99 percent removal efficiency. According to Nordberg(28), air filtration can extend turbine life by a factor of several hundred over an unprotected engine. Thus, filtration is especially effective in construction and military turbine powered vehicles, as well as in power units operating in industrial and other high-dust environments. Without filtration, erosion limits engine life to as low as a few hundred hours.

The potential magnitude of the fuel-impurity-produced erosion problem caused by fuel ash has been graphically demonstrated in past attempts to operate gas turbines directly on pulverized coal. The results shown in Table 3-5 provide representative erosion rates. Nearly 20 years of Australian effort in this area have been reported(29). The turbine inlet temperature goal for their system was approximately 1300°F (700°C). Much rig and engine test data were generated which can provide valuable insight into the more general problems of gas turbine erosion. The formation of hard deposits (rich in iron, calcium, magnesium, aluminum, silica, alkali metals and sulfur) in rig tests was primarily related to the temperature of the substrate with about 5 percent of the ash fed into the flame forming hard deposits and 0.8 percent soft deposits at 1300°F (700°C) vs. about 2 percent soft at 750°F (400°C). In another rig test, Table 3-5, coal ash erosion was measured for a number of potential airfoil materials. In addition, velocity effects on erosion were evaluated by injecting silica into a modified Rover turbine, as shown in Table 3-6. There was a marked increase in erosion with increasing velocities, and these data indicate a less rapid increase in erosion for larger particle sizes at all velocities.

The Bureau of Mines(30) and the Australian studies showed that significant levels of ash buildup could occur in a turbine. In the Bureau of Mines studies, the composition (and thus the expected hardness) of the deposits varied with location in the turbine as shown in Table 3-7. Thus, along with fuel composition, combustion gas temperature/pressure/velocity and time at temperature influence deposit formation and deposition in gas turbines.

Similar results can be implied from the Australian studies since the deposit rates on the first and second stage stators were 0.161 and 0.064 g/hr, respectively, without an ash separator but the rates reversed to material removal 0.071 and 0.146 g/hr, respectively, with an ash

TABLE 3-5 Rig Erosion of Some Airfoil Alloys

T Gas Stream = 670°C
T Specimen = 540°C

Callide Coal Ash
6μm Mean Particle Diameter

Alloy	Maximum Material Loss mg/gm Ash Fed	Incidence Angle at Maximum Erosion	Alloy Hardness at 540°C V. P. N.$_{30\ gr}$
18-8 Stainless Steel	0.18	35°	95
CM	0.12	35°	105
C242	0.09	40°	148
HS-31 (X-40)	0.07	45°	174

When alloy hardness increased by a factor of about 1.8 times, erosion losses decreased by about 2.5 times.

Note: Data from Ref. 29.

TABLE 3-6 Erosion by Silica of Rover 1S/60 Turbine (mg alloy per kg silica injected)

	Erosion Rate at Indicated Particle Size (μm)				
Velocity (fps)	6	8	10	12	14
600	0	225	390	430	460
900	0	400	650	770	820
1200	0	650	900	1040	1130

Combustion conditions, gas temperature and blade alloy not specified.

Note: Data extrapolated from Ref. 29.

TABLE 3-7 Analysis of Ash at Various Turbine Locations

			Percent in Turbine				
Constituent	Percent in Coal	Percent from Separator[1]	Inlet Gas[1]	On Blades[2]	First-Stage Stators	Loose Ash[3]	Exhaust Gas[1]
SiO_2	39.2	30.1	44.8	27.3	28.3	41.0	40.3
Al_2O_3	23.1	19.5	31.6	21.9	23.1	27.1	29.5
Fe_2O_3	17.8	34.0	5.2	6.2	5.9	7.5	7.7
TiO_2	1.7	0.7	1.3	1.6	1.9	2.1	1.3
P_2O_5	0.8	0.7	0.8	3.7	3.6	1.0	1.4
CaO	5.9	7.9	6.2	5.6	6.7	5.5	6.3
MgO	1.8	1.4	1.9	1.9	1.8	0.9	1.3
Na_2O	1.6	2.3	2.0	3.3	2.6	2.3	2.2
K_2O	1.2	0.8	1.7	4.6	4.3	1.6	1.8
SO_3	6.9	2.4	4.5	19.8	19.6	6.8	8.2

[1] Contained 12 to 25 percent unburned carbon, depending on condition of combustors. Does not include concentration of constituents other than those shown. Concentration of the solid particles in the gases entering the turbine averaged 10 to 12 grains per 100 scf of gas (60°F, 30 in. Hg).

[2] Average analysis of deposits on first- and fifth-stage stator and rotor blades.

[3] Loose ash in turbine, not hard deposits on blades.

NOTE: Data from Ref. 30.

separator. Also, with no ash separation, Nimonic 80A airfoil erosion was greater on the second stage downstream of the heavy deposits. Thus, the greater deposits upstream can contribute to erosion loss of downstream components. In some cases, however, such deposits might also protect components from erosion.

The pressurized fluidized bed concept for electric power generation is another example of an application where the primary source of erodant enters in the intake gases. The intake gases are the combustion gases from the bed and normally range from 1470-1830°F (800-1000°C) at approximately 1500 psi (10.3 MPa). Those from the carbon burnup cell (a high-temperature combustion bed to insure total combustion of recycled, partially combusted coal) will be around 2010°F (1100°C). Similar dust laden gases must be dealt with if attempts are made to combust hot, low BTU gas from a gasifier directly as a turbine fuel. Westinghouse examined the latter problem in the Energy Conversion Alternatives Study for NASA(31) at an ash concentration of .65 mg/ft^3 -- in the range of a dusty road environment. Erosion losses for a 60-blade first stage of a typical industrial turbine were estimated. The test conditions involved:

- an ash with average density of 2.5 gm/cm^3;
- a coal gas combustion gas flow 294.8 kg/s;
- a gas temperature of 1600°F (870°C);
- a gas pressure of 150 psi (1.0 MPa); and
- the factors shown in Table 3-8.

"Catch efficiency" is defined as the "estimated fractions of available gas-borne particles in the size range 1 to 10 μm that strike the surface of a blade in a gas stream."

Thus, in Table 3-8, the dust level resulted in an unacceptably high calculated erosion rate of 10 mils/year at the higher velocity to 1000 fps (300 ms^{-1}). Potential solutions primarily involve the use of high-temperature cyclones but the state of the art is not well developed for long time trouble-free particulate removal at high temperatures. Larger turbines in which gas path velocities are lower are an alternative but potentially less cost effective solution.

These same types of problems can be expected to arise in coal gasification systems that incorporate gas turbines and in most other types of power recovery systems.

TABLE 3-8 Particle Size Distribution of Ash and Estimated Erosion Losses

Size (μm)	Vol. Fract. (Percent)	Ash Flow Rate (mg/s)	Catch Efficiency (Percent)		Blade Loss (10^{-9} cm^3/s)	
			500 fps ~50 ms^{-1}	1000 fps ~300 ms^{-1}	500 fps ~150 ms^{-1}	1000 fps ~300 ms^{-1}
0 - 1	80	70	0	0.05	0	9.4
1 - 2	12.5	11	0.1	0.3	0.6	8.7
2 - 5	6.25	5.5	5.5	14	20	202
5 - 10	1.25	1.1	33	55	23.1	156
TOTAL	100	87.6	0.8	1.7	43.7	376.1
					~1.2 mils/yr.	~10 mils/yr.*

* Calculated

NOTE: Data from Ref. 31

b. Coatings: A Potential Solution. To minimize erosion (and erosion/corrosion) in power recovery turbines, the particle concentrations, particle sizes, particle hardness, and gas velocities must be kept down. Also, the harder the airfoil alloys, the lower the erosion. In addition, surface coatings offer another way to extend component life. The Australian tests included evaluation of five coatings on HS-31 (X-40) stators in a Ruston turbine (Table 3-9).

The sprayed coatings generally proved unsatisfactory (at that time the art was not well developed). However, the diffused Cr coating showed the best erosion resistance -- about one sixth that of the HS-31 -- one of the better alloys evaluated in that program. More oxidation/corrosion- resistant coatings now exist and these should be evaluated for corrosion/erosion behavior.

The hot-erosion resistance potential of the state-of-the-art aircraft utility turbine airfoil coatings -- primarily NiCrAl and CoCrAl overlay systems and a wide variety of modified diffusion aluminide systems which were developed to provide oxidation/corrosion resistance only -- is not well known. Little test data on this subject is available in the open literature. As shown by Levine(32), the bulk hot hardnesses of NiCrAl compositions similar to those found in such coatings can vary greatly with composition (see Figures 3-4 and 3-5). Figure 3-4 shows hot hardness data for nickel aluminide and some NiCrAl compositions. The bulk coating materials were either somewhat harder or softer than IN-100, a cast, high-strength nickel-based aircraft turbine blade alloy. Also note that these various temperature vs. hardness curves all exhibit a "knee" where the hardness drops off more rapidly with temperature. Figure 3-5 shows how elevated temperature hardness can vary greatly with the composition of bulk coating materials. This dropoff in hardness in the temperature range where uncooled or cooled airfoils must operate to achieve long life based on mechanical strength raises some concern. It may be that good corrosion-resistant coating compositions will need to be significantly modified to resist erosion. Thus, the compositions of coatings to resist hot erosion (or hot erosion/corrosion) will require careful tailoring to optimize resistance to all potential attack modes in the hot environment. Tradeoffs to achieve the best combination of corrosion and erosion resistance will be required.

c. Ceramics: A Potential Solution. The objective of a program at Westinghouse was to demonstrate the use of uncooled ceramic first-stage stator vanes for an industrial gas turbine. The operating goal was a peak inlet

TABLE 3-9 Test Coatings on HS-31

Coating	Hardness	Application Method
Alumina (LA2)	1100 VPN	Plasma Spray
WC + 9% Co (L.W.1)	1300 VPN	Plasma Spray
25% WC + 5% Ni + mixed W & Cr Carbides (I.W.5)	1075 VPN	Flame Plating
Diffused Cr	--	Pack
Hard Cr Plate	--	Electroplate

NOTE: Data from Ref. 29

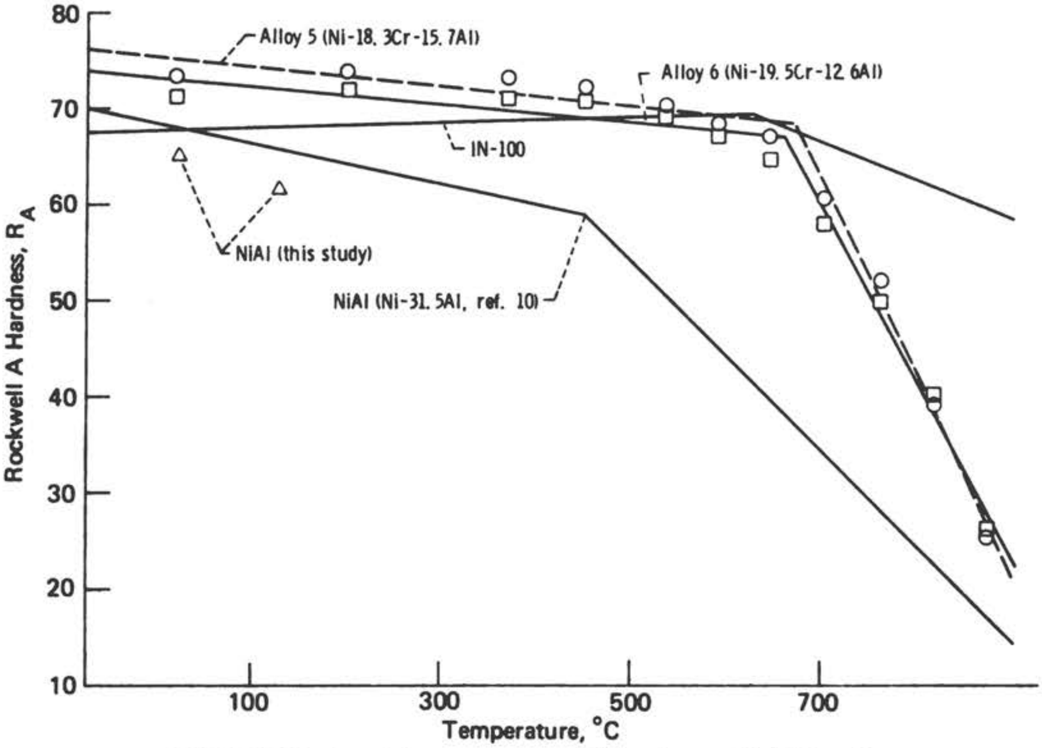
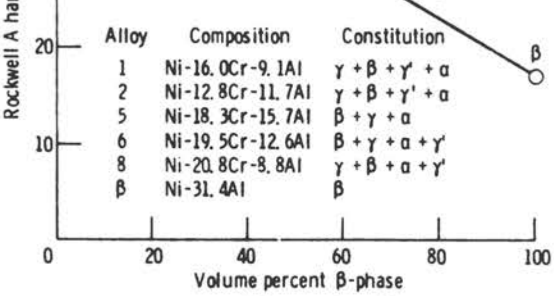


FIGURE 3-4 Temperature Effects on Hot Hardness of Bulk Coating Compositions (Data from Ref. 32.)



Alloy	Composition	Constitution
1	Ni-16.0Cr-9.1Al	$\gamma + \beta + \gamma' + \alpha$
2	Ni-12.8Cr-11.7Al	$\gamma + \beta + \gamma' + \alpha$
5	Ni-18.3Cr-15.7Al	$\beta + \gamma + \alpha$
6	Ni-19.5Cr-12.6Al	$\beta + \gamma + \alpha + \gamma'$
8	Ni-20.8Cr-8.8Al	$\gamma + \beta + \alpha + \gamma'$
β	Ni-31.4Al	β

FIGURE 3-5 Effect of Alloy Constitution on 1150 K Rockwell A Hardness for β Containing Alloys (Data from Ref. 32.)

temperature of 2500°F (1370°C) for potential use in a combined cycle system. Energy conservation and fuel cost problems have produced a renewed interest in such combined cycle systems for electrical power generation since higher thermal efficiencies can be achieved by increasing turbine inlet temperatures. Part of the program was to test the erosion/corrosion resistance of silicon nitride and silicon carbide vanes under simulated operating conditions. A test passage which reproduces the operational environment of a large stationary gas turbine was used. Temperatures of 2010°F (1100°C) and 2500°F (1370°C) were used for the erosion/corrosion experiments with flow rates of 490 fps (150 ms^{-1}). Barium-free No.2 diesel fuel manufactured by Exxon was used as the base fuel. Erosion/corrosion experiments were conducted using the base fuel and various additions of Na, V, and S to the base fuel.

In clean fuel experiments, hot pressed Si_3N_4 and SiC specimens were exposed to combustion gases for 250 hours at 2010°F (1100°C) and 45 psi (0.31 MPa) pressure at approximately 150 ms^{-1} velocity. Both Si_3N_4 and SiC form thin layers of silica and various silicates on the surfaces in the turbine environments. The impingement of high velocity combustor gases causes this surface layer to partly erode away as it is formed. However, at 2010°F (1100°C), the erosion/corrosion attack is small and the average depth of surface removal after 250 hours exposure at 2010°F (1100°C) for both materials was only 2 to 3 microns.

After 100 hours exposure at 2500°F (1370°C), under similar pressure and velocity conditions as for 2010°F (1100°C) testing, specimen surfaces were found to be covered by cristobalite and enstatite on Si_3N_4 and mullite on SiC (alumina used as an additive in the SiC). After removing the surface deposits, weight losses of 5-15 mg/cm^2 were observed.

Further experiments were carried out with additions of 5 ppm Na, 2 ppm V, 0.6 ppm Mg and 0.5 w/o S added to the diesel fuel. The magnitude of erosion/corrosion attack found after 250 hours exposure at 2010°F (1100°C) on Si_3N_4 and SiC was essentially the same as that for the cleaner fuel.

A similar test involved exposure to hot combustion gases at 2010°F (1100°C) at 45 psi (0.31 MPa) pressure using Exxon GT-2 diesel fuel to which 100 ppm V and 0.5 w/o S were added to simulate heavy residual fuels. Again, the erosion/corrosion behavior was similar to that observed using the clear fuel.

The effect of erosion/corrosion on flexural strength of hot pressed Si_3N_4 and SiC was determined using clean Exxon fuel at 2010°F (1100°C) and 2500°F (1370°C). It appeared that flexural strength remained almost unaffected by erosion/corrosion at 2010°F (1100°C) for up to 250 hours while appreciable degradation in the strength is caused by exposure at 2500° (1370°C).

High-temperature particulate filtration systems require considerably more development and long-time demonstration. Specifically, the spall resistance of castable ceramic linings and of high-temperature metallic components must be established. Fail-safe designs which prevent unfiltered hot gases from entering a recovery turbine in case of a filtration failure must also receive more attention.

d. Areas for Consideration. The actual interactions between erosion and high temperature corrosion require much better definition. Such information must be incorporated into life prediction models which can serve to guide the system designers in making life tradeoffs. It will also lead to more focused development of improved turbine alloys and coatings.

In the area of ceramics, redesign and substitution of ceramic components will be needed as another approach toward raising the operating temperature of gas turbines to increase thermal efficiency and/or toward developing multifuel capability. The ceramics used must have high resistance to thermal shock, high-temperature strength and creep resistance along with suitable erosion/corrosion properties. Major problems associated with the use of ceramics in gas turbine applications are difficulty of fabrication and designing with brittle materials. Generally, Si_3N_4 or SiC components are fabricated by slip casting, injection molding, hot pressing or chemical vapor deposition. These ceramics are considered as experimental materials and further development of properties, on a highly reproducible basis, is required. Also, machining of these materials is difficult and fabriction of components to approximate net shape is desirable.

Dense silicon nitride usually requires an additive to promote the densification process. Additives or residual impurities may diffuse to the material surface and affect oxidation and strength properties. Some surface silicates formed may react with the Si_3N_4 at the surface layer interface to produce pitting and reduce strength. Some additives may form silicates which have inferior oxidation resistance. Phase behavior studies, with particular emphasis on oxidation behavior, are required for improved Si_3N_4 materials application in high-temperature engine environments.

3. Magnetohydrodynamic Systems (MHD)

MHD systems are included here since they would most likely be coal-fired. Information on the severity of erosion in MHD systems is not readily available. Few studies involving exposure of materials under representative conditions have been conducted and reported. However, potential coal-fired MHD service conditions are considered severe and will pose serious erosion/corrosion problems for materials. The combination of high temperatures [to 4400°F (2500°C)], high-velocity reactive combustion gases containing "seed" (K_2CO_3, etc.) and particulates, and electromagnetic effects all combine to produce a harsh environment within MHD systems.

MHD studies, so far, have been devoted to the solution of system-operating problems and to the testing of relatively small scale combustors, generators and other components. In the Soviet Union, the U-02 and U-25 facilities have been used to study system performance and to develop electrode designs with emphasis on the use of clean fuels. In the United States, work at Avco Corp., University of Tennessee Space Institute (UTSI), and Westinghouse has concentrated on generator development. Some materials research is underway at the National Bureau of Standards, Fluidyne Engineering Corp., Montana State University, Westinghouse, Battelle Northwest, Massachusetts Institute of Technology, and in Japan, France and the Soviet Union. The efforts in the United States are modest in size and relatively little materials data suitable for component design use are available. Indeed, there is no long-term performance data obtained under actual operational conditions. In those cases where short time tests have been conducted, the information applies to smaller scale applications than are finally planned for base-load MHD systems. Hence scale-up difficulties are expected. Data acquired in clean fuel experiments will not be completely applicable to problems expected when coal is utilized as a fuel.

The MHD system is a complex array of components that serve specific functions and interact with each other. The generator (channel or duct) is the heart of the system. Designs vary from continuous electrode or segmented electrode Faraday generators to various cross-connected electrode generators. The high plasma temperature of 4350°F (2450°C) within the duct poses a serious materials problem. Wall protection options include liquid phase (slag) coating and possibly gas phase cooling. In coal-fired systems, coal slag is used to protect the inner construction of the generator (a slag thickness of several milimeters would be expected). In addition to control of the coal ash composition and thus fusion temperature, proper temperature control is important; too high a temperature produces a low slag viscosity and hence a very thin coating, while too low a temperature can lead to slag solidification and subsequent erosion by coal or ash particles.

Electrode designs for MHD systems vary considerably in present systems. The electric current paths at electrodes generally involve several dissimilar materials (including slag coatings). Hence, electrical arcing and erosion at various electrode interfaces has been reported. This erosion occurs in the presence of strong electric fields, steep temperature gradients, and reactive chemical environments. Attack and dissolution of electrode materials has been observed. Electrodes of ZrO_2-CeO_2 mixtures have shown poor erosion resistance. Improved electrode design may be in the direction of a gradient of materials consisting of regions of high density inert materials for corrosion/erosion resistance blended with regions of more porous texture for resistance to thermal stresses. Combinations of metals and ceramics (and cermets) are possible designs.

Boilers, heat exchangers and other downstream metallic components may be expected to suffer erosion/corrosion losses. Much will depend on the details of the temperatures, deposits that develop, and gas/particulate flow conditions. Little is known in detail about expected metal loss rates. Materials test programs are needed under representative operating conditions. Hot corrosion attack due to the potassium seed can be expected. Operating characteristics of the presently available MHD systems are summarized in Table 3-10. Note that only one system can use coal as a fuel.

C. SLURRY TRANSPORTATION

Solids (coal, ash, dolomite, etc.) must be transported in some energy systems such as coal-fed boilers, coal liquefaction, and coal gasification. The methods of transport are varied but one method which shows considerable promise is the transport of solids suspended in high concentration in a liquid. Slurry transportation is used both within the plant and between the mine and the plant.

Erosion and erosion/corrosion problems in slurry transportation systems can seriously affect the economics of

TABLE 3-10 Basic Characteristics of Open-Cycle MHD Generators*

	U-25	U-02	AVCO Mark VI	UTSI	Westing-house	Stanford	Vegas (German)	ETL (Jap.)	Poznan (Poland)
Duration (Continuous) (Hours)	~100	~100	10-20	0.2-1.0	~10	1-3	~80	~50	3 (total)
Fuel	natural gas	natural gas	toluene	coal or benzene	benzene + char	alcohol propane	propane	oil	kerosene
Mass flow (kg/s)	40-55	0.7	3	0.7	~1.5	0.136	---	0.5	---
Electric Power (MW)	up to 20.4	<0.2	up to 0.57	<0.1	~0.04	8 (thermal)	1.3-2.0 (thermal)	<<1	4 (thermal)
Seed (%)	~1	~1	1-1.5	~1	~0.8	~1.0	1.0	0.7	---
Slag (%)	---	---	~1	~10	0.5-1.0	up to 1.5	---	---	---
Gas Velocity (m/sec)	850-1000	700-800	900-1500	~1400	600	~400	650 (max)	580	700
Heat Flux (W/cm^2)	40-120	20-25	200-400	270	35-45	~100	~100	80	127
Electrode Wall Temperature (K)	1800-2200	2000	1700 (slag) 1200 (metal)	~1300 (slag) ~800 (metal)	~2000 (max.)	1000 (metal)	~1220	1100-1700	<1800 (est.)
Magnetic Field (T)	0.8-2	1.5-1.8	2.5	2	3	2.5	1.7	1.9	2.5
Dimensions (cm^2)	420 77 x 38	~100 6.2 x 30	180 20 x 15	107 5 x 20	100 7 x 12	46 3.8 x 7.6	25 5 x 5	88 2 x 8	50 3 x 10

* from "Joint US-USSR Status Report on Open-Cycle MHD," M. Petrick and V. Y. Shumiatsky. To be published by Argonne National Laboratory (ERDA), 1977.

such systems. The following components are susceptible to erosion in slurry transport systems:

- piping
- pumps
- valves
- centrifuges.

There are other components involved but the ones listed represent potential costly replacement and maintenance problems. A diagram showing the locations of these components in an existing western coal slurry delivery system is presented in Figure 3-6.

1. Pipeline

The pipeline used to transport coal from the mine site to the plant site is under serious consideration as an economically and environmentally sound transport system. It appears that projected coal delivery requirements for future conversion plants make a continuous flow single product delivery system essential. The growing interest prompted covering of two International Conferences(33,34) on slurry transport -- one at Battelle's Columbus Laboratories in February 1976, the other in Washington, D.C. (hosted by the University of Pennsylvania) in December 1976. Experience in transporting coal by slurry pipeline for long distances is quite limited. The Ohio coal slurry line of about 150 miles (240 km) length is best known. Corrosion from chemical agents associated with coal proved to be a problem until it was controlled by chromate inhibitors(35). Erosion or erosion/corrosion of a coal slurry pipeline is critical because it is known that even a pinhole can enlarge to a substantial leak in a matter of minutes by the release of high-pressure abrasive slurry(36).

Experience with the Ohio coal slurry line and the more recent 273-mile (505 km) Black Mesa pipeline supplying the 1580 MW Mohave Generating Station(37) has been quite encouraging with respect to erosion of the pipeline itself. This is the result of many years of slurry transport engineering in which it has been found that keeping the flow rate below a given level [about 5 fps (1.5 ms^{-1})] prevents serious erosion in the pipe. Experience with the Black Mesa pipeline since 1970, 5 million tons (4.5 x 10^6 metric tons) of coal per year, has been good(37). Slurry pipelines are designed to transport solids by keeping them suspended in a

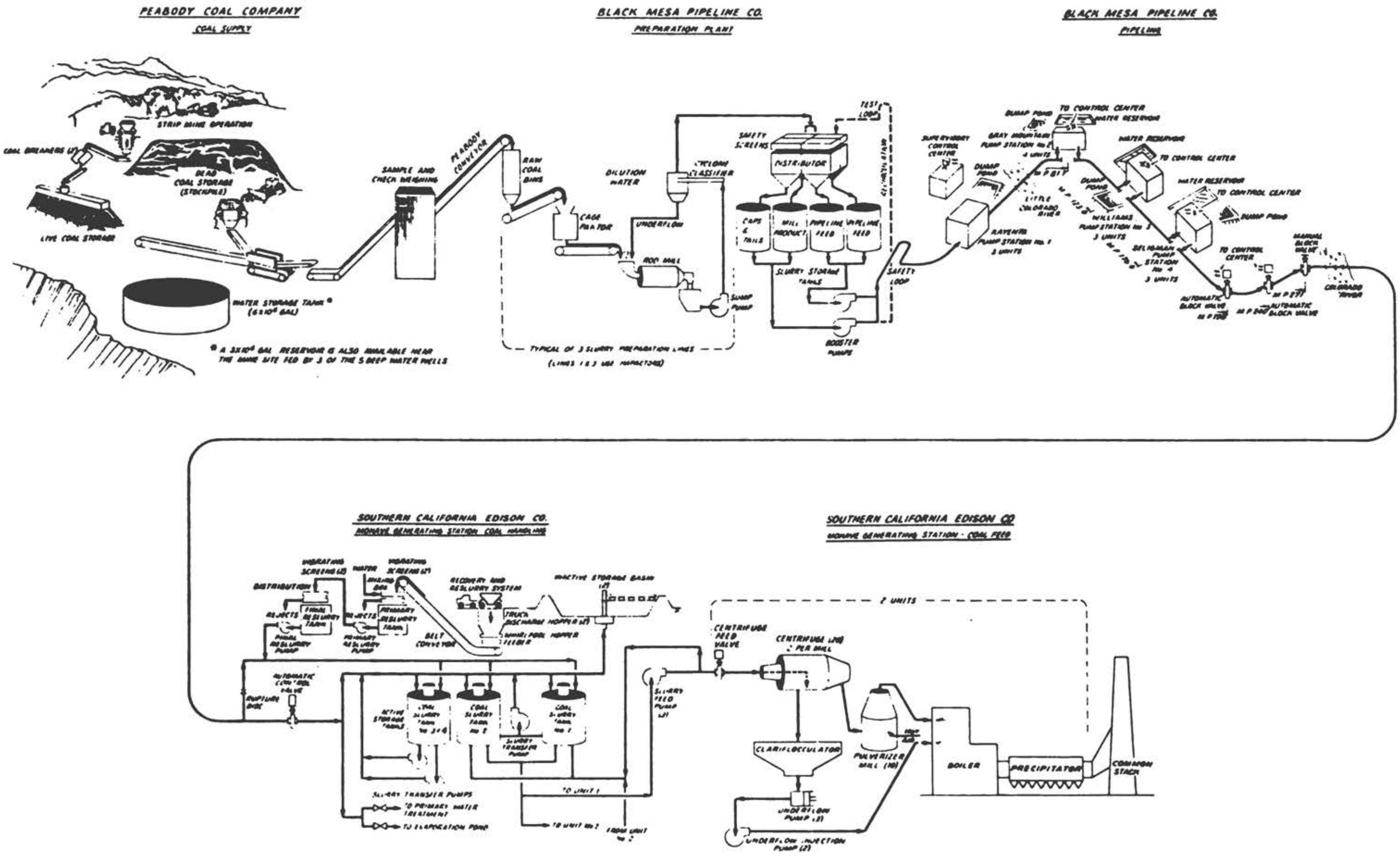


FIGURE 3-6 Coal Slurry Pipeline System

liquid flowing under turbulent conditions [(about 4 fps (1.2 ms^{-1})]. Flow velocity must be maintained above this level to prevent solids settling out and eroding the pipe as they are dragged along the bottom. The range of flow rates, therefore, is rather narrow and requires good flow control.

The Black Mesa pipeline transports about 4200 GPM (265 m^3/sec) maximum in an 18-inch (46 cm) pipe. This is small in comparison to many of the proposed pipelines. A summary of those proposed in 1976 is included in Table 3-11. Note that the Black Mesa line has a throughput of 4.8 million tons/year (4.3 x 10^6 metric tons/year) while the proposed Wytex line going from Wyoming to Texas would have a throughput of more than 6 times this amount or 30 million tons/year (27.2 million metric tons). The diameter would be 42 inches (107 cm) as compared with Black Mesa's 18-inch (46 cm) pipe. When considering the delivery required for a commercial coal gasification plant, even larger throughputs would be required. This may result in pipeline size limitations and the need to increase flow rate through pipelines of economic size.

2. Pumps

Both centrifugal and positive displacement pumps are used for pumping slurrys. The centrifugal pumps are used for relatively short distance transport where pipeline losses are negligible and high pressures are not required to keep the slurry flowing. Centrifugal pumps are used in the energy conversion plant and at the mine site where coal is prepared for transportation. Positive displacement pumps are used for pipeline systems where higher pressures are required. A comparison of operating parameters for three pump types is shown in Table 3-12. If the maximum discharge pressure desired is below 600 psi (4.2 MPa), the centrifugal compressor is generally most economical owing to its greater flow output and lower capital cost.

Piston pumps have an inherent difficulty in pumping abrasive slurries due to the continuous rubbing contact on the cylinder wall in the presence of abrasive particles. This causes rapid wear of piston rings, cylinder walls, and pistons. The plunger pump, which was designed for highly abrasive slurries has a plunger which is continuously flushed with clean water during the suction stroke to reduce ingestion of abrasive particles in the seals and bearings. The plunger is close-fitting in the cylinder and does not rub the sides of the cylinder. Clearance is selected so that particles will not become wedged between the plunger and cylinder wall. Discharge and suction valves experience the most wear and are made to be readily replaceable. Centrifugal slurry pumps experience erosion of impellers and

TABLE 3-11 Major Coal Slurry Pipelines

System	Length Miles (km)	Diameter Inches (cm)	Throughput 10^6 tons/yr. (10^6 metric tons/yr.)	Location
Black Mesa	273 (437)	18 (46)	4.8 (4.3)	Arizona to Nevada
		Proposed Pipelines		
Wytex	1260 (2016)	43 (107)	30 (27)	Montana to Texas
ETSI	1030 (1648)	38 (97)	25 (23)	Wyoming to Arkansas
Houston Natural Gas Co.	1100 (1760)	18 (46)	7 (6)	Colorado to Texas
Northwest Pipeline Corp.	778 (1244)	30 (76)	16 (15)	Wyoming to Oregon
Nevada Power Co	180 (288)	24 (61)	10 (9)	Utah to Nevada
Arizona Public Service Co.	180 (288)	16 (41)	4 (3.6)	New Mexico to Arizona

NOTE: Data from Ref. 37

TABLE 3-12 Slurry Pumps

Type	Maximum Pressure psi (MPa)	Maximum Flow gpm (m^3/S)
Plunger	3500-4000 (24-28)	920 (.06)
Piston	2500-2000 (17-14)	2700 (.17)
Centrifugal	600-800 (4-5.5)	50,000 (3.2)

casings. A split casing design is often used and wear plates attached to the casing. The plates can be removed and replaced in this design. Rubber is often used as a wear lining. For such pumps, the impeller tip speed is usually limited to 4,400 fpm (1320 ms^{-1}) and particle size limited to 2 mm to minimize erosion. This reduces the maximum head the pump can develop. Ceramic lined pumps can tolerate a higher tip speed.

Current practice in design of slurry pumps is to accommodate mechanical wear and erosion. Pump parts are made to be easily replaced and a schedule of regular replacement is part of the operating procedure. Currently, the economics of this approach appears tolerable. However, with large systems requiring much greater throughputs in coal tonnage, a new generation of more erosion and wear resistant slurry pumps will be needed.

3. Valves

Slurry systems are designed so that the pressure differential across valves is minimized. This limits erosion damage, which can be severe due to high velocity flow during opening or closing of high differential pressure valves. Plug type valves are used in high pressure applications found in positive displacement pumps. The valve design requires that flow be streamlined and not subject to sudden turns. Hard facing is used on valve seats to increase erosion resistance. Again, one feature of valve design is to provide ready replacement of parts. The design recognizes the problem of rapid erosion and replacement is assumed to be part of the operation.

4. Centrifuges

In the operation of a coal-fired electric generating plant, coal slurry containing 48 percent solids is fed into a centrifuge-pulverizing system before entering the combustion chamber. A typical centrifuge at the Mohave Generating Station has a capacity of 22 tons (19 metric tons) per hour of coal. Each boiler is equipped with 20 centrifuges. Total station design capacity is 872 tons (785 metric tons) per hour. Considerable erosion was experienced in the Mohave centrifuges when first put into service. Service lives as low as 1500 hours were typical. Several modifications were tried, including tungsten carbide hard facing but 3500 hours was the maximum service life achievable. Dense alumina wear plates finally proved effective in reducing erosion to reasonable levels. Erosion in the centrifuges, however, continues to be a serious problem.

D. GEOTHERMAL ENERGY PRODUCTION

Geothermal heat (or energy) must be transferred from the body of the earth through convection with water or water vapor. The productive areas for this transfer have been classified into three categories. The first category is vapor dominated sources which produce steam in a condition that permits direct use in equipment and steam turbines. Such sources are rare on earth. The second category is liquid dominated sources which abound throughout the world. The fluids that are delivered from such sources represent the results of centuries of circulation within the earth's interior at high temperatures and, in many cases, at high pressure. The third category is the dry rock classification where the heat must be extracted by using some convecting fluid or other heat transfer medium.

Much of the field test data on the fluids or brines are proprietary. Fluid analyses show total dissolved solids ranging from 20,000 to 300,000 ppm. The fluids contain silica, lime, CO_2 and sulfurous compounds. In the case of dry steam, H_2S is a common contaminant. Temperatures may vary between 100°F (40°C) and 450°F (230°C) delivered, and perhaps as high as 800°F (430°C) bottom hole level.

Problems in Utilization

- Many of the places where hot fluid or brine is used encounter fouling, or corrosion, or both. Fouling (deposition) seems to be a uniform experience unless water conditions are unique. Few systems escape it. Corrosion by sour brines is to be expected and pH's as low as 4 are possible. Chlorides and sulfur in the brines enter into the corrosion reactions.

- Spas around the world using hot water ranging from from 180 to 250°F (80°C through 120°C) have operated for many years with a history of pipe and equipment maintenance -- for some with almost no problems, while for others it has been close to ruinous.

- The most serious deposition problems appear apt to develop at relatively low temperatures -- a fluid starting in the system at 480°F (250°C) does not appear to deposit scale as rapidly as when cooling in the lower range of the cycle.

- The active corrosion appears to be less where deposition takes place. If deposition is controlled, then corrosion will accelerate.
- There is not enough data readily available for simple practical metal selection for geothermal service. Probably some cross fertilization with data from other fields, i.e. marine or petroleum refinery or sulfur production may be more desirable for geothermal energy systems.
- The amount of gas and air dissolved in the fluid may be an influence. Research has indicated that any contact with air seems to accelerate the deposition from geothermal fluids. Methods of fluid control in an exchange system seem to influence fouling. Any change of direction in the flow, or restrictions, appears to be bad.

Erosion/corrosion problems were predominant in materials and problems associated with geothermal systems being studied at the Lawrence Livermore Laboratory. Erosion tests are conducted at brine well sites where the erosive environment is approximtely 30 percent vapor, 70 percent liquid with a 2000 fps (600 ms^{-1}) droplet velocity and 3 micron droplet size. Although the erosion effect is small with only liquid droplets, the erosion increases significantly when ultra-fine solid particulates are present in the droplets. Gases of CO_2, H_2S, and NH_3 are mixed in with the brine liquid-vapor erosive medium to precipitate the fine particulates. Polymeric materials were found to erode considerably when subjected to the erosive stream. Other materials being evaluated for erosion resistance are nitrided Ti-6A1-4V, spray coatings of metal carbides, i.e., TaC, Stellites , ceramics (A1N, SiC, Si_3N_4), and MP35N cobalt base alloy.

E. WIND ENERGY MACHINES

The utilization of wind power for energy conversion and generation is an old technology which has recently been revitalized due to the need for alternate energy sources(38-40). Wind mills have been in use for hundreds of years and their size reached a zenith with the construction of the Putnam machine (1.25 MW) at Grandpa's Knob in Vermont in 1941. This windmill had a 175-foot (53 m), two blade rotor of steel construction on a 100-foot (33 m) tower. This device operated between 1941 and 1945 when a defect in one of the blades caused its loss due to fatigue failure. Wartime shortages prevented replacing the blade and the project was abandoned(41).

The largest facility currently operating in the United States is the 125 KW experimental wind turbine being operated by NASA-Lewis at Plumbrook near Sandusky, Ohio. This facility has a 127-foot (38 m) diameter rotor mounted on a 100-foot (30 m) tower.[42] The system is expected to generate 180,000 kwh/year in the form of 460 v, three-phase, 60-cycles-per-second alternating current output.

The most commonly used expression for calculating wind power is:

$$P = KD^2V^3$$

where P is expressed in units such as KW,

K is 0.593, a derating factor representing the commonly accepted density function,

D is the diameter of the rotor, and

V is the wind velocity.

However, the blade efficiency of modern rotor design is approximately 70 percent of the theoretical and with losses in bearings, vibration, etc., a practical power equation would be:

$$P = 0.35D^2V^3$$

Note that the power generated varies with the square of the rotor diameter which dictates that a larger diameter blade be used for increased output. This factor must be coupled with the site selection for installation of the wind machine since the power varies with the cube of the wind speed, which is totally site dependent(43).

1. Current Practice

Optimum designs for gearing and transmissions trains in large wind generators have typically employed blade velocity ratios of 6 to 7. That is, if the rated speed for the wind generator is a wind speed of 20 mph (32 km/hr) (a typical design speed), then the tip speed of the blades are 120 to 140 mph (192 - 224 km). A maximum practical design velocity is perhaps 30 mph (48 km/hr) which would result in tip speeds of 210 mph (336 km/hr).

With the desire for greater rotor diameters because of the power output dependence on diameter squared and the need for reduced weight blades to improve efficiency of the generator, these rotor blades are a natural for advanced composite construction. The large Plumbrook facility utilizes epoxy fiberglass construction with conventional erosion protection such as is utilized on helicopter rotor blades.

With velocities approaching speeds of 200 mph (320 km/hr) or greater, protection of the composites from erosion caused by rotating in rain or blowing dust/sand is essential. It is very similar to the problems of protecting composite aircraft radomes (where higher velocities are usually involved) and composite helicopter rotor blades for which erosion protective coatings and materials have been developed. The state-of-the-art materials include spray-applied elastomeric polyurethane coatings for aircraft radomes and adhesively or mechanically fastened metallic sheaths (electroplated nickel or stainless steel) for helicopter blades(44). While it is expected that these protective materials would be adequate for most wind generator designs which can be anticipated, these systems would have to consider the tradeoff of weight of the protective coatings and maintainability costs versus the benefits of the light-weight fiberglass blades.

These considerations are particularly important for future blade designs which might very likely include graphite fiber or boron-fiber reinforced epoxy composite constructions which would be highly desirable due to their strength and stiffness characteristics. These properties could be employed to minimize the dynamic response to aerodynamic, inertial and gravitational forces to provide successful, reliable, low maintenance rotors.

2. Advanced Wind Machines

One of the advanced concepts being considered for the improvement of efficiency of wind energy conversion machines is the use of a vortex concentrator. This is a small high-speed turbine located just downstream of the blade tip. A high-aspect ratio, high-lift airfoil is capable of generating the strongest trailing vortices and a rapid vortex roll-up enhances the vacuum inside the vortex. A straight blade with inverse taper and twist and a reasonably high aspect ratio will provide maximum lift coefficient and rapid roll-up. The creation of this low pressure region around a rotor increases the local wind kinetic energy and the amount of wind power harnessed per square foot of rotor area can be increased fivefold(45).

The small high-speed turbine which utilizes this vortex flow may suffer many of the erosion problems of turbines on helicopters and aircraft. Ingestion of sand or dust or even prolonged ingestion of rain can result in pitting and material loss on the tips and inboard edges of the blades. (Location is dependent on dynamics of the air flow in the turbine.) If the materials utilized in the turbine are conventional metal alloys, the erosion due to rain ingestion, probably will be minimal, based upon operating experience with airborne turbine engines which operate at considerably higher speeds. The sand/dust ingestion may result in erosion of the metal blades but this will not be too serious because of the low velocities (less than 300 fps) involved. If this proves to be a problem, then state-of-the-art erosion resistant protective coatings (borides, carbonitrides, etc.) would provide adequate protection. If these high-speed turbines were designed with composite construction blades, then both rain and sand ingestion would be a concern for the same reasons discussed previously with regard to the large wind rotors.

3. Future Designs and Materials

In view of the above, the requirements for use of advanced composite constructions appears pressing. However, with this comes an aggravation of the erosion problem since these graphite and boron fiber constructions have been shown to exhibit extreme problems with rain erosion even at low velocities due to their susceptibility to damage(44,46). In fact, this sensitivity to erosion has caused a reduction in the frequency of application of these composites in jet engine fan and compressor blades because of the weight penalties for erosion protection. Therefore, for advanced wind generator rotor applications, the erosion associated with advanced composite constructions must be taken into account and state-of-the-art protection as described earlier for fiberglass plastic constructions must be employed. If properly used, these existing materials and protection techniques can adequately protect the blades and satisfy the desired life expectations.

F. SOLAR ENERGY CONVERSION SYSTEMS

There are several approaches to converting solar energy into usable form:

- direct thermal conversion where sunlight is absorbed by collectors (i.e., black bodies);
- conversion into electricity via solar thermal-electric, photo-voltaic, wind, or ocean thermal systems; and
- conversion of biomass into fuels (i.e., methane, alcohols, or hydrogen).

Studies of all the approaches are underway. There is little current information on specific erosion/wear problems, as studies are in early phases of concept formulation and feasibility evaluation.

In direct thermal conversion systems, corrosion is a major factor where elevated temperature fluids are employed in applications such as water heat pipes, but erosion/corrosion coupling does not appear to be significant.

In conversion systems employing radiation concentrators, reflector materials (i.e., silver and aluminum) require protection against erosion by sand in desert areas subject to high winds. For example, a velocity of 100 mph (161 km/hr) was estimated as occurring once in a 50-year period at Albuquerque, New Mexico. Candidate protective materials include glass, plastic, or anodized films in the case of aluminum reflectors. Work to define the extent of the erosion problem is being conducted, under ERDA sponsorship, at Sandia Laboratories in Albuquerque and Livermore, and by other private contractors.

In addition to erosion of reflector materials, there are potential erosion problems in associated heat transfer and power generation components which are analogous to problems discussed earlier in this chapter. For instance, in steam generation systems, turbines may suffer the typical erosion caused by condensed vapor droplets.

In ocean thermal systems, corrosion and biofouling of water transfer pipes and heat exchangers may have erosive implications, particularly if abrasives are used to remove deposits.

G. OVERALL PROBLEM

A conceptual scheme that exposes the nature of the problems in energy conversion systems in a systematic way can be based on the fact that erosion/corrosion depends to a large extent on the temperature of the eroding particles, the temperature of the exposed surfaces, and the fluid in which they are carried, and the velocity of the stream. In considering these problems five kinds of particle-fluid combinations can be specified. These are: gas bubbles in a liquid, solid particles in a liquid, liquid particles in a gas, semi-hard particles in a gas, and hard particles in a gas. In each of these categories, the operating temperature range was divided into three regimes: low [up to 390°F (200°C)], medium [390° - 1110°F (200° - 600°C)], and high [above 1110°F (600°C)]. Similarly, the velocity range was also divided into three regimes: low [0-66 fps^{-1} (0 - 20 ms^{-1})], medium [61-328 fps^{-1} (20 - 100 ms^{-1})] and high [above 320 fps^{-1} (100 ms^{-1})]. There are, therefore, 45 categories, within which systems or components, materials, and problems can be categorized. These categories will be coded by the following scheme:

A - Gas bubbles in a liquid

B - Solid particles in a liquid

C - Liquid particles in a gas

D - Semi-hard particles in a gas

E - Solid Particles in a gas

V_1 - Low velocities (0 - 20 ms^{-1})

V_2 - Moderate velocities (20 - 100 ms^{-1})

V_3 - High velocities (above 100 ms^{-1})

T_1 - Low temperatures (up to 200°C)

T_2 - Moderate temperatures (200 - 600°C)

T_3 - High temperatures (above 600°C)

Thus, for example, a component exposed to solid particles in a liquid stream at moderate velocities and low temperatures will be labeled $B(V_2, T_1)$ to identify the conditions under which a system or component must function.

Using this classification, the erosion conditions stipulated for the systems and components in this chapter are classified and a judgment is made as to whether the extent of the erosion and/or corrosion will be high or low. The results of this evaluation are summarized in Table 3-13.

Table 3-13 shows that the problem of erosion/corrosion is a very general one indeed. The variety of components and materials involved is considerable, and a wide range of temperatures, velocities and environments is involved. Therefore, it is fruitful to examine these problems from a fundamental viewpoint to provide a framework within which specific problems can be examined.

TABLE 3-13 Problem Evaluation Matrix

	Condition	Corrosion	Erosion
A. COAL CONVERSION			
1. Coal Gasification			
a. Gasifier Vessels	C, D, E $(V_1, T_2 - T_3)$	$\boxed{\text{X}}$	$\boxed{\text{X}}$
b. Lockhoppers	E$(V_1 - V_2, T_1 - T_2)$	X	Ⓧ
c. Pumps	B(V_2, T_1)	X	Ⓧ
d. Valves	E$(V_1 - V_3, T_1 - T_3)$	$\boxed{\text{X}}$	$\boxed{\text{X}}$
e. Cyclones	D, E$(V_2 - V_3, T_2 - T_3)$	$\boxed{\text{X}}$	$\boxed{\text{X}}$
f. Piping (Alignment and Joining)	D, E$(V_2 - V_3, T_2 - T_3)$	$\boxed{\text{X}}$	$\boxed{\text{X}}$
2. Coal Liquefaction			
a. Agitation Equipment	B$(V_1 - V_2, T_2)$	X	Ⓧ
b. Pumps	B$(V_2, T_1 - T_2)$	X	Ⓧ
c. Valves	B, E$(V_1 - V_2, T_1 - T_2)$	X	$\boxed{\text{X}}$
d. Lockhoppers	B, E$(V_1 - V_2, T_1 - T_2)$	X	Ⓧ
B. POWER GENERATION			
1. Steam			
a. Heat Exchanger Tubes	A, B$(V_1 - V_2, T_1 - T_2)$	Ⓧ	X
b. Steam Turbines	C(V_2, T_2)	X	Ⓧ
2. Gas Turbine	C, D, E $(V_2 - V_3, T_2 - T_3)$	$\boxed{\text{X}}$	$\boxed{\text{X}}$
3. MHD	C → D → E $(V_1 > V_3, T_3)$	$\boxed{\text{X}}$	$\boxed{\text{X}}$
C. ADVANCED SLURRY TRANSPORTATION			
1. Pipeline	B(V_2, T_1)	X	$\boxed{\text{X}}$
2. Pumps	B(V_2, T_1)	X	$\boxed{\text{X}}$
3. Valves	B(V_2, T_1)	X	$\boxed{\text{X}}$
4. Centrifuges	B(V_2, T_1)	X	$\boxed{\text{X}}$
D. GEOTHERMAL	B$(V_1$ & $V_2, T_1)$ E$(V_1$ & $V_2, T_1)$	$\boxed{\text{X}}$ $\boxed{\text{X}}$	X X
E. WIND MACHINES	D(V_2, T_1)	-	X
F. SOLAR THERMAL	E(V_1, T_1)	X	X

X = Problem

$\boxed{\text{X}}$ = Problems of moderate severity

Ⓧ = Problems of high severity

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Chapter 4

MAGNITUDE OF THE PROBLEM

It is convenient to think of the erosion process in three parts: the motion of the particles in the fluid stream up to the point where they strike the surface, the impact of the particles on the surface, and the changes in the eroding materials as the result of these repeated impacts. This leads to three kinds of studies relevant to understanding erosion. These are: the fluid mechanics of particulate-laden streams, the impact process, and the behavior of the material in the imposed environment. An understanding of these three areas and the relationship among them can aid the process of materials selection and materials development and contribute to the solution of design problems. First, however, the developmental history of two systems involving erosion--the steam turbine and a small gas turbine--will be presented to illustrate the scope of the problem which must be considered and illuminate how certain specific problems have been handled in the past. This discussion indicates the need to initiate a broadly based multidisciplinary approach to erosion/corrosion problems which could limit the operational performance of future energy conversion and generation systems.

A. SOME EXAMPLES OF OVERCOMING EROSION PROBLEMS

Erosion in steam turbines has been an important consideration for many decades. The evolution of the developments involving design, materials, and operating restrictions which finally led to a reasonable solution to erosion problems is representative of the consideration required for other energy-related components where erosion/corrosion will be significant. The steam turbine example illustrates that, if a decision is made early in the planning stages to make a forthright attack on the erosion/corrosion problem, many years of hastily contrived and unsuccessful "fixes" can be avoided. Another example, involving increased operating performance for a small gas turbine when ceramic materials replaced metallic guide vanes, indicates that a new design philosophy must be developed if the full potential of ceramics is to be exploited.

1. Case History -- Steam Turbine Erosion Problems

The diagram in Figure 4-1 shows the chronological sequence of the investigations which were conducted to address the problems of steam turbine erosion. Note that the time required to develop adequate solutions covered more than a decade (from the early 1960s to 1973).

Some difficulties which were encountered in the development of solutions to the problem of erosion in steam turbines, which ERDA will face combatting erosion in other energy systems, are:

- a multi-faceted approach to the problem of erosion was required which resulted in a materials solution, a design solution, and an operating practices solution.
- after the primary problem (wet-stage moisture erosion) was identified and addressed, other problems (boiler-scale hard-particle erosion) arose and were identified which required research to provide solutions; and
- after improved materials were developed which greatly increased the erosion protection, the development of processes to permit them to be applied and of refinements in operation were necessary; procedures related to the new materials also required development.

Future problems can be forecast (in this case history, resulting from use of longer lighter blades) but extreme difficulty can arise in supporting adequate research (improved materials development, fundamental studies for improved design) so that solutions will be in hand when the problems appear.

2. Erosion of a 10kW Radial Inflow Gas Turbine*

Small gas turbines used in auxiliary power units in helicopters suffered from two principal sources of degradation. The first resulted from dust ingestion during service conditions where nozzle guide vanes, at high

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* Developmental work being carried out by the Solar Division of International Harvester Company, San Diego, California, for the U.S. Army under Contract No. DAAK02-75-C-0138 which began on 7 March 1975.

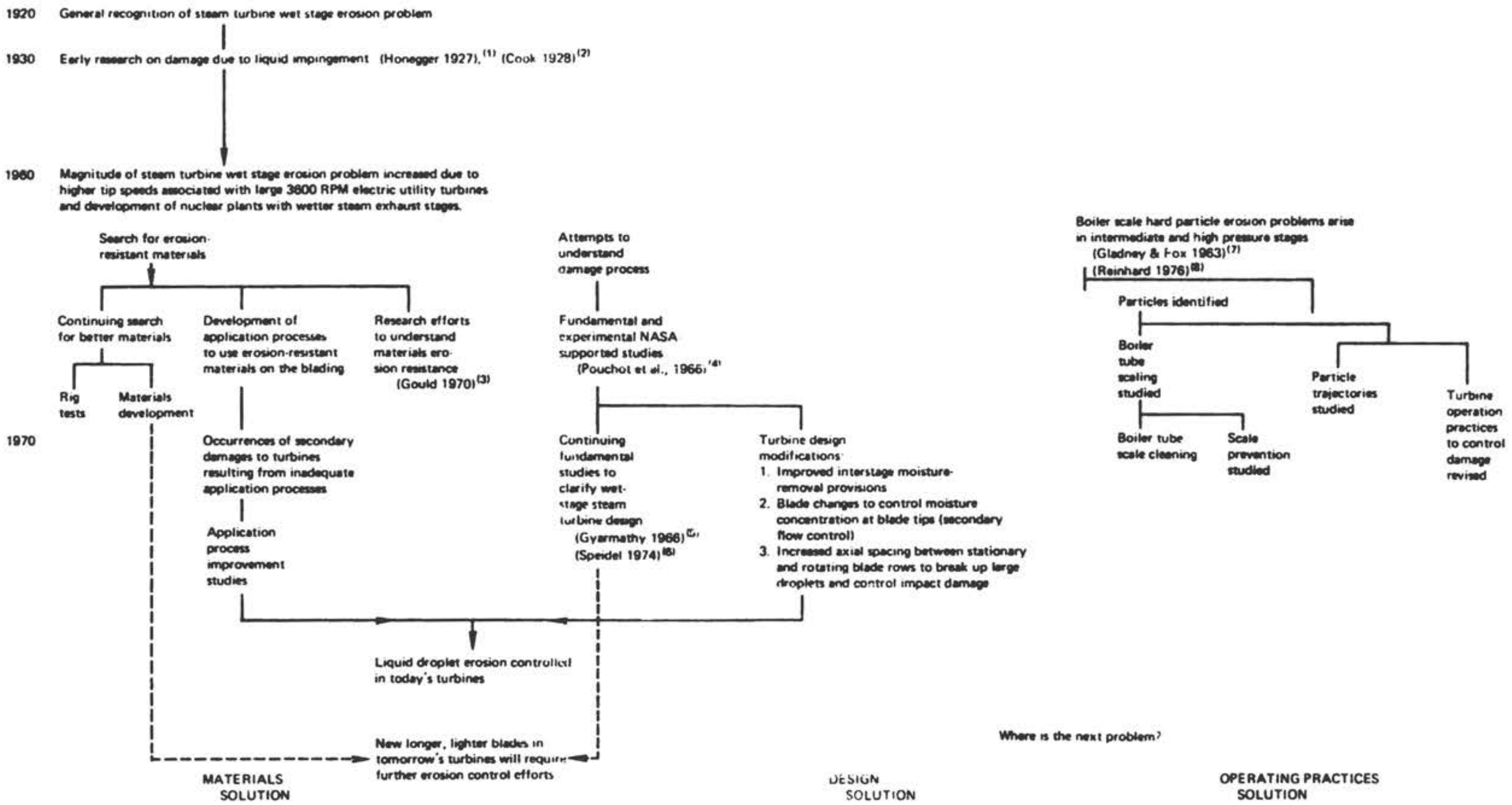

FIGURE 4-1 Case History--Steam Turbine Erosion Problems

temperature, were severely eroded. Another problem resulted from thermal degradation, or "hot spots," which developed because of environmental conditions and operation of the unit by unskilled personnel. Materials evaluation, performance testing, and engine redesign were the technical approaches used in adapting ceramics to this application.

a. Materials Evaluation. It was determined that materials for guide vanes should be resistant to thermal cycling effects, have high hot strength [to at least 2000°F (1100°C)], be resistant to oxidation and erosion by particulates, have good impact resistance, reasonable thermal conductivity, and low coefficient of thermal expansion. It was desirable to use materials which would permit increasing the turbine inlet temperature from 1700°F (925°C) to 1900-1950°F (1040-1065°C) in order to significantly increase efficiency and produce a resultant power increase. Silicon nitride and silicon carbide appeared to have the required combination of properties outlined for this application.

Erosion studies were conducted with metallic materials, hard coatings, and monolithic ceramics. It was noted that erosion results at low angles of incidence were particularly significant because, in service, the greatest erosion occurred at the trailing edges of the guide vanes. At 30° impingement angles, erosion of metals was high. Coatings were not successful due to porosity, spalling of dense coatings, or inadequate thickness. Erosion measurements with monolithic ceramics, Si_3N_4 and SiC, indicated that these might provide the desired erosion resistance and high-temperature capability. A comparison of erosion resistance of reaction bonded Si_3N_4, hot-pressed Si_3N_4, SiC, and 713LC superalloy is compiled in Tables 4-1 and 4-2 which show the effects of impingement angle and carrier gas velocity, respectively. The ceramic materials showed considerably less erosion than the metal compositions tested. Additionally, there was no deterioration of the ceramic vanes after 60 hours of exposure to a sea salt corrosive medium at 1700°F (925°C).

b. Design. In substituting the ceramic material for metallic as guide vanes, some redesign of the engine was necessary. Without detailing this aspect of technological development, some design considerations were: methods of securing and positioning shrouds, minimizing thermal stresses, developing an acceptable transition between ceramic and metallic members, and maintaining an effective but simplified ceramic vane design to keep the fabrication cost low.

TABLE 4-1 Erosion of 713LC Superalloy and Four Ceramics [600 fps (183 mps) Gas Velocity, 15 Minutes at Room Temperature, 90 mg/ft^3 of 43-74 Micron Arizona Road Dust and .0375 in. (0.95 cm) Diameter Nozzle]

Material	Erosion Volume Loss x 10^3 cc 30° Impingement Angle	Erosion Volume Loss x 10^3 cc 90° Impingement Angle
713 LC Superalloy	2.60	1.79
Hot-Pressed Silicon Nitride	0	0.12
Hot-Pressed Silicon Carbide	0.04	0.32
Reaction-Bonded* Silicon Nitride	1.65**	2.88
NC-430	0.08	0.39

* Ground surface.

** Derived from previous results.

NOTE: Unpublished data obtained with Army and Navy support at Solar Turbine International, San Diego, California.

TABLE 4-2 Effect of Carrier Gas Velocity on Erosion
[15 Minutes at Room Temperature with 80 mg/ft^3 of 43-74 micron Arizona Road Dust and .0375 in. (0.95 cm) Diameter Nozzle]

	Impingement Angle	Carrier Gas Velocity, fps			
		200 (61 mps)	400 (122 mps)	600 (183 mps)	1000 (305 mps)
713 LC Superalloy	30°	0.09	---	2.60	---
	90°	0.21	---	1.79	---
Hot-Pressed Silicon Nitride	90°	---	---	0.12	0.22
Hot-Pressed Silicon Carbide	90°	---	---	0.32	1.59

NOTE: Unpublished data obtained with Army and Navy support at Solar Turbine International, San Diego, California.

c. Engine Testing. Engine test results, thus far, have shown that hot pressed Si_3N_4 material in the ceramic vane section nozzle has erosion resistance between one and two orders of magnitude greater than 713LC superalloy at the 1700°F (925°C) test temperature. The vanes have survived 500 thermal shock cycles. The cost of the hot pressed Si_3N_4 components is quite high, however, and methods of reducing fabrication costs are being sought. It is anticipated that increasing the operating temperature from 1700°F (925°C) to 1950°F (1065°C) can increase effective power from 10 to 15KW, possibly making the expensive material cost effective.

B. FLUID MECHANICS OF PARTICLE-LADEN FLOWS

In most energy conversion systems, the eroding particles are carried in a fluid stream. The flow characteristics of this particulate-laden stream play a major role in determining the velocity and number of particles that strike pipe walls, valves, turbine blades, etc. The importance of the gas flow characteristics is readily deduced from the fact that even small irregularities in an otherwise smooth pipe are known to lead to serious erosion when solid particles are present. For flowing liquids, surface irregularities can also provide sites for cavitation erosion damage. Major erosion problems are known to occur on devices such as valves where the flow disturbances are intrinsic to the system.

Computer analyses of particulate-laden streams for a variety of concentration levels, flow velocities, particle sizes and physical configurations are needed to assist in characterizing the particle attack for particular geometries and environmental conditions. Although some work has been done in this area, the nature of turbulent flow of loaded streams is not fully understood. It is known that in perfectly smooth pipes, boundary layers exist which keep particles from reaching the walls. The conditions under which the irregularities disturb this behavior, thereby leading to particle impact and erosion, need clarification.

The turbulent flow of loaded fluids is a difficult field to study but study is necessary to provide the basis for meaningful test configurations and, subsequently, to serve as a design tool. These studies should have as their general objective the determination of particle trajectories as a function of stream velocity and physical configuration. This would give the desired base for determining the number and velocity of particles taking part in the erosion process.

There are a number of specific objectives of direct importance to practical erosion problems which should be included in such fluid mechanics studies:

- analyses of boundary layers and their effect on the rate of particle impacts;
- evaluation of boundary layer disruption by surface irregularities and the trajectories of particles near the surface under such conditions;
- determination of the particle impact rate as a function of fluid velocity, particle size, and particle concentration;
- influence of rebounding particle interactions with the rest of the loaded stream and the consequent effect on the total particle impact rate; and
- determination of the distribution of particle impact angles and velocities of impact for given stream velocities.

Such studies would be of great value in relating design parameters such as curvature of pipes, concentration of particles, stream velocities and particle sizes, to anticipated erosion problems.

C. THE IMPACT PROCESS

Several mechanisms which have been proposed for the material removal process in an erosive environment in the vicinity of room temperature are surveyed in Chapter 5. These include micromachining, in which an abrasive particle acts as a cutting tool; local melting or vaporization, in which the energy of impact melts the material which then adheres to the rebounding particle; shearing of irregularities in the surface by eroding particles or fragments of them (the irregularities can be pre-existent or formed by deformation accompanying impact); and, in brittle materials, microcracking. Investigations of the impact process should be designed to elucidate the mechanisms of material removal and make a choice among those proposed for various conditions: especially with regard to elevated temperatures and the influence of corrosive layers. Studies should also be designed to help clarify the changes in material properties that occur during the erosion process.

The development of stress wave analysis of the particle impact process would be desirable in understanding how the material responds to the imposed rapid loading conditions. Such evaluations are available for very idealized impact conditions, material behavior, and material microstructure. Computer studies of more physically-based models is costly and should be pursued with discretion. It would be helpful to have an analysis which would quantify the response of a material to the imposed loading condition and to be able to evaluate the influence of various material parameters on this response. However, similar objectives could be met by developing a well-planned experimental program. It should be kept in mind in applying continuum mechanics to the erosion of materials that differences in surface composition and material properties over small regions are important. Therefore, the unit deformation process may be different in one region of the material than in another. This observation is illustrative of the fact that continuum mechanics suffers from an inherent inability to provide an atomistic description of the deformation process. However, it is of great value in outlining general deformation modes and providing general design criteria.

Very little is known of the effect of the ambient fluid on the impact process. The impacting particle can carry a boundary layer with it and must penetrate the boundary layer at the exposed surface. Continuum mechanics studies obviously must account for the presence of the fluid phase: especially for reactive and liquid media. It is important that the fluid mechanics of the stream should be coupled with an understanding of the particle impact process.

A basic experimental technique involves impact erosion tests in which particles in a controlled environment impinge on a target. Multiple-particle tests are used to measure the rates of erosion and should be a part of any materials evaluation program. The importance of erosion testing was indicated in the Introduction (Chapter 1) and the general procedures employed for engineering applications are described in Chapter 8. Collection and analysis of the debris resulting from steady-state erosion tests would be useful in documenting such processes as incident particle fragmentation, surface film fragmentation, wear particle formation processes, etc. Single particle impact tests offer a better opportunity to identify impact damage regimes and study the process of material removal. This is particularly true for materials in which several damage modes exist. Furthermore, in some cases the total erosion of a stream of particles is approximately the sum of the erosion for each impact. Single particle tests can, therefore, be useful in predicting erosion. In many soft metals, low velocity impact damage is primarily dependent on the interaction between successive impacts, and damage is not a simple sum of the effects of individual impacts. In this case, single particle tests are not as useful in predicting erosion. However, single particle tests of pre-eroded surfaces as a function of degree of erosion can still be valuable in studying the mechanisms and materials changes occurring during the process.

Material removal under the combined influence of a corrosive environment and particle impact is poorly understood. Single particle studies can be an important aid in examining the erosion/corrosion interaction as described in Chapter 7.

D. MATERIAL BEHAVIOR IN AN EROSION/CORROSION ENVIRONMENT

Dramatic changes in material properties take place during erosion, not only in the later stages but even in the earliest stages. The impact process can give rise to the following phenomena in the underlying material, all of which have an effect on material properties; migration and resegregation of impurities, twinning, phase changes, dislocation multiplication and migration, local melting and recrystallization, work hardening and microembrittlement, and void microcrack formation. Sorting out these effects constitutes a major task of materials and metallurgical analysis. Understanding their role in the erosion process is essential for a rational erosion-resistant materials development program.

A major part of a materials study of erosion should be the characterization of the surface damage accompanying the impact process. Traditional metallography and electron microscopy are important tools in determing microstructural changes. Experiments should be designed to make profile analyses of the microstructure below the surface when studying resegregation and impurity migration. Some of the more modern surface analysis tools can be used. These include: Auger analysis (AA), electron spectroscopy for chemical analysis (ESCA), secondary ion mass spectroscopy (SIMS), and ion scattering spectroscopy (ISS). The first three methods give information on chemical composition at a high scale of resolution for the first five to ten angstroms in the surface. SIMS includes ion milling which provides the capability to explore surface composition. ISS identifies the composition of essentially the first atom layer. The objective of these studies would be to determine the nature of the near-surface region as a function of the degree of erosion. This would be of great help not only in understanding the erosion mechanisms, but also in designing new erosion-resistant materials. For example, if it were found during the erosion process that micromigration of impurities to grain boundaries occurred with a resulting microembrittlement which led to crack formation and surface failure, then the design of future materials would be able to take this into account and hopefully eliminate future conditions of this type. Again these studies would have to account for elevated temperature and corrosive effects on the material.

A more detailed program for investigating erosion/corrosion is developed in Chapter 8. Some general considerations of the coupled problem are presented here. Depending upon the corrosion process, the environmental variables can be systematically changed (environment, temperature and thickness of corrosion layer) and the resulting single-particle impact damage can be compared with that on a pristine surface. The corrosion processes to which this procedure would be appropriate are those where the surfaces are such that the damage can be adequately observed and documented. For example, this could involve passive layers developed during aqueous corrosion and the dense, adherent α-Al_2O_3 scales that are formed during high temperature oxidation in gas turbines. For such cases, post-impact damage characterization can be performed immediately after impact and after continued exposure to the test environment. This would distinguish the effect of corrosion on impact damage from the effect of impact damage on corrosion.

In those corrosion processes where very severe degradation takes place even in the absence of impacting particles, as can be the case in gasifier internals, the value of single-particle impact studies may be limited. There optical metallographic studies as a function of exposure time using multiparticle conditions appear to be more appropriate. In many alloys, particularly those that undergo hot corrosion attack, very severe corrosion takes place only after an incubation period during which corrosion occurs slowly. For such metals, single particle studies could prove to be especially useful in helping to identify those processes which are important for the initiation of hot corrosion attack.

Model materials that have some of the characteristics of materials from which commercial units would be constructed should also be studied. For example, hot pressed alumina or silicon nitride can be chosen as ceramic model materials, a Cr-Mo steel and a nickel base superalloy for moderate- to high- temperature applications.

E. CONCLUSION

A considerable increase in basic research is necessary. This conclusion will be reinforced when the state of the art in erosion and corrosion is reviewed in the next two chapters. The proposed research effort should view the problem in a global sense and draw upon a variety of disciplines. This program should be oriented toward understanding the fluid mechanics of particulate-laden flows and the physical and material processes resulting in erosion and erosion/corrosion effects. This effort as outlined above would be important in overcoming the erosion/corrosion problems in energy systems on an intermediate time scale.

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Chapter 5

MECHANISMS OF PARTICULATE EROSION OF MATERIALS

Solid-particle erosion of metals and ceramics are reviewed here in terms of the information available in order to assess the current state of the art, to indicate where additional work is required, and to highlight some of the experimental techniques used in obtaining erosion rates.

The general erosion behavior of a generic material eroded under a specific test condition has the characteristic response illustrated in Figure 5-1. The erosion exposure time curve has a general form which consists of an incubation period, an acceleration period, and a steady state period. Although stages beyond the steady state rate of material removal have been defined, the material is by then so badly eroded that its usefulness for most applications is no longer of interest. Most of the evaluations made for solid-particle erosion continue the test until the steady state rate of erosion has been established. This is accomplished by running the test for successive equal time increments and obtaining the same value of the mass loss for these increments. Most of the results reported for solid-particle erosion evaluations are expressed as the ratio of the mass of material removed to the mass of the impacting particles for a known exposure time increment. The ratio of the volume of material removed to the mass of the impacting particles is also used as a measure of the erosion rate. Thus, a single number is obtained to represent the rate of material removed for a material exposed to a specific erosion condition.

Two types of response to multiple solid-particle impacts have been noted. The first is a ductile response generally associated with metals, while the second is brittle response associated with glasses and ceramics. The general form of the mass removal rate as a function of the angle of attack for each response is shown in Figure 5-2.

It is a general observation, however, that normally brittle materials exhibit ductile behavior when the particle diameters are less than 100μm. Sheldon and Finnie(1) state that this phenomenon occurs when the zone of material affected by an impacting particle is smaller than the spacing between material flaws or inhomogeneities. Experimentally this transition from brittle to ductile behavior is shown by plotting the erosion rate versus impact angle relationship for different sizes of impacting particles. For larger particles, the typical brittle curve is found with its maximum at normal incidence. For very

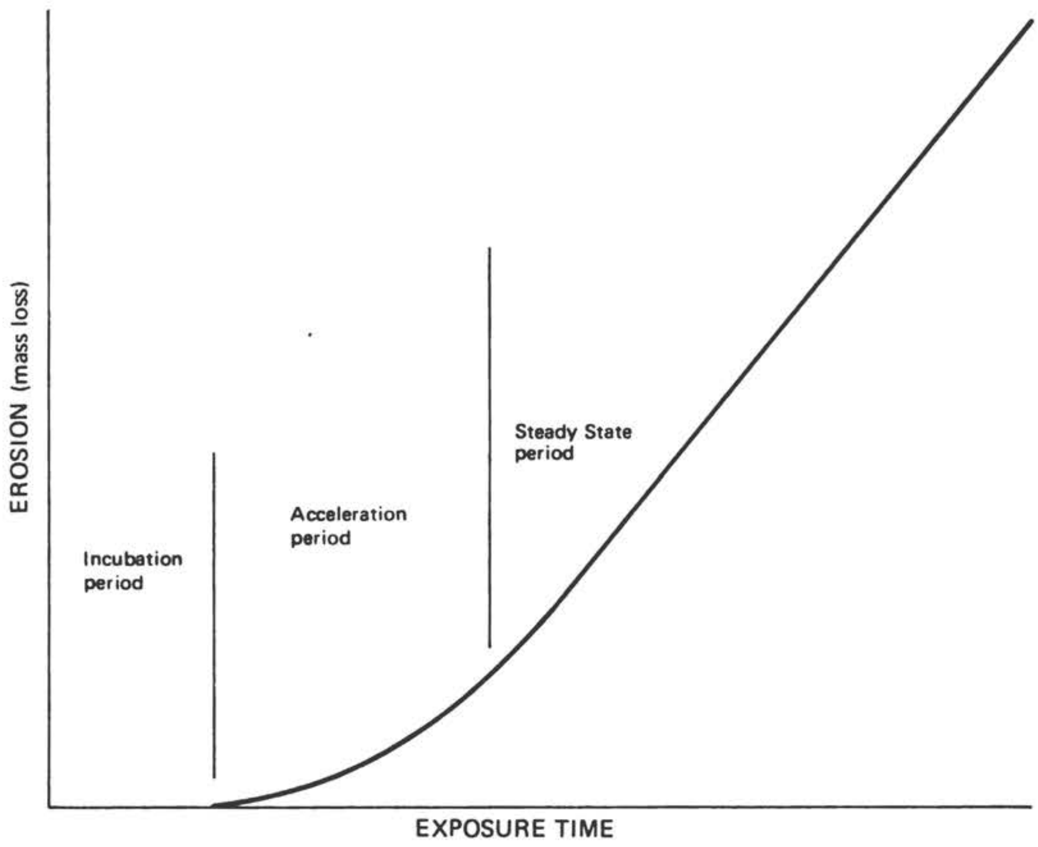
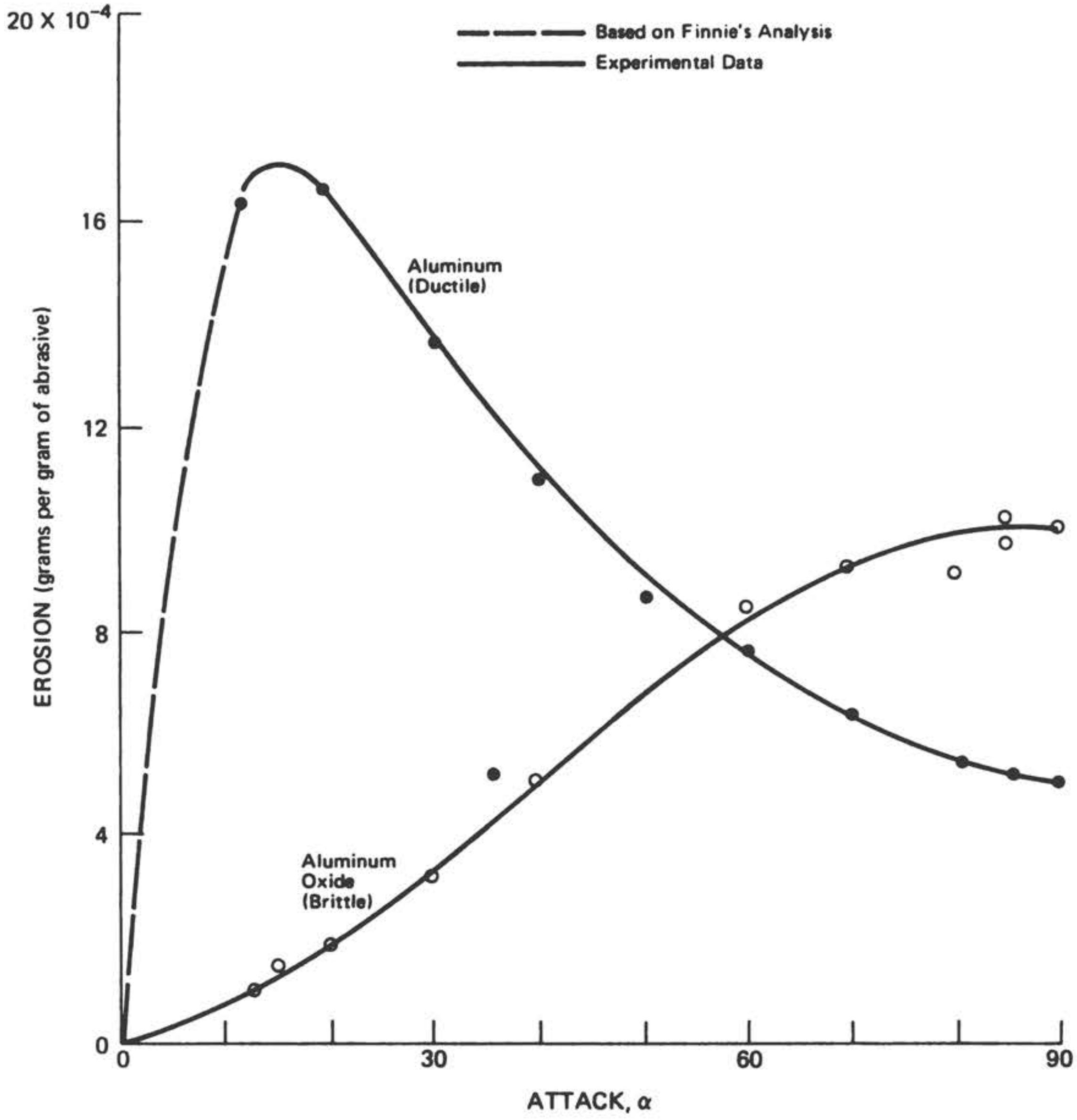


FIGURE 5-1 Erosion as a Function of Time of Exposure



(--- based on Finnie's Analysis
— experimental data)

FIGURE 5-2 Erosion as a Function of Angle of Impingement for Aluminum (Ductile) and High-Density Aluminum Oxide (Brittle). (Data adapted from Ref. 1.)

small particles the same material may show a dependence more like the typical ductile curve having a maximum at other than normal incidence. Another indication of ductile behavior is the formation of surface ripples (which is characteristic of ductile erosion around the impact angles at which the maximum rate of erosion occurs) on brittle materials eroded by very small particles.

Many of the previously discussed findings have been experimentally confirmed by Wood(2,3), who also found that the erosion rate per particle decreased with the concentration of particles in the fluid carrier stream. Moore(4) has demonstrated the formation of a protective umbrella of rebounding particles which interferes with the impinging particles at high concentrations.

A. ANALYTICAL DEVELOPMENTS

Most analytical approaches which can be found in the literature are based on hypothesized models of the material removal mechanisms. Until recently, comparatively little work has been devoted to identification of the actual mechanisms responsible for the attrition of material from an eroded surface. From the program listing in the Appendix it is seen that there are investigations currently underway directed toward this objective.

The basic analytical and experimental work on this subject during the period from 1960 to 1970 is due to Finnie, Tilly, and their associates. Finnie's earliest papers(5,6) reviewed previous work on this subject, most of which was of a practical and empirical orientation. Several of the previous investigators had already found that hard steel better resisted particles impinging obliquely, whereas soft steel appeared more resistant to normal impingement. This gave the first clue that rather different mechanisms were predominant in these two cases. Finnie then presented a theory for the erosion of ductile materials by angular particles impinging obliquely on the surface. This theory treats each particle as a small cutting tool which gouges into the surface by virtue of its momentum. The volume of eroded material per particle is related to the depth and length of the groove cut by the particle before it is brought to rest or rebounds from the surface. The main results of the theory are that, for typical particles at a given velocity, the erosion rate should be at a maximum when their direction of approach makes an angle of about 20° with the surface, and that erosion should be proportional to the square of the impact velocity. These predictions were generally confirmed by experiment, although later, more complete tests(7) showed that the erosion rate varied with a somewhat higher power of velocity in the range of 2 to 2.5. This was explained as a consequence of the size effect in metal strength: at lower velocities, the depth of the cut of each particle is smaller and the effective flow stress of the material is greater. Similar effects have been demonstrated in grinding and micromilling(8). The size effect was also evidenced by a reduced rate of erosion per gram of impinging particles when the size of particles was reduced.

Finnie(9,10) analyzed the erosion of ductile metals by writing the equations of motion for a single abrasive grain interacting with a surface and assuming the volume of material removed was proportional to the particle's traverse along the surface. Introducing a set of assumptions concerning the particles and the target material, Finnie solved the equations of motion to obtain the relation(10)

$$V \propto \frac{\rho_p}{p} R^3 U^2 \; f(\alpha) \qquad (1)$$

where V is the volume of material removed from the surface

ρ_p is the density of the particle

p is the horizontal component of the flow stress

R is the average particle radius

U is the particle velocity, and

$f(\alpha)$ is the functional dependence of V upon the impact angle of attack α.

Finnie suggests, on the basis of these equations, that the angle of attack associated with the maximum erosion rate is shifted to 13°, whereas the value of 20° (actually 17° for the magnitude of the parameters used to evaluate $\alpha = 13°$) is a value often quoted in the literature. Another prediction of this theory(5,10) is that at an angle of 90°, (normal impact), the erosion rate should be zero (as indicated in Figure 5-2) since there is no tangential cutting action of the particles. Experiments show, however, that the erosion rate declines from its maximum toward a smaller but nonzero value, thus indicating that another mechanism of erosion is operative.

More general, but less mechanistically oriented, models have been proposed by Bitter(11,12) and Neilson and Gilchrist(13). They included both cutting wear (proposed by Finnie) and erosion due to repeated deformation. In these correlations, the mechanism by which deformation wear occurs is not at all clear. These equations provide a better fit to the experimental data than Finnie's correlation. These models include the idea of a particle energy threshold below which deformation erosion ceases, and a minimum effective angle of impingement below which ductile erosion ceases. Implementation of Bitter's model requires knowledge of the energies necessary to remove a unit volume of a material by cutting wear and deformation wear, respectively. These parameters are determined by performing at least two tests and back-calculating to determine the required values. Nielson and Gilchrist(13) provided simpler equations for deformation wear than those of Bitter(11). They were able to account for the angular dependence of the erosion process and included another parameter to be evaluated experimentally, namely the normal velocity component below which no erosion takes place.

A theoretical analysis for the erosion of brittle materials was presented by Sheldon and Finnie(14). Whereas Bitter's deformation wear analysis is based on an elastic-plastic model which he also applied to brittle materials, Sheldon and Finnie's analysis is based on an elastic brittle model. The penetration of the particle into the specimen is calculated from the Hertzian theory of impact(15-17) and cracks are assumed to spread around the impact point. The volume of material removed by brittle fractures is based on the particle geometry and penetration depth and on the statistical strength properties of the target material. While the theory(14) involves too many unknown parameters to predict the absolute value of the erosion rate, it suggests that the erosion resistance of brittle materials should be related to the square of their fracture strength in bending. Experimental results on various materials showed that the erosion per particle varied from the 2.5 to 4.4 power of impact velocity, and from the 3.1 to the 5.1 power of particle size. Results with angular silicon carbide particles seemed more consistent than those with spherical steel shot.

An important conceptual difference between Bitter's deformation wear theory and Sheldon and Finnie's brittle erosion theory -- even though both begin by analyzing the penetration of a normally impacting particle into the surface using the Hertzian theory of impact -- is that the former adopts an energy balance approach; the latter explicitly rejects the energy viewpoint for brittle materials for which the energy actually causing the fracture is described as a small and unpredictable fraction of the total energy expended.

Hertzian impact theory has been used by several investigators(11,12,14,18) to establish relations describing the response of the material for localized particulate impacts. The Hertzian theory is used, since explicit expressions are derived for the relations between the surface stress components and the mass, impact velocity, and elastic properties of the impinging particle. The theory assumes that impact conditions are essentially a sequence of quasi-static stress states. The validity of this approach must be established for the highly transient stress states associated with small particles impacting at moderate velocities. Furthermore, the physical basis for the application of the Hertzian theory of impact applicable to rounded bodies has not been established in the development of semi-empirical correlations for erosion by irregularly shaped particles to which it is applied(11,14,18). The details of erosion of brittle materials by rounded particles, where Hertzian concepts are shown to be relevant in the initial stage of the erosion process, have been studied(19). The mechanisms of material removed for 70- to 290-μm glass beads impacting glass plates were observed microscopically for progressively eroded specimens. The erosion process was described in terms of a general pit nucleation and growth model(20,21). The identification of the damage modes due to impacts by highly angular solid particles remains an active area of investigation. It should be noted that Hertzian fracture analysis -- that is, the form of fracture associated with indentation of a brittle surface by a rounded indenter, is important in the evaluation of several material properties that are significant in brittle solids: for example, fracture toughness of near-surface material and surface crack size densities.

Two regimes of fracture-induced erosion have been identified in polycrystalline ceramics: a plastic response regime and an elastic response regime(22). The former response induces radial and lateral cracks. This is an elastic-plastic problem and, hence, the hardness H (which determines the amplitude of the elastic strain) and the fracture toughness K_c (which determines the materials' resistance to fracture) are the prime material parameters that control the extent of the fracture (and thereby the erosion). The mechanism of material removal is also relatively well-defined in this regime, where the subsurface lateral cracks are independent sources of chip formation. A semi-empirical characterization of lateral fracture indicates that the erosion V (the average volume of material removal per particle) is given by(23);

$$\bar{V} \approx \chi U^{5/2}\ R^{4}\left[\frac{\rho_{p}}{K_{c}^{5}\ H}\right]^{1/4} \qquad (2)$$

where χ is a constant (but could be a material dependent variable) and H is the quasi-static Vickers hardness in the macro-indentation load independent regime. The predicted trends in erosion with target and projectile properties are typical of the trends observed in brittle materials; also, the numerical exponents fall within the experimental range.

Several types of fracture have been observed in the elastic response regime, from single cone (Hertzian) cracks(14,24,25) to arrays of short circumferential surface cracks(22). Material removal occurs by the interaction of these cracks(24,25), but the details of the process are complex and, as yet, poorly defined. It is evident that the fracture threshold depends on target parameters such as(22) the surface flaw size distribution, the fracture toughness and the elastic wave speed. However, the equivalent parameters involved in the erosion process have not yet been seriously explored. Intuitively, it would be anticipated that the toughness is very important, but the roles of microstructure (grain and pore size and morphology) and the elastic properties cannot be meaningfully presupposed. The analysis of erosion in this regime presented by Sheldon and Finnie(14) predicts reasonable velocity and size exponents, but the analysis is not based on a material removal mechanism that is consistent with experimental observation.

Sheldon and Kanhere(26) present an interesting study of single particle impacts. They support their contention that steady-state material removal can be determined from single spherical bead impacts on the target material on the basis of two observations. The first is that the normalized weight loss measurement for a single 3 mm diameter glass bead impacting annealed 6061 aluminum is "approximately equivalent" to the measured erosion rates quoted from the literature for multiple glass bead impacts on aluminum alloys. The second observation is that the erosion characteristics are quite similar when either spherical or very angular particles are used. Neither of these observations can be supported, even using the sources referenced in their paper. They proposed that material removal by spherical bead impacts on ductile metals occurs by plastic flow of the material along an arc in the direction of the advancing particle until it is strained to fracture. An analysis of this material removal process using Meyer's empirical indentation relation(27) to represent the resistance of the material to penetration gives

$$V \propto \frac{R^3 \; U^3 \left(\rho_p\right)^{3/2}}{H^{3/2}} \qquad (3)$$

where the hardness H is the Vickers hardness of the material. This is the only derived relation for ductile erosion which shows a velocity exponent other than 2; however, hardness to the -3/2 power does not provide a very good correlation with the erosion data for pure metals.

Hutchings, Winter, and Field(28) have also described the correlation between mass removal due to single bead impacts and that due to both multiple spherical and irregular shaped particles. The orientation of a single abrasive particle was investigated by Winter and Hutchings(29,30). The deformations which the particle can produce are based on the rake angle. At positive rake angles above a critical value, ϕ cutting occurs as defined by Finnie(10). In this case, material flows up the face of the tool and is removed along a cutting plane. For negative rake angles greater than ϕ ploughing is dominant. For this case, material flows down the face of the particle and the flow is continuous along the cutting plane. Depending on the impact conditions, it is possible for the particle to rotate and roll along the surface rather than result in a ploughing action. The ploughing action associated with irregular shaped particles produces damage morphologies similar to those associated with spherical bead impacts.

Hutchings and his associates(28-31), ascribed material removal to the raised shear lip around the crater and the hinterland deformation which spread over a large area around the crater. Subsequent particles removed the raised material around the crater along a band of intense shear deformation formed beneath the surface near the lip. The resultant strain concentration was calculated to be associated with the temperature rise due to plastic flow. They also found that a velocity-dependent fraction of the displaced material was removed, whereas former models of material removal assume that all of the material displaced is removed as a single event.

Finnie's theory of ductile erosion indicates that the erosion resistance is inversely proportional to the flow stress of the material which in turn is directly related to the hardness. The results of Finnie, et al.(7), for a variety of pure metals and some steels, are reproduced as Figure 5-3. Note that on this log-log plot there are two distinct and parallel lines, both having a slope which represents a direct proportionality between erosion resistance and Vickers hardness. The one line, which the authors regard as the "main trend," is established by tin, aluminum, silver, copper, tantalum and (with slight deviation) by cadmium and nickel. The other line can be imagined to pass through or close to the points for bismuth, magnesium, the ferrous materials and molybdenum, and represents an erosion resistance about one third that of the "main trend," for the same hardness. The authors propose explanations for these results in terms of the microstructure, work-hardening properties and dynamic properties of the various materials, and make comparisons with corresponding results from abrasive wear tests. Goodwin, et al.(32) and others have also shown that hardness in combination with other properties may provide some correlation for the erosion resistance of alloys.

Finnie, et al.(7) also investigated the effect of prior work-hardening on the erosion resistance of several pure metals and found no effect. Furthermore, the hardening by heat treatment of several steels not only showed no beneficial effect, but actually reduced the erosion resistance slightly. The lack of improved erosion resistance through coldworking and heat treatment of alloys was also found by Smeltzer, et al.(33) and to a lesser extent by Sheldon and Kanhere(26).

Brauer and Kriegel(34) and Truitt(35) found a correlation between erosion resistance and the melting point for pure metals(7). Ascarelli(36) improved the correspondence by defining the thermal pressure of pure metals, such that

$$\rho_T = \frac{\alpha_t\left(T_m - T_R\right)}{X} \qquad (4)$$

where

α_t is the linear coefficient of expansion,

T_M is the melting temperature,

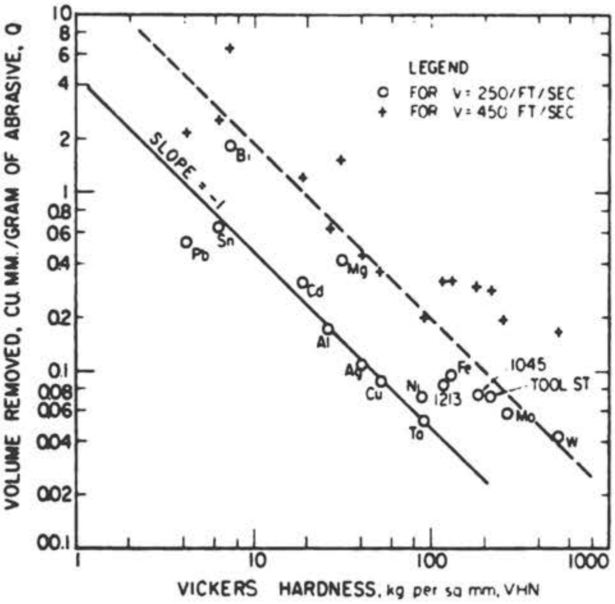


FIGURE 5-3 Volume Removed as a Function of Vickers Hardness When Annealed Metals Are Eroded by 60-Mesh SiC at $\alpha = 20°$ and U = 250 fps (76 ms^{-1}). (Data from Ref. 7. Reprinted by permission of the American Society for Testing and Materials, Copyright.)

T_R is room temperature, and

x is the isothermal compressibility.

By introducing the concept of thermal pressure, Ascarelli states that isothermal compressibility is the primary parameter characterizing the erosion resistance of both brittle and ductile metals. Hutchings(37) found (Figure 5-4) that the data of both Finnie, et al.(7) and of Tadolder(38) for pure metals can be correlated with the product, $C_{\rho}(T_m - T_R)$, where C is the specific heat of the material at room temperature, and ρ_t is the density of the target material. Hutchings stated that the data of Finnie et al.(7) can be fitted to within 25 percent by Ascarelli's thermal pressure, but that comparable agreement is not found for Tadolder's results. The applicability of these thermally oriented relations to metallic alloys has not been determined.

B. EROSION PROCESSES IN METALS

Some information on the erosion of ductile metals has been presented in the preceding discussion. A comparison of the response of various metals to the separate conditions of abrasion and erosion can be made using data on the relative wear or erosion resistance of several materials(7,39). Those results are plotted as a function of static indentation hardness in Figures 5-5 and 5-6. Both figures show that there is a linear increase in resistance to material removal with increasing hardness. However, Figure 5-5 shows that with steel alloys, the efficiency of abrasion resistance is reduced when hardness is increased by heat treatment and that no improvement is produced by cold working. Figure 5-6 shows the same anomalous behavior of materials subjected to erosion. That is, materials with the same intrinsic hardness do not necessarily exhibit similar erosion resistance. It also shows that heat treating steels to increase hardness has virtually no influence on erosion resistance (even with a fourfold increase in hardness). A study of the microstructures in metal alloys resulting from various combinations of strain rate and temperature by the use of deformation mechanism maps(40) shows that most metals have a capacity to deform by several alternative mechanisms. Therefore, depending on the temperature generated by impact and the velocity of impact, the plastic response can be much different from that of static indentation. More importantly, the kind of damage imparted to the near surface microstructure by particle impact can be unique under impact

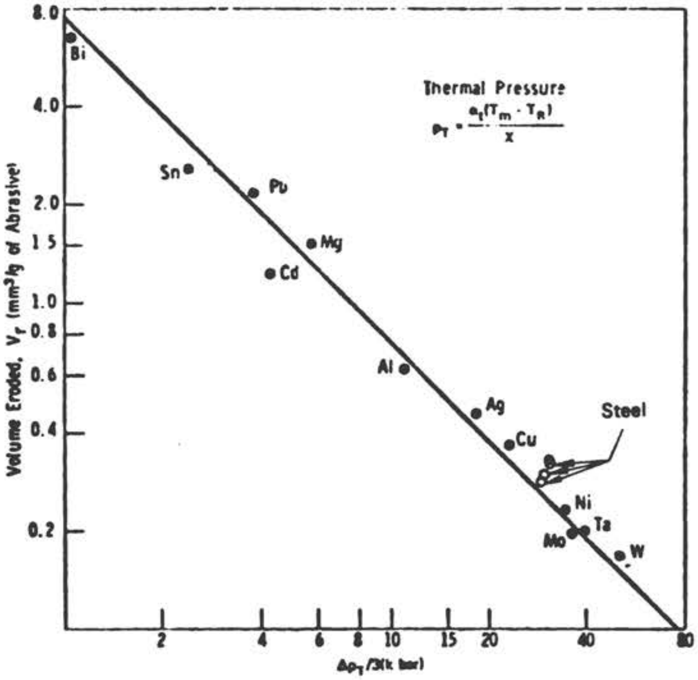


FIGURE 5-4 Correlation of Erosion Data with Thermal Pressure as Defined in Eq. (4). (Data have been taken from Ref. 7 for metals eroded by 60 mesh SiC particles at 20° and 139 ms^{-1}. All the metals were in the annealed state except cadmium.)

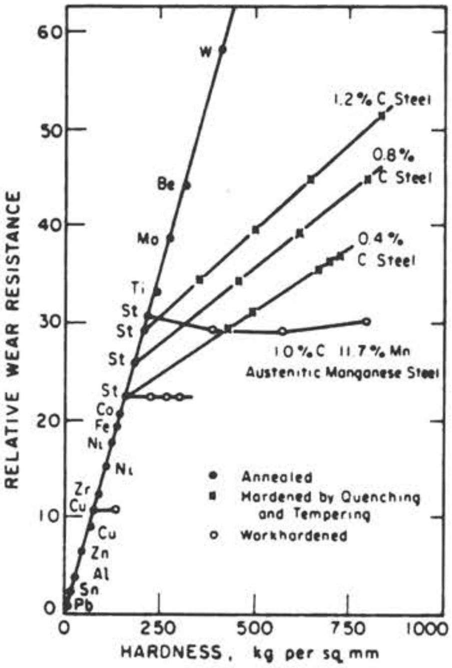


FIGURE 5-5 Relative Wear Resistance as a Function of Indentation Hardness for Metals Rubbed Against Abrasive Paper, from Krushchov (39). (Data from Ref. 7. Reprinted by permission of the American Society for Testing and Materials, Copyright.)

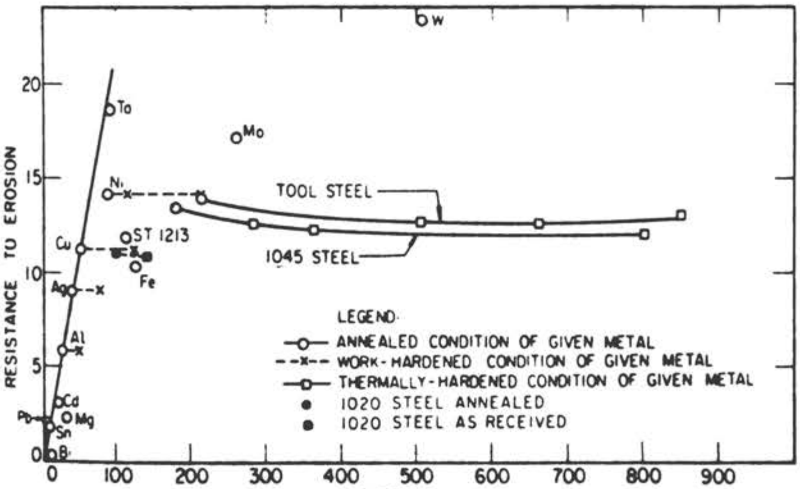


FIGURE 5-6 Resistance to Erosion (Grams of Eroding Particles Per Cubic Millimeter Removed) as a Function of VHN for Erosion by 60-Mesh Silicon Carbide Particles at $\alpha = 20°$ and a Velocity of 250 fps. (Data from Ref. 7. Reprinted by permission of the American Society for Testing and Materials, Copyright.)

conditions, and ultimately will determine the way in which surface material is removed.

Several conjectures have been made regarding the basic erosion process in metals. Finnie(5,6,9,10) hypothesized that angular particles cut into the surface and remove material by a micromachining process. Smeltzer, *et al.*(33,41) claimed to have found support for localized melting of the surface: material being removed as a portion of the molten material adheres to the rebounding particle. Tilly and co-workers(42,43) observed that raised lips of material surround the cavity formed by the impacting particle, especially in the direction of the particle's velocity tangent to the surface of the target. The elevated material is then removed through collisions with the fractured fragments of the impacting particle which shatters upon impact. Hutchings and Winter(28,29,31) have also made the raised lips surrounding the impact site the basis for their mechanism. They assumed that the raised lips are removed by shear during subsequent encounters with impacting particles.

Probably the simplest mechanism for the removal of material by erosion can be deduced from scanning electron microscopy studies of eroded soft materials like aluminum or copper. These materials often develop a cratered surface with thin lips of material extruded from the edges of the craters. These lips are easily knocked off by other impacts and material removal proceeds by cratering and loss of severely displaced material(29). The process of almost unrestricted plastic flow which characterizes cratering has been likened to a phenomenon observed in machining known as thermoplastic shear(44). In this process, plastic flow is localized in bands of heavy slip and, as a result of the high strain rates associated with erosion, localized heating occurs, allowing climb and cross slip of dislocations, essentially nullifying the work-hardening process. This allows extensive flow on slip bands. Ductile materials exhibit a critical strain rate above which thermoplastic shear takes place. The critical strain rate is a function of thermal conductivity, specific heat and strain-hardening properties. Titanium exhibits a remarkable sensitivity to this phenomenon(44). This effect has not been explored nor verified as an aspect of erosion, however, it is suspected that it would be most evident in cases where particles are relatively large and where oxide scale or surface coatings do not exert a major influence on surface deformation.

A more general approach to the erosion of ductile materials involves the accumulation of large amounts of plastic strain and damage in a thin surface zone. Cratering would be a special case involving gross plastic flow in a localized region. In fact, the process of strain accumulation and subsurface fracture leading to release of debris from the surface has been likened to a fatigue process(45). The accumulation of strain and the loss of ductility of near-surface material is currently under investigation to explain the processes of wear and machining(45-47). Erosion, being a surface deformation process, has a fundamental similarity to wear but may exhibit some unique aspects as a consequence of mechanical shock and high strain rates. The shock wave associated with impact on a surface probably produces fast-moving dislocations in the substrate. Transmission electron microscope studies of dislocations formed at impact craters have been reported(49). Such studies can indicate the dislocation processes that are avoided. For example, point defects can form as a result of jogs located on dislocations that cannot move conservatively. As the dislocation velocity approaches that of sound, vacancy generation increases appreciably(49). Vacancy formation is energetically more likely than interstitial formation in this situation. It has been observed that high shock pressures produce vacancies in profusion(50) and this effect can be detected in changes in density of the material subjected to shock. The phenomenon of shock hardening can be related to vacancy formation. The efficiency of jog formation increases with materials having high stacking fault energy or materials with multiple slip systems. This effect has been observed in molybdenum which satisfies both of these requirements(51). The accumulative effect, then, on a material subjected to multiple impacts by particles would be an increase in vacancy concentration in a thin surface layer, leading to coalescence of vacancies into voids and the formation of subsurface cracks. Propagation of the cracks between voids would lead to separation of material from the surface. This process would be influenced by material properties such as stacking fault energy, slip habit, and dynamic-elastic properties (e.g., speed of sound in the material, acoustic impedance). Furthermore, complex wave interactions resulting from reflections from internal defects and multiple wave fronts from simultaneous particle impacts could cause localized nonuniform stress distributions which could propagate cracks or produce cavitation-like effects. Improvement of the erosion models by using material properties more related to the basic mechanisms involved (i.e., dynamic elastic-plastic properties) is needed and should result from further research.

The influences of the target temperature and environment appear to have received little attention for metals. Smeltzer, et al.(33,41), conducted a series of tests on type 2024 Al, Ti-6Al-4V, type-410 stainless steel, and type 17-7 PH stainless steel at temperatures of 70, 400 and 700°F (21, 204, and 371°C). The trend of the data showed a significant reduction in the erosion rates compared with the room temperature values. In order to assure that the erosion was only due to the mechanical interaction of the particles with the surface, the test condition was repeated without particles in the gas flow. No measurable weight gain due to oxidation was found for any target material. In general, there was a complex response pattern at elevated temperatures with regard to perturbation of the room temperature curves of the erosion rate as a function of attack angle.

Tilly and Sage(43) report erosion rates for Ti-6Al-4V, 11 percent chromium steel, a nickel alloy, an aluminum alloy, a beryllium copper alloy, and mild steel exposed to 60-125μm quartz sand at temperatures up to 1110°F (600°C). The erosion resistance of the titanium, aluminum, beryllium copper, and mild steel alloys all decrease with increasing temperature. The erosion resistance of 11 percent chromium steel is slightly improved at elevated temperatures; however, the nickel alloy displays a significant improvement in erosion resistance at temperatures between 932°F (500°C) and 1472°F (800°C). Recently(52,53), measurements on stainless steels and other Ni- and Cr-containing alloys have found that erosion rates usually increase with temperature, although surface films that form can alter that trend for small impacting particles.

Ascarelli(36) suggested that the temperature dependence of erosion results from the competition of two contrasting effects: with increasing temperature, the ductility of metals increases. This leads to larger deformations (for constant impinging particle velocity) and reduces the probability of energy localization. However, this is contrasted by the reduced energy necessary to get a region of the metal to the melting point. In view of the difficulty in predicting or describing the ductility of metals, it is indeed a difficult problem to make predictions for the temperature dependence of erosion for temperatures higher than say 0.5 T_m.

C. EROSION PROCESSES IN CERAMICS

As noted above, several separate erosion processes occur due to the impingement of solid particles including a plastic flow process and localized fracture processes. The plastic material removal process can occur in ceramics at high temperature(54) and/or with small particles(55). This process is characterized by a peak in the material removal rate at an angle of incidence of from 15° to 20°, and a primary functional dependence on the inverse of the target hardness. Material removal by localized fracture is, however, a more commonly encountered erosion mechanism in ceramics. These processes are characterized by a maximum erosion rate at 90° incidence, a functional dependence on the inverse of the fracture toughness; and, in some instances, on the hardness of the target, as seen from Equations (2) and (3).

Erosion by soft or liquid projectiles is less well understood. Although the impact damage threshold is known to depend on the toughness, longitudinal wave velocity, and near-surface flaw size distribution of the target(22,56), the quantitative relations between these parameters and the damage or erosion have not been elucidated. Further, the steady-state erosion may depend on additional parameters such as the grain size, porosity, etc.

In general, it is possible to conclude that a high toughness and hardness are desirable properties for erosion resistance, with high wave velocities (large modulus or low density) and small surface (or near surface) flaw sizes as other possible considerations. The optimization of these properties should be a useful guide to the selection and development of materials for use in erosive environments. For multiphase materials (which typify most refractories), or for particles smaller than the microstructural dimensions, the properties of the least resistant phase (which erodes preferentially and then causes the more resistant phase to fall out) are of importance(54,57).

Values of room temperature hardness and toughness of several ceramics as reported by A. G. Evans based on work for the Office of Naval Research are listed in Table 5-1. Note, that the macrohardness is used as the important deformation parameter (and not the microhardness) and that this property exhibits important dependencies on the microstructure (e.g. reaction-bonded and hot-pressed silicon nitride). Unfortunately, these properties have not been measured for most of the materials presently being used in energy systems, and little information is available for any of the important ceramic materials at elevated temperatures.

Although there is insufficient information available concerning the erosion of ceramics, it is informative to discuss certain general trends. The hardness and toughness generally decrease as porosity increases, e.g., reaction-bonded compared with hot pressed silicon nitride (Table 5-1). Nearly fully dense materials are thus to be preferred. This accounts for the relative success of fusion-cast alumina. However, high internal stresses are present near the grain boundaries in coarse-grained alumina; these reduce the effective local toughness and can lead to

TABLE 5-1 Erosion-Related Parameters for Ceramic Materials at Room Temperature

Material	Fracture Toughness K_c $(MPa)m^{\frac{1}{2}}$	Macro-hardness H (GPa)
Hot-Pressed Si_3N_4	5	16
Reaction-Bonded Si_3N_4	2.2	3.3
Sintered Al_2O_3 (AlSiMag)	4.1	12
Hot-Pressed Al_2O_3	3.5	19
Sintered SiC	3.0	23
Hot-Pressed SiC	3.9	21
Sintered BC	5.9	41
Sintered WC/Co	13.2	13

premature material removal. In noncubic materials (e.g. alumina, silicon nitride) the grain size is also important; for example, the maximum toughness occurs at intermediate grain size (20-40μm in alumina). There may be a major incentive for grain size refinement, especially in the fully dense materials, provided that the grain boundary phases which induce high temperature deformability and toughness degradation can be averted. The ideal material for high erosion resistance would thus be a fully dense, fine grained, single phase material with the appropriate grain morphology (e.g. elongated grains); hence, the excellent erosion resistance of the hot-pressed alumina, sapphire, and hot-pressed Si_3N_4. Fabrication problems are a major constraint on the development of some ideal materials, except for the more sophisticated high-cost components that can be fabricated by hot pressing or sintering. It may be necessary to settle on compromise materials that have the optimum microstructure consistent with the specified fabrication procedure and to allow for the erosion of these materials in the system design.

Turning to the effects of environments, there is, as yet, no significant understanding of erosion/corrosion interaction effects in ceramics. The preliminary information needed to address this problem includes the phase relations between the constituents of the material, microstructure, and the corrosion products, and the thermodynamic relation between the material constituents and the corrosive species. Only a fraction of the information required is available, mostly for the oxide systems. This paucity of the knowledge of the basic chemistry of the systems will impede the rational selection of pertinent erosion/corrosion resistant materials.

Again, however, certain underlying principles for materials selection are apparent, and these should guide the initial materials development studies. Chemical reactions occur rapidly in the presence of liquid phases and, hence, systems with low eutectic temperatures should be avoided(58). Low temperature eutectics are frequently encountered when a significant proportion of silica that forms silicate is present. The silica content of the material should be carefully controlled and, where possible, eliminated, However, not all silicates develop unacceptably low eutectics and good properties might be obtained in certain compatibility triangles between SiO_2 - M_1O - M_2 (SiO_2), where M_1 and M_2 are two different metal constituents. Silica can also lead to problems in low-oxygen partial pressure environments, where volatile silicon monoxide forms and causes the silicate to disassociate rapidly.

An erosion/corrosion interaction phenomenon that has recently been encountered, principally in nonoxide materials, is the adherence of particulates to a viscous oxide surface layer that forms in many high-temperature environments. This prevents erosion but particulate agglomeration eventually leads to clogging of the gas ducts. Therefore, it is not yet apparent whether this type of interaction could be used to advantage or whether it is another detriment.

D. SUMMARY OF GENERAL OBSERVATIONS

Erosion studies in metal systems have produced a substantial amount of data involving exposures at normal ambient temperatures. However, relatively little experimental work has been reported involving elevated temperatures and reactive environments. With regard to coal conversion applications, the environmental effects such as slag deposition and slag corrosion may even dominate the particulate erosion process. Clearly more basic information is needed involving elevated temperature effects and environment effects under simple, controlled conditions. In addition, realistic exposure studies of materials in an appropriate testing program should be undertaken.

Development of erosion models and identification of the mechanisms of material removal have had limited success so far in terms of adequately explaining dependencies of such parameters as particle size and velocity. Less adequate is the understanding of the importance of material parameters. More information obtained from fundamental erosion studies should contribute to more detailed knowledge of the significance of material properties in erosion. This would lead to the ability to model and predict at least relative erosion rates of materials and such effects as the incubation period. Quantitative prediction of erosion rates from basic material properties could require a much greater understanding than is expected for some years. However, a sufficient understanding of the basic erosion process could develop soon and be effective in terms of materials design and improvement for greater erosion resistance.

Several regimes of erosion have been identified in ceramic systems, but the mechanics of material removal have only been sufficiently defined in one impact regime to enable a meaningful initial relationship to be developed between erosion and the primary target and projectile variables. Equivalent studies in the other principal erosion regimes are urged. One material parameter that pertains in all fracture-controlled erosion regimes is the fracture toughness of the near surface. An approach for enhancing erosion resistance in these regimes is to design a microstructure which maximizes the near-surface toughness, for example though grain size refinement and grain morphology modification (multiphase microstructures are not normally effective because the lower toughness constituent can be preferentially eroded).

Erosion/corrosion effects have not been systematically studied in ceramic systems and, hence, quantitative guidelines for microstructural design are not available. There is an urgent need to initiate studies of erosion/corrosion phenomena along the lines discussed in Chapter 7. However, one preliminary guideline that can be deduced from available information is the need to avoid systems that produce low melting point eutectics in the presence of the operating environment.

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Chapter 6

CORROSION

A large portion of the environments to be encountered in energy systems will involve both erosion and corrosion effects. However, relatively little information can be found in the literature pertaining to coupled erosion/corrosion interactions. A general methodology for investigating erocion/corrosion interactions is outlined in Chapter 7. For completeness, a review of corrosion is provided in this chapter for the interested reader and as a reference for future work on combined erosion/corrosion phenomena. Due to the sparsity of understanding pertaining to the combined effects, the relevant aspects of the coupled process as they are known at the present time are summarized in Chapter 7. The remainder of the report can be read without the general corrosion background provided in this chapter.

Corrosion is the change in materials that takes place as a result of chemical reaction with their environment. In many instances these changes are such that materials are eventually deteriorated and destroyed. The conditions that cause corrosion of materials are numerous. The three dominant parameters are temperature, the environment and the material. Depending on the material, corrosion can occur at all temperatures and practically all environments are corrosive to some degree. Even though the consideration of corrosion generally involves an unlimited number of processes and reactions, the conditions which must prevail in order to obtain corrosion resistance are comparatively few. In particular, it is necessary to have conditions such that chemical reaction between the material and the environment does not take place, or reaction does occur but the product of this reaction inhibits all subsequent reaction.

In order to discuss corrosion it is necessary to make some classifications. Corrosion has been classified in many different ways.(1) One method divides corrosion into low- and high-temperature corrosion. The preferred classification has been wet and dry corrosion, where wet corrosion occurs when a liquid is present. Historically, wet corrosion has usually involved aqueous solutions or electrolytes and dry corrosion vapors and gases. Consequently, dry corrosion has been most often associated with high temperature. In recent years, however, high temperature corrosion involving layers of liquids on the surfaces of materials has become a significant means of materials degradation. The presence of the liquid layer produces some effects similar to those of wet corrosion. However, transport of the gaseous reactants through the liquid also occurs and processes similar to those observed in dry corrosion are common. In fact such corrosion consists of processes common to both wet and dry corrosion. In this chapter, corrosion will be discussed by considering first wet and then dry corrosion. The case of corrosion involving layers of liquids on materials will be treated in the dry corrosion section. Finally, within each of these two sections it is necessary to make divisions according to different types of materials. Metallic systems will receive the major emphasis. Ceramics will be the only other type of material given any consideration; however, the environmentally induced deterioration of other nonmetallics such as carbon, glass, plastics, rubber and synthetic elastomers may be of importance in some systems.

A. WET CORROSION*

In discussing wet corrosion it is useful to first consider aqueous corrosion and then examine other types of corrosion involving liquids.

1. Aqueous Corrosion

In all corrosion processes, oxidation and reduction reactions take place. In fact, if there is nothing in the environment that can be reduced, then oxidation of metals and alloys will not take place. When metals are exposed to gases at low temperatures a very thin film of reaction product is formed on the metallic surfaces and the corrosion reaction becomes negligible before the film even becomes visible. In the presence of an aqueous salt solution, however, the oxidation of the metal and reduction of a species in solution occur at different areas on the metallic surface with consequent electron transfer through the metal or alloy from the anode to the cathode. The stable phases formed at the alloy/solution interface may be transported away from the interface by processes such as migration, diffusion, convection, and agitation. Under these circumstances the reactants will not be separated by a reaction-product barrier and the corrosion rate will tend to be linear. Subsequent reaction with the solution may result in the formation of a stable solid phase, but since this is

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* Some of the material contained in this section was adapted from Corrosion Engineering(1).

usually formed away from the alloy/solution interface, it will not afford protection. Such conditions give rise to active corrosion.

A metal surface is said to be passive when (although it is exposed to an electrolyte solution under conditions such that reaction of the metal with the solution should occur with decrease of the free energy of the system) it remains visibly unchanged for an indefinite period. Faraday suggested that passivation is caused by an invisible oxide film on the metal surface, or by an oxidized state of the surface, that prevents contact between the metal and the solution. The oxide-film theory in its modern form, due largely to Evans(2), has been challenged by proponents of theories of change of the metallic surface involving, not film formation, but allotropic modification, electronic modification, or adsorption of ions or molecules. However, it has been supported and extended, with modifications of detail, by great weight of the experimental evidence accumulated since it was proposed.

The question as to whether active corrosion or passivity will develop depends on which one of two possible reactions will prevail; namely, whether metallic ions will move into the solution giving a soluble salt or some non-protective product, or whether some type of barrier-formation, leading to passivity, will predominate. Most metals will suffer active corrosion, yielding soluble salts, in slightly acid solutions, but will become passive in mildly alkaline solutions. Passivity may also occur in neutral solutions but the consumption of OH^- ions renders the liquid acid and conditions can become favorable for active corrosion.

Pourbaix(3) and his co-workers have considered all the possible equilibria between metal and cations, and anions and solid oxides (or hydroxides) of the metal for a given M/H_2O system and have consolidated these data into potential/pH diagrams such as that presented in Figure 6-1.

In these diagrams active corrosion has been defined as an equilibirum activity of metals ions in excess of 10^{-6} gram ion/liter. On this basis, the diagrams can be subdivided into zones of active corrosion, passivity and immunity. It should be noted that the passivation area represents a type of protection entirely different from that met within the immunity area of the diagrams. Within the latter area of the diagram, corrosion will be impossible for reasons of energy whereas in the passivation area corrosion is obstructed for reasons of geometry. In the immunity area, corrosion cannot occur whereas in the passivation area it can occur but it does not occur to any extent because of the barrier that is developed. The diagrams are developed considering equilibria between the metal, ions of the metal,

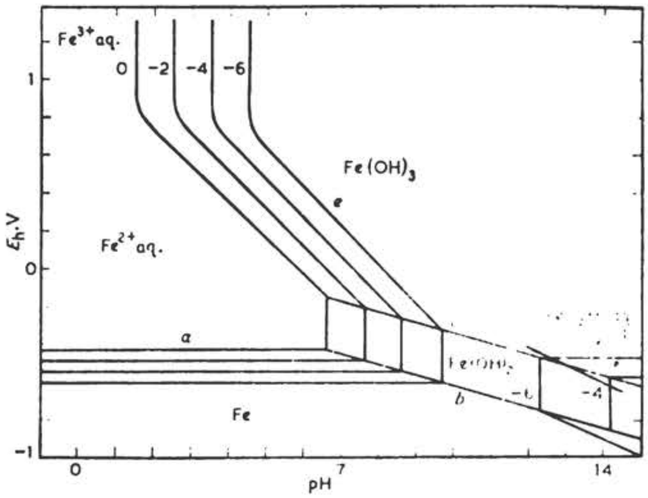

FIGURE 6-1 (a) Simplified Potential/pH Diagram for the Fe/H_2O System Showing the Zones of Thermodynamic Stability of Cations, Anions and Hydroxides of Iron. (The numbers refer to values of isoactivity lines for different ionic species.)

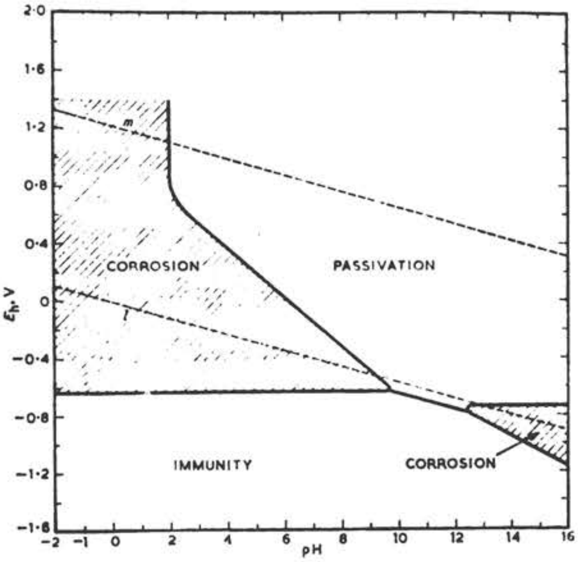

FIGURE 6-1 (b) Diagram Showing Zones of Active Corrosion, Passivity and Immunity for Diagram Presented in (a). (Curves l and m show the reversible hydrogen and oxygen electrodes at $P_{H_2} = P_{O_2} = 1$.)

NOTE: Data from Ref. 5.

and solid oxides or hydroxides for systems in which the reactants are the metal and water or hydroxyl ions. In real solutions a change of pH can be effected only by additions of acid or alkali, and in the case of the former the effect of the addition of an anion may be very significant owing to the formation of metal complexes. Anions like chloride, cyanide, citrate, tartrate, which tend to form soluble complexes may thus extend the zone of corrosion; on the other hand, phosphates, carbonates, silicates, etc., which tend to form insoluble basic compounds, may increase the extent of the zone of passivity. Provided the thermodynamic data are available, diagrams similar to the M/H_2O systems can be evolved for M/H_2O-X systems.

It is convenient to classify wet corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. There are eight forms of aqueous corrosion. Some of these forms are interrelated as will become apparent in the following discussion.

a. Uniform Attack. Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. For example, a piece of steel or zinc immersed in dilute sulfuric acid will normally dissolve at a uniform rate over its entire surface.

b. Galvanic or Two-Metal Corrosion. A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them. Corrosion of the less corrosion-resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal cathodic. Usually the cathode or cathodic metal corrodes very little or not at all in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic, or two-metal corrosion.

c. Crevice Corrosion. Intense localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. As a result, this form of corrosion is called crevice corrosion or, sometimes, deposit or gasket corrosion. Until recently, it was believed that crevice corrosion resulted simply from differences in metal ion or oxygen concentration between the crevice and its surroundings. Consequently, the term concentration cell corrosion has been used to describe this form of attack. More recent studies(4) have shown that although metal-ion and oxygen-concentration differences do exist during crevice corrosion, these are not its basic causes. Oxygen depletion in the crevice tends to cause an excess of positive charge in the solution since oxygen is not available for reaction. This excess of positive charge is balanced by the migration of anions, for example chloride ions, into the crevice. Except for alkali metals, metal salts hydrolize in water and consequently hydrogen ions are also produced in the crevice. For reasons which are not yet understood, both chloride and hydrogen ions accelerate the dissolution rates of most metals and alloys. Consequently, the dissolution rate of the metal or alloy is increased and this increase in dissolution causes increased migration of anions into the crevice as well as the production of hydrogen ions in the crevice. Therefore, the result is a rapidly accelerating or autocatalytic process.

d. Pitting. Pitting is a form of extremely localized attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases they are relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth. Pitting is one of the most destructive and insidious forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. It is often difficult to detect pits because of their small size and because the pits are often covered with corrosion products. The mechanism of pit growth is virtually identical to that of crevice corrosion. However, in the case of pitting, it is necessary to account for the initiation of pitting, whereas in crevice corrosion the reason for changes in solution composition is caused by the crevice itself. At present the cause of pit initiation has been proposed to be momentarily high metal dissolution in localized areas which allows anions (e.g. chloride ions) to migrate to these areas which stimulates metal dissolution and consequently a pit is developed.

e. Intergranular Corrosion. Under certain conditions, grain interfaces in alloys are very reactive and intergranular corrosion results. Localized attack at, and adjacent to, grain boundaries, with relatively little corrosion of the grains, is intergranular corrosion. The alloy disintegrates (grains fall out) and/or loses its strength. Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain-boundary areas. Small amounts of iron in aluminum, wherein the solubility of iron is low, have been shown to segregate in the grain boundaries and cause intergranular corrosion. It has been shown that based on surface-tension considerations, the zinc content of a brass is higher at the grain boundaries. Depletion of chromium in the grain-boundary regions results in intergranular corrosion of stainless steels.

f. Selective Leaching. Selective leaching is the removal of one element from a solid alloy by corrosion processes. The most common example is the selective removal of zinc in brass alloys (dezincification). Similar processes occur in other alloy systems in which aluminum, iron, cobalt, chromium, and other elements are removed. Selective leaching is the general term to describe these processes, and its use precludes the creation of terms such as dealuminumification, decobaltification, etc. Parting is a metallurgical term that is sometimes applied, but selective leaching is preferred.

g. Erosion/Corrosion. Erosion/corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. Generally, this movement is quite rapid, and mechanical wear effects or abrasion are involved. Metal is removed from the surface as dissolved ions, or it forms solid corrosion products which are mechanically swept from the metal surface. Sometimes movement of the environment decreases corrosion, particularly when localized attack occurs under stagnant conditions, but this is not erosion/corrosion because deterioration is not increased. Erosion/corrosion is characterized by the appearance of grooves, gullies, waves, rounded holes, and valleys and usually exhibits a directional pattern. Figure 6-2 is a sketch representing erosion/corrosion of a heat-exchanger tube handling water. In many cases, failures because of erosion/corrosion occur in a relatively short time, and they are unexpected largely because evaluation corrosion tests were run under static

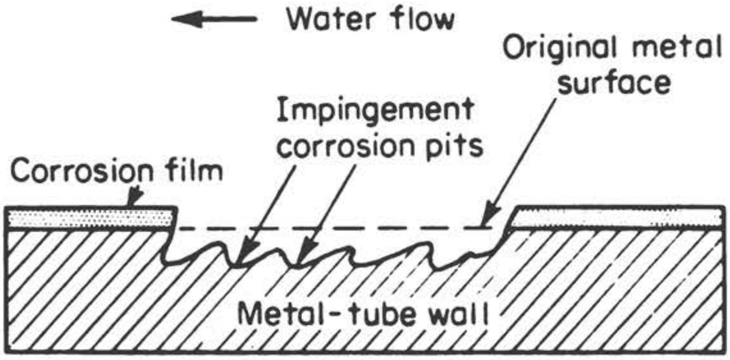

FIGURE 6-2 Schematic Illustrating Erosion/Corrosion of Condenser Tube Wall. (Data from Ref. 1. Copyright 1967 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Book Company.)

conditions or because the erosion effects were not considered.

h. Stress Corrosion. Stress-corrosion cracking refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. Many investigators have classified all cracking failures occuring in corrosive mediums as stress-corrosion cracking, including failures due to hydrogen embrittlement. However, these two types of cracking failures respond differently to environmental variables. To illustrate, cathodic protection is an effective method for preventing stress-corrosion cracking whereas it rapidly accelerates hydrogen-embrittlement effects. Hence, the importance of considering stress-corrosion cracking and hydrogen embrittlement as separate phenomena is obvious. For this reason, the two cracking phenomena are discussed separately in this chapter.

During stress-corrosion cracking, the metal or alloy is virtually unattacked over most of its surface, while fine cracks progress through it. This cracking phenomenon has serious consequences since it can occur at stresses within the range of typical design stress. The stresses required for stress-corrosion cracking are compared with the total range of strength capabilities for type 304 stainless steel as shown in Figure 6-3. Exposure to boiling $MgC1_2$ at 310°F (154°C) is shown to reduce the strength capability to approximately that available at 1200°F(650°C).

The two classic cases of stress-corrosion cracking are "season cracking" of brass, and the "caustic embrittlement" of steel. Both of these obsolete terms describe the environmental conditions present which led to stress-corrosion cracking. Season cracking refers to the stress-corrosion cracking failure of brass cartridge cases. During periods of heavy rainfall, especially in the tropics, cracks were observed in the brass cartridge cases at the point where the case was crimped to the bullet. It was later found that the important environmental component in season cracking was ammonia resulting from the decomposition of organic matter.

Many explosions of riveted boilers occurred in early steam-driven locomotives. Examination of these failures showed cracks or brittle failures at the rivet holes. These areas were cold-worked during riveting operations, and analysis of the whitish deposits found in these areas showed caustic, or sodium hydroxide, to be the major component. Hence, brittle fracture in the presence of caustic resulted in the term caustic embrittlement. While stress alone will react in ways well known in mechanical metallurgy (i.e., creep, fatigue, tensile failure) and corrosion alone will react to produce characteristic

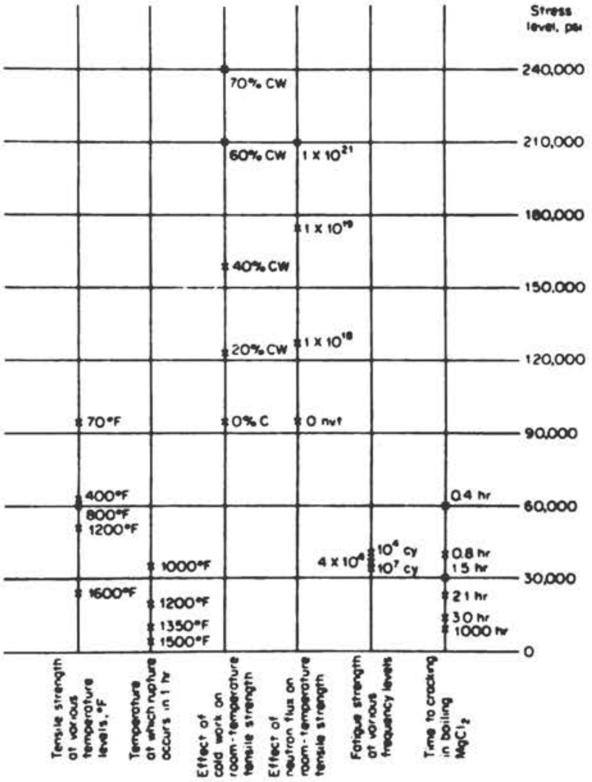

FIGURE 6-3 Comparison of Fracture Stresses by Various Techniques Compared with Stress-Corrosion Cracking. Material: type 304 stainless. (Data from Ref. 1. Copyright 1967 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Book Company and author, R. W. Staehle, Ohio State University.)

dissolution reactions, the simultaneous action of both sometimes produces disastrous results.

Not all metal-environment combinations are susceptible to cracking. A good example is the comparison between brasses and austenitic stainless steels. Stainless steels crack in chloride environments but not in ammonia-containing environments, whereas brasses crack in ammonia-containing environments but not in chlorides. Further, the number of different environments in which a given alloy will crack is generally small. For example, stainless steels do not crack in sulfuric acid, nitric acid, acetic acid, or pure water, but they do crack in chloride and caustics. The important variables affecting stress-corrosion cracking are temperature, solution composition, metal composition, stress, and metal structure.

Although stress corrosion represents one of the most important corrosion problems, the mechanism involved is not well understood. This is one of the big unsolved questions in corrosion research. The main reason for this situation is the complex interplay of metal, interface, and environment properties. Further, it is unlikely that a specific mechanism will be found that applies to all metal-environment systems. The most reliable and useful information has been obtained from empirical experiments. Corrosion plays an important part in the initiation of cracks. A pit, trench, or other discontinuity on the surface of the metal acts as a stress raiser. Stress concentration at the tip of the "notch" increases tremendously as the radius of notch decreases. Stress-corrosion cracks are often observed to start at the base of a pit. The role of tensile stress has been shown to be important in rupturing protective films during both initiation and propagation of cracks.

i. Hydrogen Damage. Hydrogen damage, although not a form of corrosion, often occurs indirectly as a result of corrosion attack. Therefore, hydrogen damage is not one of the eight forms of aqueous corrosion but it must be considered when discussing the deleterious effects of aqueous solutions on metals.

Hydrogen damage is a general term which refers to mechanical damage of a metal caused by the presence of, or interaction with, hydrogen. Hydrogen damage may be classified into four distinct types:

- hydrogen blistering
- hydrogen embrittlement

- decarburization
- hydrogen attack

Hydrogen blistering results from the penetration of hydrogen into a metal. The result is local deformation and, in extreme cases, complete destruction of the vessel wall. Hydrogen embrittlement also is caused by penetration of hydrogen into a metal, which results in a loss of ductility and tensile strength. Decarburization, or the removal of carbon from steel, is often produced by moist hydrogen at high temperatures. Decarburization lowers the tensile strength of steel. Hydrogen attack refers to the interaction between hydrogen and a component of an alloy at high temperatures. A typical example of hydrogen attack is the disintegration of oxygen-containing copper in the presence of hydrogen. Decarburization and hydrogen attack are high-temperature processes. Hydrogen blistering and hydrogen embrittlement may occur during exposure to petroleum, in chemical process streams, during pickling and welding operations, or as a result of corrosion. Since both of these effects produce mechanical damage, catastrophic failure may result if they are not prevented.

2. Acid Corrosion

Most of the severe corrosion problems encountered involve the mineral acids or their derivatives. Sulfuric, nitric and hydrochloric acids are the three most important inorganic acids. In acidic corrosion, the cathodic reaction is frequently the reduction of hydrogen ions. In all cases hydrogen may not be evolved since it may react to form another compound. For example, when magnesium is attacked by HCl, hydrogen is evolved; but when it is attacked by nitric acid, ammonium nitrate is formed.

The choice of metals and alloys for nitric acid services is quite limited as far as variety is concerned. For plant applications, the choice is usually between only two general classes of materials -- the stainless steels and the high-silicon iron alloys. The choice is further limited because a minimum chromium content is required in the stainless materials, and the high-silicon alloys are available only in cast form. The beneficial influence of chromium on the resistance of low carbon steel to boiling 65 percent nitric acid is evident in data presented in Table 6-1.

Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of construction. Extreme care is required in the selection of materials to handle the acid by itself, even in

TABLE 6-1 Influence of Chromium on Resistance of Low-Carbon Steel to Boiling 65 Percent Nitric Acid

Percent Cr	Average Corrosion Rate, mils per year
4.5	155,000
8.0	1,700
12.0	120
18.0	30
25.0	8

NOTE: Data from Ref. 1. Copyright 1967 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Book Company.

relatively dilute concentration, or in process solutions containing appreciable amounts of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys.

When aeration or oxidizing agents are also present, corrosive conditions may be very rugged. Many unexpected failures in service are explained by the presence of ostensibly minor impurities. The commercial or muriatic acid often behaves very differently from the chemically pure or reagent grade hydrochloric acid as far as corrosion is concerned.

Hydrofluoric acid is unique in its corrosion behavior. High-silicon cast irons, stoneware, and glass are generally resistant to most acids, but all of these materials are readily attacked by hydrofluoric acid. Magnesium shows rather poor corrosion resistance to many acids, but this metal resists attack by hydrofluoric acid; in fact, some shipping containers for this acid are made of magnesium. Below 1 percent concentration some attack occurs, but in concentrations of 5 percent and over the magnesium is practically immune to corrosion because of the formation of a surface fluoride film, and corrosion of the metal is retarded. This same surface effect also applies to other metals and alloys which resist corrosion by hydrofluoric acid.

Corrosion by phosphoric acid depends somewhat on the methods of manufacture and the impurities present in the commercial finished product. Fluorides, chlorides, and sulfuric acids are the main impurities present in the manufacturing processes and in some marketed acids. For example, the high-silicon irons, the austenitic stainless steels without molybdenum (added for pitting resistance), ceramics, and tantalum are appreciably affected by the presence of hydrofluoric acid. Two of the most widely used alloys are type 316 stainless steel and Durimet 20® (and similar alloys). These alloys show very little attack in concentrations up to 85 percent and temperatures including boiling.

Acetic acid is the most important organic acid from the standpoint of quantity produced. Many other organic acids show similar corrosion behavior and, in the absence of data, one must assume that they all behave alike. Types 316 and 304 stainless steels, copper and bronzes, 1100 and 3003 aluminum, Durimet 20®, Duriron®, and Hastelloy® alloy C are widely utilized for handling acetic acid. Type 316 SS is preferred for the more severe conditions involving glacial (98%+) acid at elevated temperatures. Aluminum, copper, and type 304 are good for room-temperature glacial acid and for more dilute acid. Copper was the early work horse for acetic acid, but has lost much ground to the stainless steels, partly because of the reduced cost differential between these materials. Durimet 20 is used for pumps and Duriron for pumps, lines, and columns. Hastelloy alloy C and Chlorimet® alloy 3 are used for the most severe conditions.

Organic acids are "weaker" than the inorganic acids because they are only slightly ionized. Formic acid is one of the strongest organics and is the most corrosive. Aluminum is not suitable for formic acid. Maleic and lactic acids are more aggressive than acetic with regard to intergranular attack on stainless steels. The fatty acids, e.g., stearic, are less corrosive, but 316 is required at high temperatures. Naphthenic acid presents a corrosion problem in petroleum refining mainly because of the high temperatures involved. Citric and tartric acid are found in food products. Table 6-2 lists data on corrosion of metals by organic acids.

The common alkalies such as caustic soda (NaOH) and caustic potash (KOH) are not particularly corrosive and can be handled in steel in most applications where contamination is not a problem. However, one must guard against stress corrosion in certain concentrations and temperatures. Rubber-base and other coatings and linings are applied to steel equipment to prevent iron contamination. Nickel and nickel alloys are extensively used for combating corrosion by caustic.

3. Liquid Metal Corrosion

The corrosion of metals and alloys by liquid metals generally follows the pattern of the formation of metallic alloys, i.e. solution and intermetallic compound formation. Although electron transfer may be involved, the oxidation and reduction processes which characterize corrosion by ionic solutions are absent except in a few special cases. The nature of liquid-metal corrosion varies depending on whether the fluid is static or is moving relative to its container, on whether the temperature is constant or varying throughout the system, and on whether the container is a single metal or a composite of two or more metals. As in other corrosion processes, the presence of impurities in the fluid may also be of importance. All the processes, however, involve solution as a first step.

No adequate theory is yet available to explain the variation in the solubilities of metals in molten metals. It has been observed(5) that plotting the solubilities of metals in a number of solvent metals showed a periodic variation with the solute and not the solvent, i.e. a given metal such as manganese showed a consistently high solubility in molten magnesium, tin, bismuth, and copper,

TABLE 6-2 Corrosion by Organic Acids

Acid	*Concentration*	*Temperature, °F*	*Aluminum**	*Copper & bronze†*	*Type 304*	*Type 316*	*Durimet 20*	*Duriron*
Acetic	50%	75	●	●	○	●	●	●
Acetic	50%	212	×	○	□	●	●	●
Acetic	Glacial	75	●	●	●	●	●	●
Acetic	Glacial	212	○	×	×	○	○	●
Citric	50%	75	○	□	○	○	●	●
Citric	50%	212	□	□	×	○	○	●
Formic	80%	75	○	○	○	●	●	●
Formic	80%	212	×	○	×	○	○	●
Lactic	50%	75	○	○	○	●	●	○
Lactic	50%	212	×	○	×	○	○	○
Maleic	50%	75	○	□	○	○	●	●
Maleic	50%	212	×	—	○	○	○	○
Naphthenic	100%	75	○	○	●	●	●	—
Naphthenic	100%	212	○	×	●	●	●	—
Tartaric	50%	75	○	□	●	●	●	●
Tartaric	50%	212	×	—	●	●	●	●
Fatty	100%	212	●	□	○	●	●	●

LEGEND: ● Less than 2 mpy, ○ less than 20 mpy, □ from 20 to 50 mpy, × over 50 mpy.

* More than 1% water for napthenic and fatty acids.

† Aeration greatly increases corrosion rate.

SOURCE: Corrosion Data Survey, Shell Development Co., 1960.

NOTE: Data from Ref. 1. Copyright 1967 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Book Company and Shell Development Co.

compared with iron or chromium. This variation has been correlated with the solute lattice energy and hence with the latent heat of fusion. This correlation is useful in making qualitative predictions.

In the more practical sense, solution may be uniform or localized. Preferential solution can take two forms:

(i) leaching: one component of an alloy is preferentially dissolved, an example being nickel which is leached from stainless steels by molten lithium and by bismuth, sometimes to such an extent that voids are left in the steel.

(ii) intergranular attack: the liquid penetrates along the grain boundaries, owing either to the accumulation of soluble impurities in the boundaries or to the development at the junction of a grain boundary with the metal surface of a low dihedral angle to satisfy surface-energy relationships. When this process is accompanied by stress, catastrophic failure can occur, a classical example being the action of mercury on brass.

The solubility of metals, S, in molten metals generally varies with temperature according to the relationship $\log S = A - (B/T)$ where A and B are constants for a given system. Therefore, it is possible for more material to dissolve from a container at its highest-temperature end than at the low-temperature end, and, if the melt flows round the container by natural or forced convection, the liquid arriving at the cold region will be supersaturated and will precipitate solute until equilibrium is attained. If it is then recycled to the hot end, it dissolves more metal until saturated and then returns to the cold end to precipitate this excess. This process is termed "thermal gradient mass transfer."

In a container or a "loop" in which a molten metal is flowing but where there is not necessarily a temperature gradient, a type of corrosion can occur by transfer of material along an activity gradient. It is convenient to discuss this phenomenon by considering metal and nonmetal transfer.

a. Metal Transfer. When two different metals are separated by a third, liquid, metal and one or both solid metals dissolve in the liquid, an alloying action may be observed. The liquid metal itself may form an intermetallic compound on the surface of one or both of the solid metals, in which case a diffusion barrier will build up and the reaction will gradually slow down. If, however, this does not occur, an alloy of the two solid metals will be formed either in the melt or on the surface of one of the solids. The most common effect is the formation of a layer at the surface of the less soluble of the two solid metals, this layer being made up of all or some of the compounds which are formed between the two solids. The rate-controlling step is the diffusion of the less soluble metal through this surface layer to react with the other species of solute atom.

b. Nonmetal Transfer. The elements of primary importance in this context are oxygen, nitrogen, carbon, and hydrogen. They play a predominant role in the technology of the liquid alkali metals. Their origin is not, in general, a massive constituent but rather leakages in the circuit or impurities remaining after construction. These nonmetallic contaminants can produce corrosion effects similar to those observed in gaseous corrosion. The transfer of a nonmetal, X, dissolved in a molten metal, M', to another metal, M", will depend on the relative free energies of formation of M'X and M"X. Thus, sodium will give up oxygen to Zr, Nb, Ti, and U, as the free energy of oxide formation of these metals is greater than that for sodium; on the other hand, sodium will remove oxygen from Fe, Mo and Cu.

4. Corrosion in Fused Salts

There are two cases in which a metal can be attacked by a salt melt: if it is soluble in the melt, or if it is oxidized to metal ions. In the first case, attack occurs by direct dissolution without oxidation of the metal and the mechanism is likely to be closely similar to attack by liquid metals. If the solubility is appreciable, excessive corrosion can be expected, but with few exceptions metals appear to be appreciably soluble only in their own salts. The main exceptions are certain noble metals, such as gold, for which there is evidence of some metal solubility in molten alkali chlorides. Most of the metals of the first and second groups of the periodic table are soluble in their own halides, and in certain cases there is complete miscibility at high temperatures.

Electrochemically, the system metal/molten salt is somewhat similar to the system metal/aqueous solution, although there are important differences, arising largely from differences in temperature and in electrical conductivity. Most fused salts are predominantly ionic, but contain a proportion of molecular constituents, while pure water is predominantly molecular, containing very low activities of hydrogen and hydroxyl ions. Since the aqueous system has been extensively studied, it may be instructive to point out some analogues in fused-salt systems.

Setting aside for the moment effects due to passivity, a metal can be oxidized (corroded) only if it is in contact with something it can reduce. In an aqueous electrolyte, either hydrogen ions are displaced to form hydrogen gas, or some other solute (often dissolved oxygen) is reduced; in a salt melt, either one of the metal cations (corresponding to hydrogen ions in the aqueous solution) is displaced to produce metal, or some molecular species (such as dissolved chlorine or oxygen) or an ion (such as nitrate or ferric ion) is reduced. In aqueous electrolytes, therefore, metals which are too noble to displace hydrogen corrode only if dissolved oxygen or some other reducible substance is present, and when the reducible material has been used up, corrosion ceases; the metal has become "immune," i.e. has reached electrochemical equilibrium with its environment. The position is similar in fused salt corrosion, and the relative nobilities of the salt melt and the metal are important. A noble metal in contact with a pure melt of a base-metal cation can react only to a very limited extent (provided the anion is not reducible); for example, nickel cannot displace sodium from a sodium chloride melt to any appreciable extent and hence nickel will not corrode in molten sodium chloride unless some other reducible impurity is present.

In practice, the conditions under which metals are exposed to fused salts will be of three types:

- conditions under which equilibrium between metal and salt melt can be reached and maintained;
- conditions under which equilibrium cannot be reached; and
- conditions under which passivity is possible.

In metal/melt systems, just as in aqueous systems, one possible way of ensuring adequate corrosion resistance is to choose conditions such that the metal is passive, which requires that it should become covered with an adherent, compact, insoluble film or deposit, preventing direct contact of the metal with its environment. Any melt which reacts with a metal to give a corrosion product insoluble in the melt is, in principle, capable of passivating the metal -- for example, passivity can be expected to occur in oxidizing salts in which metal oxides are sparingly soluble. Thus, iron is highly resistant to alkali nitrate melts because it becomes passive, and passivity has also been observed by electrode potential measurements of an iron electrode in chloride melts containing nitrates, although in this case the oxide corrosion product is not particularly protective.

In cases where passivity is impossible, corrosion can be prevented if the metal can reach equilibrium with the melt. The system usually undergoes some corrosion initially, when traces of oxidizing impurities are reduced and the redox potential of the melt falls. Finally, after a certain amount of corrosion has occurred, the metal becomes immune and corrosion ceases.

Under certain conditions, it will be impossible for the metal and the melt to come to equilibrium and continuous corrosion will occur, this is often the case in practice when metals are in contact with molten salts. Rates of corrosion under conditions where equilibrium cannot be reached are controlled by diffusion and interphase mass transfer of oxidizing species and/or corrosion products; geometry of the system will be a determining factor.

The obvious method of reducing corrosion in fused salts is to choose a system in which either the metal can come to equilibrium with the melt, or else truly protective passivity can be attained. In most cases in industry, neither of these alternatives is used. In fact, fused salt baths are usually operated in air atmosphere, and the problem is the prevention of excessive corrosion. This can be done in two ways: (a) by reducing rates of ingress of oxidizing species (mainly O_2 and H_2O) from the atmosphere, and rates of their diffusion in the melts, and (b) by keeping the oxidizing power (redox) potential of the melt low by making periodic additions to the bath.

5. Ceramic Materials

Ceramic materials generally have better resistance to wet corrosion than metallic systems. Some acids and numerous molten salts can attack ceramics. In the case of molten salts corrosion usually involves solution of the oxide in the salt via the formation of various ionic species. The corrosion process can be controlled, as in the case of metallic systems, by developing passivity via barrier formation or by having the salt melt and the ceramic achieving equilibrium with each other (i.e. immunity). Some ceramics having industrial applications are as follows:

a. Acidbrick. This material is made from fireclay with a silica content about 10 percent greater than in ordinary firebrick. A common application is lining of tanks and other vessels to resist corrosion by hot acids or erosion corrosion. A brick-lined steel tank usually contains an intermediate lining of lead, rubber, or a plastic. Acid-resistant cements and mortars join the brick. Floors subject to acid spillage are made of acidbrick.

b. Stoneware and Porcelain. Both of these find many applications because of their good corrosion resistance. Porcelain parts are usually smaller in size than stoneware, and the porcelain is less porous. Both can be glazed for easy cleaning. Stoneware and porcelain show tensile strengths of about 2000 and 5000 lb/in^2, respectively. Stoneware sinks, crocks, and other vessels, absorption towers, pipes, valves, and pumps are available. Porcelain can be made into similar equipment (e.g., acid nozzles) and is widely used as insulators and spark plugs.

c. Structural Clay. These clay products include building, fire, sewer, pipe, paving brick, terracottas, and roofing and wall tile. Hot acids sometimes attack these materials.

d. Glass. Glass is an amorphous inorganic oxide, mostly silica, cooled to a rigid condition without crystallization. Glass laboratory ware, such as Pyrex, and containers are well known. Piping and pumps are available. Transparency is utilized for equipment such as flowmeters. Glass fibers are widely used for air filters, insulation, and reinforced plastics. Hydrofluoric acid and caustic attack glass, and it shows slight attack in hot water.

e. Vitreous Silica. This material, also called fused quartz (almost pure silica), has better thermal properties than most ceramics and excellent corrosion resistance at high temperatures. It is used for furnace muffles, burners, reaction chambers, absorbers, piping, etc., particularly where contamination of product is undesirable.

f. Concrete. Tanks and pipes made of concrete are well known for handling mild corrosives. If aggressive environments are involved, the concrete is protected by coatings or linings.

B. DRY CORROSION

Dry corrosion has analogs to active corrosion, passivity and immunity of wet corrosion. For example materials could be called immune when the compositions of the gas environments are such that reactions with the materials are not thermodynamically possible. Passivity would correspond to the case where the corrosion products are effective in inhibiting subsequent reaction between the materials and their gas environments and active corrosion would apply to the case where the reaction products were ineffective in inhibition. In dry corrosion, the reaction products determine whether or not a material will be resistant to a particular environment. Resistance to corrosion is achieved by having the reaction products formed as a barrier on the surface of materials separating them from the corrosive environments.

A great variety of dry corrosion reactions are possible. In the following paragraphs, metallic systems will be emphasized. More importantly, dry corrosion will be discussed by first considering the stability of reaction-product barriers on the surfaces of alloys and then examining the protectivity of such barriers. Finally, dry corrosion processes in general will be compared.

1. Stability of Reaction-Product Barriers

a. Thermodynamics. When a multicomponent alloy containing elements A is reacted in a gas environment containing reactants X (subscripts m and n are used to identify the components of the reactions; for simplicity, only products of the type AX are considered), the following reactions can initially occur on the alloy surface:

$$A_i + X_j = A_iX_j \tag{1}$$

$$i = 1, 2, 3, \ldots, M; \; j = 1, 2, 3, \ldots, n$$

provided that the activities of the reactants exceed the values of the equilibrium constants for these reactions. For example, A_1X_1 will be formed provided

$$a_{A_1} a_{X_1} > 1/K \tag{2}$$

where

$$K = \exp\,(-\Delta G^{\circ}_{A_1X_1}/RT) \tag{3}$$

and $\Delta G^{\circ}_{A_1X_1}$ is the standard free energy of formation of A_1X_1.

However, this condition is necessary but not sufficient for the permanent stability of the phases, since displacement reactions must also be considered. Displacement reactions can occur because certain elements in the alloy have a greater affinity for the oxidant than do other elements, and reactions of the following type can occur:

$$A_1 \text{ (alloy)} + A_2X_1 = A_1X_1 + A_2 \text{ (alloy)} \qquad (4)$$

The direction of such displacement reactions is determined by the values of the activities of A_1 and A_2 in the alloy in comparison to the equilibrium values defined by the equation

$$a_{A_2}/a_{A_1} = \exp\left[(\Delta G^\circ_{A_1X_1} - \Delta G^\circ_{A_1X_1})/RT\right] \qquad (5)$$

where it should be noted that the activities of A_1 and A_2 at which the three-phase equilibrium described by Equation (4) will exist are determined by the difference between the standard free energies of formation for A_2X_1 and A_1X_1. If the standard free energy of formation for A_1X_1 is much more negative than that for A_2X_1, then the value of a_{A_2}/a_{A_1} will be a large number and the displacement reaction described by Equation (4) will proceed to the right even when the activity of A_1 in the alloy is small compared to that for A_2. Similar conditions hold for the case where a certain oxidant in the gas has a greater affinity for an element than other oxidants, and therefore displacement reactions of the following type can also occur:

$$a_1X_2 + X_1\text{(gas)} = A_1X_1 \times X_2\text{(gas)} \qquad (6)$$

In view of these displacement reactions, thermodynamic factors in even complex systems favor the formation of the most stable compounds on the surfaces of alloys; in particular, conditions are such that the oxidation of one element in the alloy by one oxidant in the gas environment is favored.

In many applications for alloys at elevated temperatures, oxygen is present in the gas environment. Moreover, the affinity of most metallic systems for oxygen is usually greater than that for other oxidants. Therefore, it is thermodynamically favorable to have oxide barriers formed on alloys in multicomponent gas environments. Even though oxide barriers may be developed on the surface of alloys, phases can be formed by reaction with other oxidants in the gas. For example, when a continuous oxide barrier is developed on the surface of an alloy, the oxygen activity at the alloy-oxide interface is substantially reduced and reaction of the alloy with other oxidants can occur providing the other oxidants can penetrate the oxide barrier.

The stability of different phases on the surfaces of alloys in various environments can be identified by constructing stability diagrams. In Figure 6-4 the oxide phases stable on different nickel-chromium alloys are identified. Figure 6-5 shows the phases stable on nickel in gases containing different amounts of sulfur and oxygen. Such diagrams can become complicated for multicomponent alloys exposed to multicomponent gases, but it is usually possible to simplify the diagrams by considering only the most thermodynamically favorable reactions.

b. Kinetics. In the previous section, it has been shown that dry corrosion reactions favor the formation of the most thermodynamically stable reaction products. The spatial distribution of the reaction products is determined by kinetic processes. The spatial distribution of the reaction products is crucial to the subsequent course of the corrosion process. For example, even though the initial stages of the corrosion process are thermodynamically selective, if the resulting reaction products do not influence the corrosion process, then all of the stable phases will be eventually formed. In order for reaction products to influence the corrosion process they should be present on the surfaces of alloys. In some instances, the corrosion products are formed away from metal or alloy surfaces and exert little effect on the corrosion process. For example, when zinc is heated at 400°C in a low oxygen partial pressure, ZnO is formed as a smoke above the metal. However, in most instances, the vapor pressures of metals and the metallic reaction products are sufficiently low such that the reaction products are formed on the surfaces of alloys.

In considering how kinetic processes affect the spatial distribution of corrosion products on the surfaces of alloys, it is worth noting that prior to reaction the stable phases are determined solely by thermodynamic factors. As corrosion begins, due to kinetic factors, the compositions of the alloy and the gas adjacent to one another can change and other phases therefore become stable. To consider these effects it is convenient to first examine the case where the gas composition is constant and the alloy composition changes and then discuss the case where the gas composition changes and the alloy composition is fixed.

As reaction between an alloy and oxygen takes place, it is frequently the case that the alloy does not

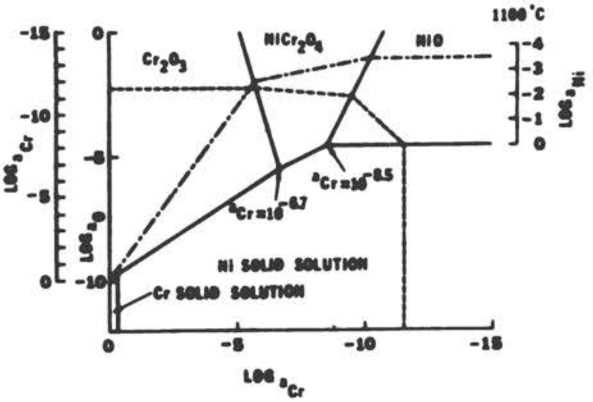

FIGURE 6-4 Isothermal Section of the Ni-Cr-O Phase Diagram Showing Oxide Phases That May Be Stable on Ni-Cr Alloys. (Chromium (---) and nickel (–·– –) isoactivity lines are shown.)

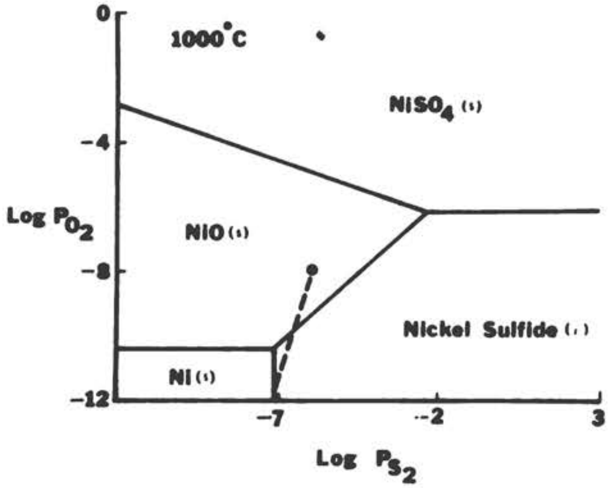

FIGURE 6-5 Stability Diagram for the Nickel-Sulfur-Oxygen System at 1000°C. (The dot indicates the composition of the gas phase, and the dashed line indicates a possible compositional gradient for which a sulphate can be stable on nickel beneath a layer of NiO.)

contain enough of that element whose oxide is the most thermodynamically stable to cover the surface of the alloy completely until some enrichment of this element at the alloy surface occurs due to diffusion. Consequently, during the initial stages of oxidation, the elements with the greater affinities for oxygen are selectively removed from the alloy surface and the composition of the alloy surface is modified such that other less stable oxides are formed. As oxidation is continued, the enrichment of the oxide with the element having the greater affinity for oxygen can be sufficient to permit the development of a continuous layer of this oxide over the surface of the alloy. The theory for such a process has been developed by Wagner(6-8) and by Rapp(9,10). It is sufficient here to use the diagrams for the oxidation of NiCrAl alloys presented in Figure 6-6 to illustrate the important, practical features of this theory.

Reaction-product barrier formation chronologically goes through two stages. In Figure 6-6(a), (b) and (d), the first stage is a transient stage, since oxides are formed which may not continue to grow. The second stage involves the growth of one of the oxide products as a layer, Figure 6-6(c) (NiO layer), (e) (Cr_2O_3 layer), and (f) (Al_2O_3 layer). It is to be noted that for those alloys with compositions such that a continuous barrier of the most thermodynamically stable oxide is formed, no other oxides are formed after this barrier becomes continuous, Figure 6-6(f). On the other hand, when less stable oxides are formed as the continuous layer, discontinuous particles of the more stable oxide are developed in the alloy, Figure 6-6(c) and (e).

The previous discussion has shown that the oxidation of alloys tends to produce layers of reaction products. The corrosion of metals and alloys in multicomponent gases also tends to produce layered reaction products, Figure 6-7. In some instances, however, intermixed rather than layered reaction products can be formed, Figure 6-8. Intermixed reaction products can be formed, in principle, when the gas composition corresponds to a multiphase region of the stability diagram. However, if the step controlling the reaction resides in the gas or at the reaction product-gas interface, then intermixed reaction products can be formed even though all the phases may not be stable in the bulk gas. The case in which transport in the gas controls the reaction rate is straightforward. As a result of such a condition, the gas composition is changed from the bulk to one over the alloy in which the observed multiphase scale is stable. The case where the reaction rate is controlled by a phase boundary reaction at the reaction product-gas interface does not cause the gas composition to be changed from its bulk

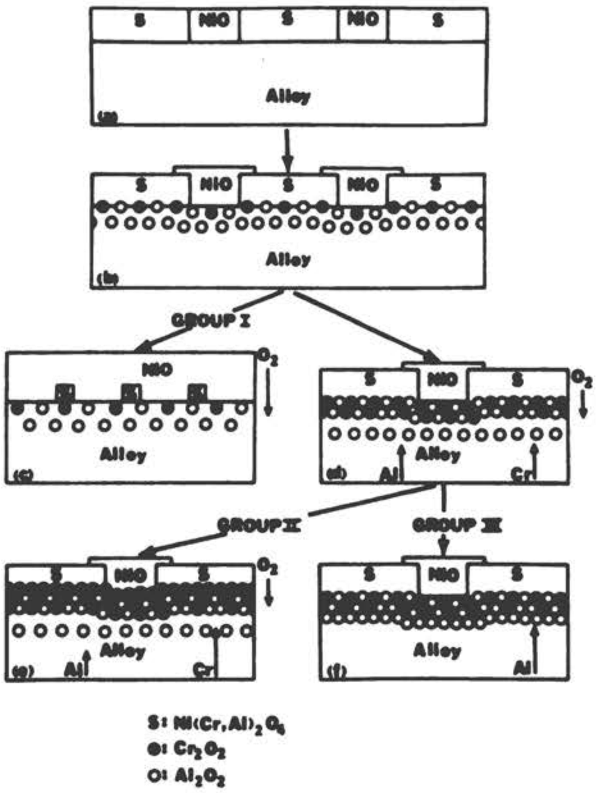

FIGURE 6-6 Schematic Diagram Illustrating the Three Oxidation Mechanisms for Nickel-Chromium-Aluminum Alloys. (S, ●, and O indicated $Ni(Cr, Al)_2O_4$, Cr_2O_3 and Al_2O_3 respectively.)

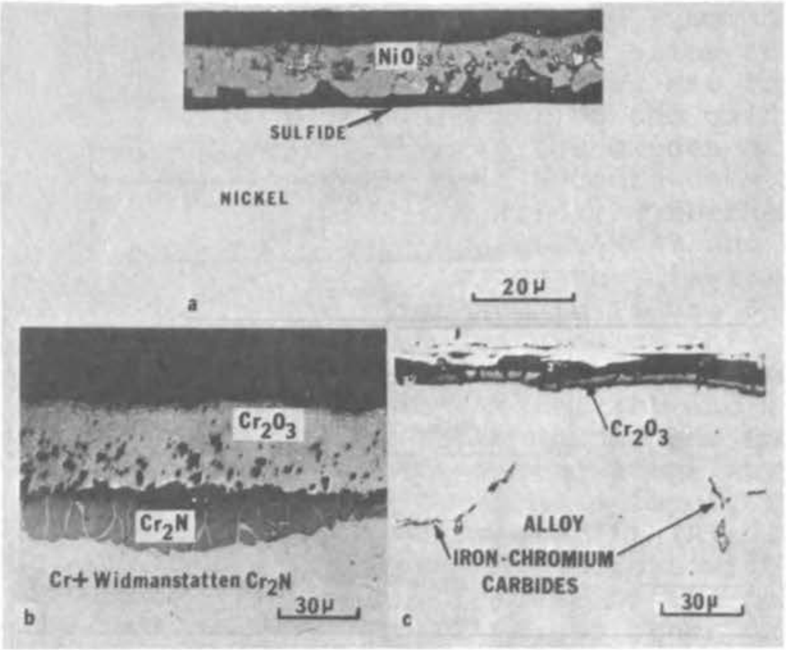

FIGURE 6-7 Photomicrographs Showing Structures Developed after Simultaneous Attack by Two Oxidants:

(a) Nickel after 8 hours in flowing SO_2 at 1000°C
(b) Chromium after 17 hours in air at 1200°C
(c) Fe-25Cr after 20 hours at 900°C in a $CO\text{-}CO_2$ mixture with $CO/CO_2 = 5$

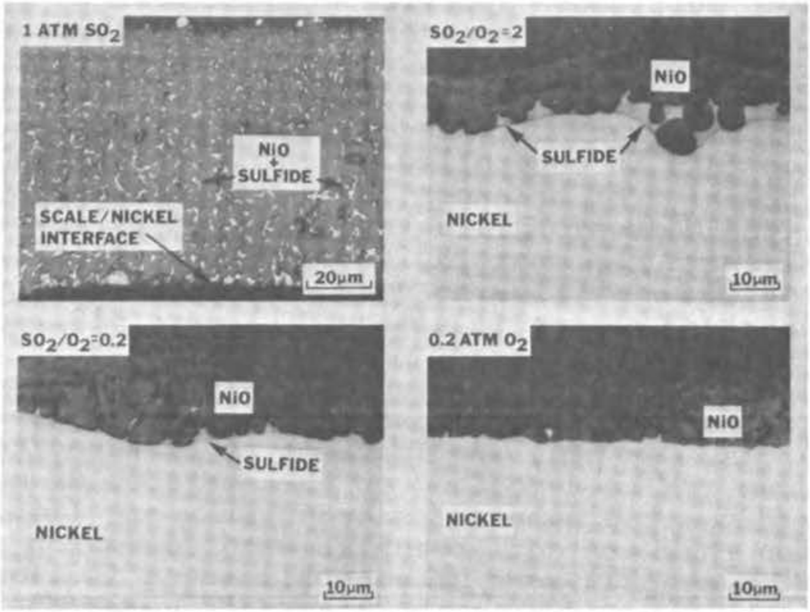

FIGURE 6-8 Photographs Showing Microstructures Developed on Nickel after 6 Hours Exposure at 900°C in SO_2-O_2 Mixtures or Pure O_2 Where These Phases Are Formed as Discrete Layers

composition. Since the supply of one of the oxidants is less than that with which the alloy can react, the phase that is formed on the metal is not in equilibrium with the gas but has a surplus of metal which reacts with the second oxidant. The influence of such phase boundary reactions may be very important to corrosion of metals and alloys in CO_2 or SO_2 at the oxide-gas interface(11,12,13).

While the factors which determine whether a particular multiphase reaction product will be layered or intermixed may not be apparent, the point to be emphasized is that intermixed reaction products are much less effective barriers than layered reaction products. In layered barriers, the transport process is in series and the corrosion rate is controlled by diffusion through the layer having the slowest transport. In barriers having intermixed phases, the corrosion rate is determined by movement through the phase with the most rapid transport. This latter condition can give rise to very rapid corrosion when one of the intermixed phases is a liquid, Figure 6-8.

c. Ash Deposition. Thus far in this discussion of dry corrosion, the corrosive environment has been assumed to be a gas. In many applications at elevated temperatures, substances can be deposited on the surfaces of materials. The ash-deposited substances frequently are liquids, but even when they are not, reaction with corrosion products present on the surfaces of alloys results in liquid formation. The corrosion of materials under the combined influence of a liquid surface deposit and a gas environment frequently is much more severe than that which occurs from the gas environment alone and is called hot corrosion. Substances that in practice have been observed to be deposited on the surfaces of alloys and produce hot corrosion are molten oxides (e.g. V_2O_5), molten sulfates (e.g. Na_2SO_4, K_2SO_4) and molten chlorides (e.g. NaCl, KCl).

Liquid layers influence the corrosion behavior of alloys in gases because these layers affect the nature of the reaction-product barriers. Since these layers frequently separate the alloys from the gas environments, the thermodynamic potentials established over alloys are different from those established when the layers are not present. Consequently, phases can be formed which would not be stable in the absence of the liquid. For example, when Na_2SO_4 is present on the surfaces of alloys in air, sulfides can be formed in the alloys which eventually can result in more rapid oxidation of the alloy. Another undesirable effect produced by liquid layers arises because the reaction-product barriers react with the liquids to produce less effective barriers. Reactions of this type are those where oxide barriers are fluxed by acid or basic melts by either donating or accepting oxide ions. Liquid layers also affect dry corrosion processes by causing the spatial distribution of phases in the reaction products to be changed. Layered reaction product barriers can be changed to less protective intermixed barriers, and dense, adherent barriers can become porous and nonadherent.

2. Protectivity of Reaction Product Barriers

The previous section has considered the stability of reaction product barriers but little discussion has been given to comparing the protectivity of different barriers. In addition, the previous discussion has not considered the destruction of surface barriers in use. In this subsection, the protectivity of barriers will be compared and the ability of barriers to reform will be discussed.

Continuous reaction product barriers of oxides are usually more protective than barriers of sulfides, nitrides or some other type of barriers that can be formed in practical environments since diffusion through oxides is usually slower than through these other materials. Parabolic rate constants for the growth of sulfide and oxide barriers on some alloys are compared in Table 6-3 where it can be seen that the oxides grow more slowly than sulfides. Sulfides usually melt at lower temperatures than oxides, and therefore at temperatures where the sulfide is liquid the difference in growth rate can be extremely large. Since oxides are usually more stable than sulfides, carbides, or nitrides, the most corrosion resistance is achieved, even in complex gas environments, by having the reaction-product barrier contain a continuous zone or layer of oxide.

Parabolic rate constants for the growth of different oxide barriers as a function of temperature are compared in Figure 6-9. This figure does not contain data for the growth of many other oxides, but the rate constants for such oxides are greater than those for cobalt. Alternatively, such oxides are not easily formed as continuous barriers on practical alloys. It can be seen in Figure 6-9 that Al_2O_3, SiO_2 and Cr_2O_3 are the more effective barriers to inhibit oxidation. This condition is also true for hot corrosion induced by ash deposition since, as discussed previously, the added problems incurred by such a condition do not involve transport through protective barriers but rather avoiding physical breakdown of such barriers.

The degradation of corrosion-resistant alloys consists of two stages. In the first stage, a barrier of the most protective reaction product is formed. In the second stage, the alloy becomes degraded to the extent that other less protective reaction products begin to be formed. These two stages of alloy degradation can be said to involve

TABLE 6-3 Parabolic Rate Constants of Sulfidation and Oxidation of Some Binary and Ternary Alloys

Alloy	Temperature °F (°C)	kp ($g^2 cm^{-4} min^{-1}$) Sulfidation	Oxidation
Fe-20 Cr	1830 (1000)	5.9×10^{-4}	1.2×10^{-9}
Fe-20 Cr	1650 (900)	1.1×10^{-4}	1.0×10^{-10}
Ni-20 Cr	1830 (1000)	5.3×10^{-4}	3.0×10^{-9}
Co-20 Cr	1470 (800)	1.6×10^{-5}	5.0×10^{-11}
Fe-25Cr-5Al	1830 (1000)	6.5×10^{-5}	1.6×10^{-11}
Ni-20Cr	1470 (800)	6.0×10^{-5}	1.2×10^{-10}

NOTE: Data from Ref. 14. Reprinted by permission of Verlag Chemie GmbH.

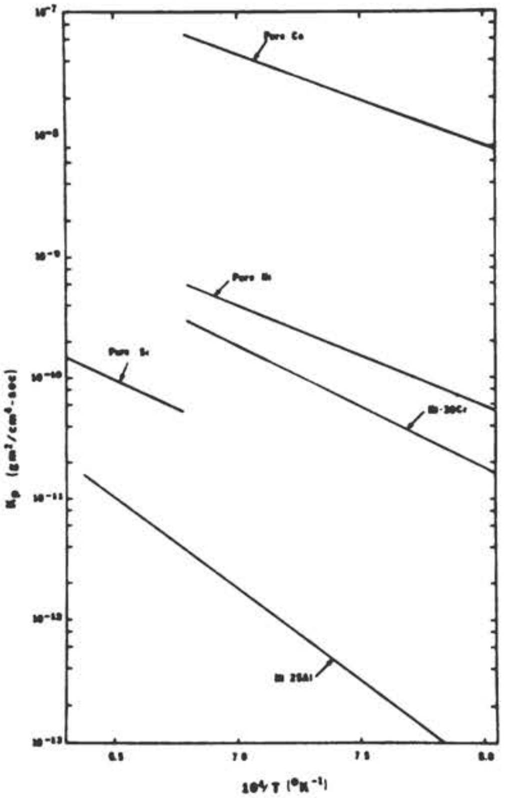

FIGURE 6-9 Temperature Dependence of the Parabolic Rate Constants Obtained for the Growth of Various Oxide Barriers on Pure Metals [CoO on Co, NiO on Ni, SiO_2 on Si and alloys (Cr_2O_3 on Ni-30Cr, Al_2O_3 on Ni-25Al). The oxidizing environments for the data presented were 0.1 atm oxygen for Ni, Ni-30Cr, and Ni-25Al; 0.125 atm oxygen for Co and 1 atm oxygen for Si.]

initiation processes and corrosion propagation processes. Therefore, the first stage can be called the initiation stage because processes are taking place which eventually result in the development of other phases in addition to the one which gives the most protection. The second stage is the propagation stage because the corrosion process involves transport through barriers other than the one with the slowest rate. The length of the initiation stage defines the period over which the alloy retains its corrosion resistance. The initiation time is not a parameter that can be precisely defined because the transition from the initiation to the propagation stage takes place gradually over the surface of the alloy. Corrosion via the propagation stage is usually developed in localized areas and then the transition spreads laterally across the specimen surface from the initial sites.

It is important to emphasize that initiation times are greatly dependent upon experimental or operating conditions. For example, initiation times for cyclic corrosion are always much smaller than those for isothermal corrosion because cracks are developed in the barrier in the cyclic test as a result of thermally induced stresses. When ash or salts are deposited on the surfaces of alloys, the length of the initiation stage is usually shortened and the processes involved in the propagation stage are frequently modified but the barrier developed in the initiation stage is the same as that formed in the absence of the deposit. Since the barrier established on the surface of the alloy in the initiation stage is the determining factor in regard to corrosion resistance, the most significant effect of the ash deposit is shortening of the initiation stage of the degradation process.

Certain techniques are available for extending the initiation times for alloys. In the case of oxide barriers, spalling is inhibited by using an oxygen active element or oxide particle additions, Figure 6-10. A variety of approaches are used to negate effects produced by hot corrosion. These approaches extend from washing the deposits off alloys to modifying the alloys to make them more resistant to the particular type of ash that is being deposited. Substantial changes in alloy composition frequently are not possible because of attendant changes in physical or mechanical properties of the alloys. In such cases, the necessary compositional modifications are developed through the use of coatings on the surfaces of the structural alloys and the desired reaction-product barriers are developed on the surfaces of the coatings.

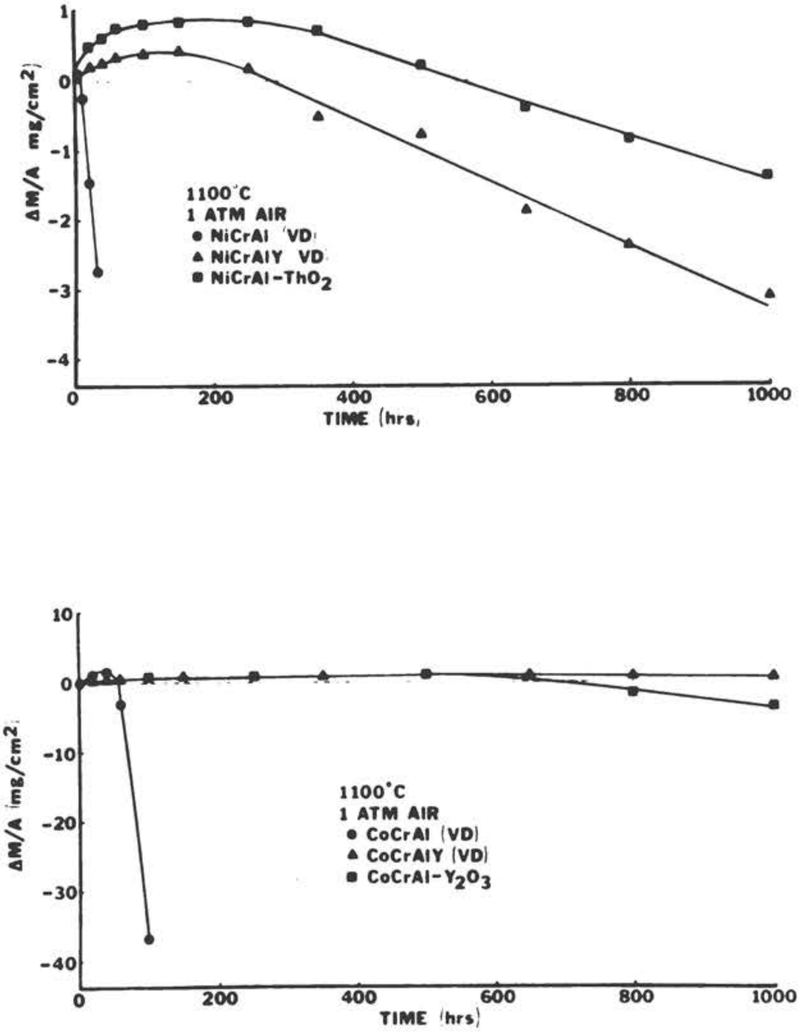

FIGURE 6-10 Weight-Change Versus Time Data for the Cyclic Oxidation (1 hr. cycles) of NiCrAl and CoCrAl Alloys and Alloys Containing Oxide Particles or Yttrium. [These data show that yttrium and oxide particles improve the adhesion of the Al_2O_3 barriers. (VD indicates alloys prepared by vapor deposition.)]

3. Dry Corrosion Resistance

In concluding this section on dry corrosion, it would be helpful to categorize and to compare the various types of dry corrosion reactions that are possible. It is believed that any attempt to categorize dry corrosion reactions becomes cumbersome as this categorization approaches completeness. Therefore, it may be more constructive to simply identify those conditions which, when developed, give rise to corrosion resistance:

- development of solid reaction products on the surfaces of alloys;
- the difficulty in developing and maintaining protective barriers on alloys depends on the environment; environments encountered in practice in order of increasing difficulty of developing protective reaction product barriers are:
    - oxygen,
    - oxygen and other oxidants (e.g. S, C, N),
    - cyclic gas pressures: oxygen and other oxidants,
    - liquid layers and oxygen,
    - liquid layers and oxygen and other oxidants, and
    - cyclic gas pressures: liquid layers, oxygen and other oxidants;
- in the case of multiphase reaction products, layered barriers are preferable to intermixed;
- adherent reaction barriers are preferable to nonadherent;
- oxide barriers are preferable to other types of reaction-product barriers;

- the most desirable oxide barriers in order of preference are: α-Al_2O_3, SiO_2 and Cr_2O_3; and
- in environments where no oxide products can be developed, it is necessary to determine what reaction product phase has the slowest transport properties and attempt to use an alloy on which this phase will develop as a continuous layer.

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Chapter 7

EROSION/CORROSION INTERACTIONS

In the previous chapters erosion and corrosion have been considered separately. It is now necessary to examine combined effects. Before discussing possible interactions between erosion and corrosion, it is constructive to identify the following limiting cases.

- Corrosion Negligible Compared to Erosion

  When the particle diameter is large compared to the thickness of the corrosion product, as may occur when the corrosion rate is small or the time between subsequent impacts in a given area is small, the corrosion products will have a negligible effect on the erosion process. The material removal rate will therefore be controlled by the erosion process.

- Erosion Negligible Compared to Corrosion

  When the thickness of the corrosion product is great compared to the size of the particle diameter, as may occur for very rapid corrosion processes, the erosion of the corrosion product by the particles will have a negligible effect on the rate of material degradation. The material removal rate can be considered to be controlled essentially by the corrosion process.

- Interaction Between Erosion and Corrosion

  When the particle diameter and the thickness of the corrosion product are of the same order of magnitude, the material removal or degradation rate can be influenced by both corrosion and erosion.

The remainder of this chapter will consider the synergism between erosion and corrosion.

A. EROSION/CORROSION IN ENERGY SYSTEMS

The effects produced by interaction between erosion and corrosion can be varied. The corrosion process could cause the rate of erosion to be decreased. For example, in the absence of corrosion, the material removal rate may be controlled by ductile or brittle erosion. The development of a corrosion product will involve erosion of this product rather than the substrate and the rate of erosion of the corrosion product can be greater or less than that of the substrate. The erosion rate relative to that of the substrate is determined by such properties as the microstructure (porosity and grain size) of the corrosion product, its chemical composition and its adherence. For example, a dense, fine grain, adherent layer can be substantially more erosion resistant than the substrate, by virtue of its superior hardness and good toughness; whereas a porous, coarse-grained or poorly adhering layer could be rapidly eroded. Even when the corrosion product is not developed as a distinct layer, the solution of elements from the environment in the substrate can produce effects either favoring or inhibiting the erosion process.

The erosion process can also affect the corrosion process, and such effects are almost always deleterious in that more material is removed than would be removed without the erosive component. This increased material removal occurs because the corrosion product, which normally inhibits reaction with the environment, becomes thinner or it cracks and spalls under the influence of the erosive component.

Certain corrosion reactions can be considered further which are of special importance to specific energy-related systems and involve erosive processes.

In processes whereby coal or liquid fuels are combusted, the oxygen activity in localized areas of the combustion gases can be reduced to levels where oxides, such as NiO, CoO and FeO are not stable. Such conditions are likely to develop in coal gasifiers and pressurized fluidized beds. Lack of oxygen permits other components in these gases, such as sulfur, to react with materials. Liquid sulfides or liquid sulfide-oxide mixtures can therefore be formed. Another source for this liquid slag formation on the surfaces of alloys can be deposition of sulfides or oxides from the gas where the deposited material was originally present in the fuel. The formation of slags of this type on alloys results in very severe corrosion. The addition of an erosive environment can be expected to make the situation more severe.

In gas turbines the two principal modes of alloy or coating degradation are oxidation and hot corrosion. The average oxygen pressure in gas turbines is on the order of one atmosphere. With this abundance of oxygen, the corrosion products are oxides except when salts or ash are deposited on turbine hardware and then sulfide phases can also be developed. In cases where high temperature oxidation is a problem, coatings are used upon which dense, adherent scales of α-Al_2O_3 are developed during the oxidation process. An erosive component may be expected to decrease the lives of such coatings by causing the scales to crack or spall. The coatings used to achieve resistance to hot corrosion attack also depend upon the formation of Al_2O_3 scales; erosion damage of these scales will cause hot corrosion to be initiated after shorter exposure times. Furthermore, once hot corrosion attack has been initiated, oxides other than Al_2O_3 are formed on the surfaces of alloys. These other oxides (e.g. Cr_2O_3, NiO, CoO) are not developed as continuous layers on the surfaces of alloys but they do afford some protection. The erosive component can be expected to make the scales formed during hot corrosion attack even less protective.

In systems that operate at temperatures where water is stable (for example, heat exchanger tubes and slurry pipelines) the corrosion processes described in Chapter 6 must be considered.

Material removal under the combined influence of a corrosive environment and particle impingement is a poorly defined phenomenon. Virtually no data nor theoretical analyses are available to describe it. There is an urgent need to address two basic issues: 1) a definition of the mechanisms of material removal which would allow the various erosion regimes to be identified and the primary material parameters that control material removal in each regime to be isolated, and 2) an evaluation of the functional relations which characterize the material degradation process over the domain of interaction of corrosion and particle impingement conditions. To address these topics experimental work is required. Parallel studies of single and multiple particle impact damage and the associated material removal processes are described for this purpose.

B. SINGLE-PARTICLE IMPACT TESTS

Single-particle impact tests offer a unique opportunity to identify impact damage regimes and to separate the contributions to material removal that derive from the corrosion process and the particle impingement process. Ideally, since the results of these studies can assist in the selection of the most pertinent multiple-particle tests, the single-particle tests should be the first series of tests to be initiated. The relative importance of single particle tests in the study of erosion is determined by the nature of the impact damage. In many soft metals, for example, low velocity impact damage at the angle of inclination for maximum erosion (approximately 15° to 20°) occurs by a single mechanism (plastic penetration and ploughing) and the mechanics of material removal are primarily dependent on the damage interaction between successive juxtoposed impacts. Single-particle tests are not, therefore, very informative, either for defining damage regimes or for predicting the characteristics of the erosion process. Conversely, for brittle materials (such as ceramics) several modes of damage and material removal can operate; a plastic process applies to materials of intermediate hardness impacted by small, hard particles; a fracture process, involving lateral and radial cracking, pertains when harder materials and/or larger particles are used; a different fracture process, involving circumferential cracking, occurs for materials impacted by relatively soft particles. The single particle studies thus identify damage regions that enable erosion behavior to be rationalized. Further, in the case of the lateral/radial fracture process, erosion predictions can be made, because multiple-particle material removal is primarily determined by a simple summation of the damage that occurs at each impact site. For material removal under the combined influence of a corrosive environment and particle impact, the surface being impacted will be a brittle corrosion product. The prior knowledge of the damage processes that prevail in brittle materials thus indicates that several damage mechanisms are likely when a corrosive medium is present, ranging from fracture processes to deformation processes. It is presumed, therefore, that single-particle studies will occupy a central role in the evaluation of erosion/corrosion interaction effects.

The sequence and the extent of the single-particle tests will be determined by the results of the initial test series, and it is not meaningful to outline a detailed test matrix. However, it is already apparent that impacting certain particle environment and target variables should be explored and that careful damage characterization is an essential component of an effective single particle study.

1. Test Variables

The impact damage invariably exhibits strong dependencies on the size and velocity of the particle and its angle of incidence. These particle attributes should be systematically varied in order to characterize their effects on the damage morphology and the extent of the damage. The particle type and shape are other important variables, but a few carefully selected tests will determine the extent to which these variables should be explored. Thus, the particle type, especially its hardness (or compressibility), is certainly important because (as noted above) it can influence the damage mechanism; but, within a specific damage regime, the projectile type tends to be a secondary consideration. Similarly, the influence of the particle shape is minor in certain damage regimes -- such as fracture regions that involve the plastic penetration of the target (entering the erosion problem only through the effect of angularity on the suppression of the erosion threshold). More substantial effects might pertain, for example, for fully elastic contact conditions.

The environmental variables can be systematically studied by varying the thickness of the corrosion layer (within reasonable bounds) for each environmental condition and temperature. The damage would be compared, where possible, with the damage created on a pristine surface. The post impact damage characterization would be performed both immediately after the impact, and after continued exposure to the test environment, in order to distinguish (a) the effect of corrosion on impact damage, and (b) the effect of the impact damage on corrosion. This aspect of the study would be critical to the interpretation of erosion/corrosion interaction effects. It is important to emphasize that the environmental variables and the compositions of the materials control the type of corrosive layer that will be formed. On the same material, it is possible to obtain corrosive layers with dramatically different properties (e.g. sulfides compared to oxides) by changing the environment. The initial environment probably should be air but environments containing oxygen and sulfur as well as carbon must eventually be considered.

The material variables for single particle studies are the most difficult to define. It is evidently preferred that, initially, well-defined model materials be used that have known microstructural characteristics and relatively simple corrosion products and morphologies. Yet, the model materials selected for this initial study should exhibit most of the important characteristics of the materials that will be used in each application. Thus, for ceramic systems, a hot-pressed alumina or a hot pressed silicon nitride may be appropriate; whereas, for metal systems, a Co-17Cr-11Al-0.5Y alloy (overlay coating alloy) may be pertinent. Thereafter, the studies can be extended to include actual ceramic and alloy compositions. One important constituent of the study on actual materials would be the incorporation of the effects of microstructural and compositional changes that are likely over the extended periods that these materials are exposed to the service environment. For example, the effects of the depletion of certain elements in subsurface layers caused by corrosion could be examined by pre-corroding the material, removing the corrosion product, and then looking at the effects of subsequently formed corrosion layers on the impact damage; whereas, the effects of temperature-dependent microstructural changes could be explored by developing these microstructures prior to the corrosion/impact sequence.

2. Damage Characterization

The impact damage should be characterized by first summarizing the damage that occurs on the impacted surface by optical and scanning electron microscopy (including chemical analysis using energy dispersive x-ray techniques). Analytic techniques, such as electron spectroscopy for chemical analysis should also be contemplated. Thereafter, the sample can be polymer impregnated to preserve the state of damage and sectioned to successive locations through the damage zone. The sections can again be studied using optical microscopy (polarized light reflected microscopy or transmission microscopy on thin sections are especially informative) and scanning electron microscopy. Thin sections normal and/or parallel to the impact directions can also be prepared by ion beam thinning techniques for transmission electron microscopy.

The effects to be looked for using these techniques are primarily the incidence and location of fracture, the morphology and extent of fracture, the structure and chemical composition of the surface and near-surface layers, and the incidence, character and extent of plastic deformation. Pressure-induced phase transformations are another possible consequence of the impact process that should not be ignored.

C. COMPUTER STUDIES

The interpretation of single-particle impact damage observations often requires some knowledge of the dynamic stresses generated by the impact process, and the effects of certain target and particle variables on these stresses, i.e. the effects of a corrosive layer, the deformation susceptibility of the target material and particle, the elastic properties of the target material and particle, etc. These stresses can be accurately determined in the fully elastic, elastic-plastic and hydrodynamic ranges, by using numerical finite difference techniques, provided that the constitutive equations describing the plastic and elastic response of the materials and the corrosion layers are known. The latter are rarely known in adequate detail; yet numerical stress calculations can provide information about trends in the dynamic stress fields that are invaluable for interpretation of the damage process. Such calculations are expensive and, therefore, each calculation has to be carefully planned to ensure that it effectively addresses one of the critical issues raised by the single particle tests. The incidence and growth of fracture can also be incorporated in the numerical analysis by applying crack initiation criteria (e.g. a statistically varying crack activation condition) and crack propagation criteria (e.g. a critical strain energy release rate).

D. MULTIPLE-PARTICLE TESTS

The thrust of the multiple-particle tests is somewhat different from the single tests in that the interaction effects between adjacent impacts and gross material removal can be studied. This interaction effect is necessarily included in the resultant damage morphology, but the damage sequence can be obscured if the experiments are not carefully designed. It is thus important to conduct some studies with small particle loadings that allow only a fraction of the original surface to be impacted. Then, interaction effects will occur at those sites where impacts have juxtaposed. These studies should be conducted in the same spirit as the single-particle tests and demand a careful characterization of the damage in the interaction zone. The test matrix will be determined by the initial studies which indicate the importance of the interaction effects. Where such effects are shown to be minimal, only a few tests will be required. However, if the interaction is the dominant removal process, the significance of all of the particle environment and target variables described for single-particle tests will have to be explored and each damage characterization technique will need to be used to determine the damage interaction process and the material removal sequence.

Another critical series of multiple-particle tests involves a study of the gross material removal and damage that results from the impact of a multitude of particles. Initially, these tests could be used to assess the validity of the erosion/corrosion rates predicted by the single and low concentration particle impacts. Whenever these predictions are verified, it simply remains to generate data in each damage regime that provide absolute functional relations between the material removal rate and the particle environment and target parameters which have been shown to exert the primary influence on the removal rate. Here, it would be recognized that the particle flux is an important test variable because, by changing this flux, the conditions can be changed from pure corrosion to pure erosion (these effects should, of course, be predictable from the damage characterization). For systems where the observed erosion/corrosion rates are not predictable, additional many-particle interaction effects must be occurring, and attempts must be made to infer the character of these interactions from examinations of eroded surfaces or erosion debris. This study is the least definitive in terms of erosion prediction, and it may be required that erosion in these regimes be characterized by a very comprehensive, systematic empirical study of the functional dependence of the erosion rate on the system parameters.

E. FOULING

Throughout this chapter, it has been assumed that the erosive particles impact with materials and are then removed by rebounding. It is possible that the particles may accumulate at the surfaces of the materials. Such a condition can occur with submicron particles by entrapment in stagnation zones. It appears that even much larger particles may accumulate under high flow rate conditions for erosive materials with low coefficients of restitution. Deposition of the erosive particles prevents erosion and may also affect the corrosion processes.

F. MODELING STUDIES

It is implicit in the multiparticle studies that modeling activities be used to relate the behavior observed at interaction sites to the final erosion/corrosion characteristics of the material. These activities can range from the quite simplistic (simple summation) to the complex (cumulative damage) depending on the observed character of the interaction. It is not possible to make, a priori judgments about the character and extent of the modeling efforts. Researchers with the appropriate background and expertise must be integrally involved in interfacing with the physical erosion/corrosion process as this knowledge is acquired from materials-oriented investigations.

Chapter 8

TESTING PROCEDURES

Test evaluations are a significant factor in materials selection, materials improvement, and in the development of design guidelines for energy-system components exposed to severe erosion/corrosion environments. Since advanced energy systems impose new challenges for operating efficiency, it is important that proper attention be given to an integrated testing program. It is also important that the test environments be adequately characterized. This is necessary if the data generated are to be in accordance with the conditions specified and thus, by truly reflecting plant operating conditions, be usable in design.

Materials testing of erosion/corrosion resistance for use in various types of energy-related systems is a crucial aspect of any program directed towards obtaining materials with improved properties. Ideally one attempts to develop a test that duplicates the service conditions. However, such a test typically cannot be developed because frequently the service conditions are not well defined, and more importantly these conditions vary during extended periods of exposure. It is, therefore, necessary to use a combination of testing procedures. Some of these tests should examine the performance of the material under conditions supposedly encountered in practice. Other tests should be of a more sophisticated nature and be concerned with mechanistic interpretation of material behavior under well controlled and well-defined conditions. It is also very important to have these tests supplemented by results obtained from analyses of service hardware. By using these three sources for material response data, the performance of various materials in specific applications can be well documented.

A. GENERAL TEST PROCEDURES

In Chapter 3, three temperature regimes for erosion/corrosion attack in energy systems were designated: room temperature to 390°F, 390°F to 1110°F, and greater than 1110°F (200°C, 200°C-600°C, and above 600°C). The complexity of assessing materials performance in the various combinations of erosive/corrosive and elevated temperature environments requires that a four-level scheme of testing be employed. The recommended types of tests are based upon procedures very successfully utilized in the jet engine industry.

The four levels of testing are:

1. Screening

The purpose of screening tests is to rank materials. Usually a large number of specimens of simple geometry are tested. Erosive environment approximation includes typically sized and constituted particles at a selected velocity (in the range of the anticipated environment) with provision for elevated temperatures (at least two) and variation of impact angles (at least two). The test variables are tightly controlled to allow accurate models or corrections of the material removal rates to be developed with respect to the test variables. This may be an accelerated test.

Another screening test would employ a corrosive environment only. Environmental approximation would include principal corrosive elements or atmospheres and appropriate elevated temperatures (at least two) within the ranges indicated above.

2. Bench Tests

Additional complexity is introduced in these tests by adding a realistic corrosive environment to the erosive environment and by introducing particle-impact velocity, concentration, and size variations. This is usually an accelerated test. The number of materials represented is usually smaller than used in screening tests and the specimen geometry approximates that of the actual component. These tests establish a more realistic ranking than obtained in the screening tests and so must be conducted with complete objectivity.

3. Component Tests

This level of testing is conducted on components to examine the geometrical and environmental effects which represent the final service application under the best feasible simulation of the environments. Because of expense, only a small number of components are so tested and for times much less than those associated with service requirements. This is a final proof of readiness test and assures that no unexpected behavior will be observed in actual in-service evaluation.

4. Life Prediction and Verification Tests

Because of the very large scale of the equipment in energy conversion processes, these tests, which require service conditions for full-scale components, must be conducted in pilot plants or demonstration units. Confidence in application of specific materials and constructions for advanced designs is high from such test results because the failure analysis includes many of the geometric, scale-up and operating parameters which apply for the full-scale equipment.

A comparison of the four levels of testing is presented in Figure 8-1. This table highlights the fact that as complexity or scale of the test increases so, of course, does the cost and the closeness of the information one obtains from the test to actual service. Thus, the risk of generalized extrapolation from the higher level tests is reduced, as is the risk that some material or aspect of the problem has been overlooked. Remember, however, these higher level tests offer less control over test variables and so offer only a generalized corroboration of any models developed from lower level tests. A good screening test, for instance, may satisfy very few designers, and it is extremely critical that materials or designs not be developed just to pass one particular test. This is especially true for the erosion/corrosion/elevated-temperature coupled conditions of interest in energy systems. Examples of the type of facility at each test level are also indicated in Figure 8-1.

It should be emphasized at this point that the above testing scheme may involve several different kinds of conditions at each level depending upon the application involved. For instance, to meet the data needs for fluidized beds, gasifiers, and turbines, many different types of corrosive environments, fuels, particle characteristics and velocities must be introduced into the tests.

B. STANDARDIZATION ACTIVITIES

Materials developers are the greatest users of screening tests. A standardized screening test for a particular application should be established to reduce confusion and simplify comparison of results from several sources. This would eliminate some of the difficulties which arise in trying to transfer results from one apparatus to another or from one application to another.

TYPE OF TEST		COST	NUMBER OF TESTS REQUIRED	CONTROL OF ALL VARIABLES	USEFULNESS FOR MECHANISM DEVELOPMENT	USE SERVICE EXTRAPOLATION RISK	EXAMPLE FACILITY
I.	Screening	Low	Many	Good	High	High	Sand Blast Nozzle Corrosion Chamber
II.	Bench	↓	Reasonable Number	↓	↓	↓	Burner Rig Equipped With Particles
III.	Component	↓	Reasonable Number	↓	↓	↓	Process Unit for Experimental Hardware
IV.	Life Prediction and Verification	High	Few	Poor	Low	Low	Pilot Plant or Demo Unit

FIGURE 8-1 Recommended Testing Scheme

Standardized reporting procedures are needed in view of the extent of the erosion/corrosion testing which will be carried out in the next decade. The minimum number of descriptors and properties to be reported should be established for reproducing the test conditions and fully characterizing the specimen prior to testing. For example, properties of interest may include hot hardness, melting point, corrosion/oxidation at temperature, erosion rates (cold and hot). Tests should be conducted at a number of independent laboratories to provide objectivity in the bench level or component level testing and to provide a meaningful data base.

Testing for research studies must of necessity be very specific and is discussed in Section C of this chapter. Standardized reporting of the results obtained (in specified format perhaps), reporting all test variables, and identification of gaps that remain are needed to increase confidence in the data base.

C. MECHANISM EVALUATIONS

Research involving the study of basic mechanisms of erosion is concerned with the effect of particle impingement on surface microtopography, near-surface microstructure, surface chemistry, and localized heating. That is, emphasis is on the microscopic and localized events rather than bulk material loss. Testing, therefore, involves bench tests using model materials (single crystals, simple solid solution alloys, glasses, plastics) selected for consistency in composition and physical properties. The specimens are subjected to a "standard" eroding medium or to single-particle impacts. The eroding medium is usually a single constituent (silica, alumina, steel shot) of high purity and screened to a narrow size distribution. The particulates used should have characteristics representative of the particulate of concern -- for example, the hardness and angularity of fly ash or the deformable nature of a molten or partially molten slag particle.

The bench test apparatus is designed to provide a controlled gaseous environment and control over particle velocity and angle of impingement. If single particles or multiple particles are accelerated in a gas stream, sufficient path length must be provided to allow the particles to reach the equilibrium particle velocity. The particle velocity rather than the stream velocity should be measured directly. Particle velocity measuring instrumentation for gas entrained particles is varied and depends in part on the size of the particles being used. A high-speed photography setup is an example of one velocity measurement scheme which can be used for this purpose. Individual particles are photographed on the same photographic plate during a series of strobe flashes and the distance of travel measured between flashes used for velocity calculation. The impact area is often monitored by high-speed photography to measure rebound angles and detect fragmenting of particles and secondary surface damage.

Various particle acceleration devices are employed currently. Gas guns have been used by several investigators for single-particle experiments. Particle velocities of up to 1500 fps (450 ms^{-1}) can be achieved with relatively small facilities. These velocities are suitable for most of the impact problems of energy systems. In general, particles are carried down the gun tube mounted in a sabot and exit from the gun as the sabot hits a stop at the end of the gun. Several particles can also be propelled at once with this arrangement(1,2). Another technique utilizes an exploding wire as a means of propelling the particle against the target(3). Also, impact velocity can be controlled by mounting the material specimen on a rotating disk or arm(4,5). For small arm radii the specimen is rotated at high speed in a partial vacuum; particles are allowed to drop in front of the specimen, which impacts them. Vacuum conditions are necessary in small rotating arms since gas turbulence generated in the vicinity of the rotating specimen will either deflect particles or influence impingement angle in an uncontrolled way. Longer radius arms can be operated at atmospheric conditions using particle sizes above 50μm(6). However, most experiments involve injection of solid particulate matter into an air stream.(7)

Specimens are removed and examined by microscopy (both scanning electron and optical microscopy) after single or relatively few particle impacts. The microtopography of the impact craters or pits is analyzed and compared with the average particle size and shape. For single crystal material, slip lines and dislocation arrays can be revealed by etch-pitting processes. Subsurface strain patterns can be observed in transparent single crystals, glasses, or plastics by polarized light. Metallographic sections of eroded samples also provide information on the subsurface microstructural changes.

Thin foil transmission electron microscopy has been used in a limited number of studies to reveal dislocation configurations associated with individual particle-impact sizes(8). Surface replication techniques can also be used to examine the damage at the same location on the surface of a progressively eroded specimen without destroying the specimen(9). Transmission electron microscopy can be used when the damage is in its earliest stages of development.

If the mechanistic studies are concerned with flowing systems such as pipeline slurries or particles entrained in gaseous streams, the addition of a well-characterized flow may be necessary to induce appropriate particle-impact characteristics (rebound, etc.) or coupling effects such as flow-surface asperity interaction. Flow simulation techniques include engine ground tests with particle ingestion, burner rig tests, and wind tunnel tests with particle injection.

D. ACCELERATED-LIFE TESTING

Perhaps the most difficult question pertaining to testing procedures is that of accelerated-life testing for energy systems. Such systems are designed to have very long lifetimes (hundreds of thousands of operating hours). This is in contrast to the nearly ten thousand hours (at most) of design life for many aerospace power systems. With more than an order of magnitude increase needed in extrapolating test results for life prediction, the necessity for meaningful accelerated tests is apparent.

The erosion process can involve long-term effects where eventual failure does not occur until five or ten years have passed. The formation of pin holes in a piping system, for instance, may take years to develop. In order to predict this type of failure, it would be impractical to run tests to failure. Therefore, some reliable way must be found to either speed up the process leading to failure after reasonable test times or to extrapolate the results of relatively short tests with the required confidence. A third alternative would be to use both approaches --- accelerate the erosion rate and extrapolate data from truncated tests. The scaling for combined erosion/corrosion effects would have to be established or alternatives would have to be sought. Fundamental understanding of the various corrosion damage modes would certainly contribute to reliable life prediction evaluations.

Accelerated-life testing requires the following series of steps:

(1) define the failure;

(2) select a reliable model for the failure process;

(3) select the confidence band needed for fail safe or reliable service;

(4) determine operating conditions which can safely accelerate the process without causing a change in failure mode;

(5) determine minimum length of tests required to get extrapolative data (using a model);

(6) determine statistically the valid number of data points required for confidence limits required; and

(7) extrapolate data for expected operating conditions assuming a cumulative damage type process if operating conditions are variable

Definition of the failure may seem obvious. However, there are many mechanical failures which arise from several independently operating processes, viz: corrosion, wear, fatigue, and it is important to determine which one will ultimately dominate the failure of a particular component. In the erosion of a pipeline, for instance, failure might be defined as the point at which local wall thickness is reduced to the point where it will blow out, producing a small hole, which then will enlarge to a substantial leak very rapidly. This might be the combined effect of corrosion on the outer surface of the pipe and localized erosion/corrosion on the inner surface.

Modeling the erosion process is extremely important. Modeling presents many difficult problems owing to the lack of understanding of the parameters controlling erosion and how they are influenced by outside conditions. There are at least two relationships which should be considered. One is the steady-state equation discussed in Chapter 5, which can be discussed in general form as follows:

$$V = KR^3U\gamma f(\alpha)$$

where

V is the rate of removal per particle

K is an erosion coefficient

$f(\alpha)$ is a function of impingement angle,

R is the radius of the particle

U is the particle velocity, and

γ is the velocity exponent.

If the erosion coefficient and f(α) were known for the target material and erosive medium, then the most efficient impingement angle for accelerated erosion tests could be selected and the effect of increasing particle velocity on erosion rate estimated. Something would have to be known about the response of the material to be eroded to impact velocity so that changes from purely impact deformation to shock-induced vacancy formation (change in damage mechanism) or impact heating to a critical temperature could be avoided in the accelerated test. Some materials show a significant change in the incubation period with moderate increase in particle velocity.

The second relationship required would be the erosion rate-time curve (Figure 8-2) obtained under constant and controlled conditions. Material removal as a function of time changes with time in erosion processes. Often there is an incubation period characteristic of each material where little measurable loss can be detected. This is followed by a rapid increase in the removal rate and then a leveling off to a much lower removal rate under approximately linear conditions. It would be essential to design the test so that the essentials of the erosion-time characteristics would be covered in order to define the full curve. The effect of changing such parameters as particle velocity and impingement angle on the erosion-time characteristics would have to be known.

Figure 8-2 serves to show that running a short-term test of two hours would give data, if extrapolated out to 1000 hours, which obviously would be alarming to say the least. If the test were run-in for the first two hours without recording erosion loss and then measurements made for the next two hours, the periodic fluctuation which appears over the 10-hour period would not be detected. This example shows the importance of knowing the erosion-time characteristic of a system before an abbreviated test can be designed. Incidentally, some materials (aluminum for example) show a weight gain during an extended incubation period. This is caused by imbedding of the erosive medium in the surface.

It is obvious that more research is needed to help improve the accuracy of erosion models and to develop techniques for investigating material response to coupled erosion/corrosion environments. In addition to the items mentioned in the above example, it is essential to know the effects of particle size and shape, ambient temperature, and corrosive environment on the erosion rate-time characteristics. When the model is better defined, then Steps 3 through 7 can be carried out with some degree of confidence.

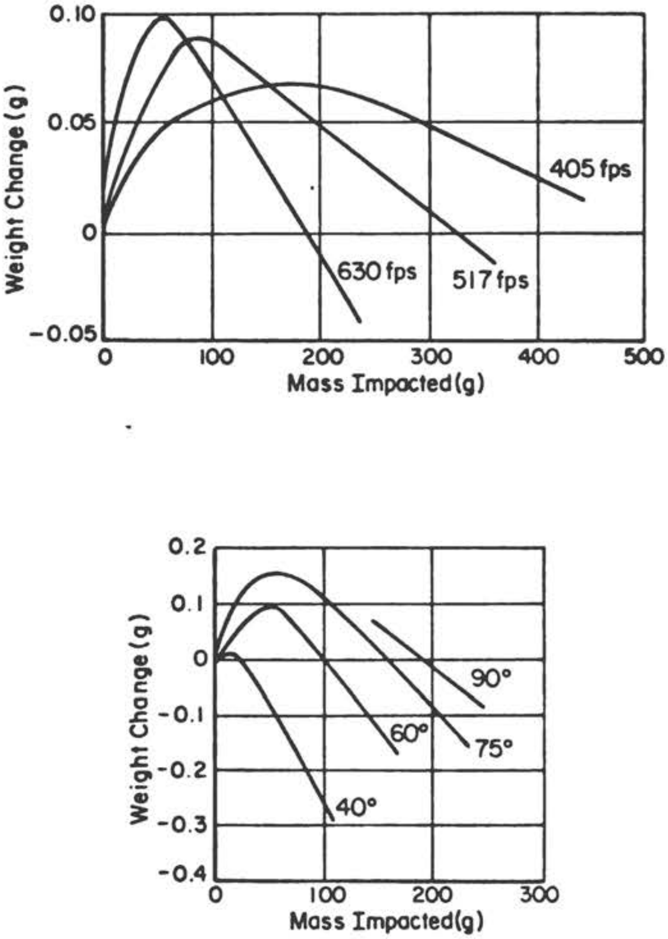

FIGURE 8-2 Example of Erosion-Time Characteristics for Different Particle Velocities (Data from Ref. 10.)

Initial detailed system designs are lacking, fuel and other input materials are of widely varying composition, and initial cost compared to repair costs are not well established. Which environment (temperature, gas composition, particle velocity, etc.) does one change to accelerate the degradation process? Since both corrosion and erosion occur simultaneously, perhaps both should be accelerated but then oxide scale removal/reformation kinetics (as an example) may be completely unrealistic. It is clear that this subject requires immediate attention by this country's leading corrosion and erosion research groups.

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Chapter 9

ENGINEERING FOR CONTROL OF EROSION DAMAGE

Erosion of system components will be a problem in making reliable new processes to extract energy from coal. Because erosion damage limits the life of components critical to the operation of the system, the ability to achieve an engineering design that is operable and economic early in the process development demonstration may be decisive in determining the value of a system or a concept. All of the "new" processes compete with current technology. To illustrate, high BTU coal gasification processes are being developed to augment the natural gas supply. The ultimate products, heat for homes and businesses and process heat for industry, can also be supplied by burning coal in a conventional steam-electric generating plant (with stack gas cleaning), distributing the electricity and using I^2R electric heating. This basically "here now" technology establishes a floor on the process efficiency and a ceiling on the economics which the new technology must meet to be useful.

The engineer must arrive at a workable and reliable system design within the performance and economic constraints. He is faced with four problems:

- identifying the critical erosion-limited components or problem areas;
- devising effective erosion control strategies;
- evaluating both the cost of his design and the effect of his design on the system performance to permit choices between his options; and
- understanding the effect of process scale on his design so he can properly test commercial scale solutions in pilot-scale plants and time frames (or have sufficient confidence in his design that commercial scale demonstration units do not become unreliable).

The engineer has available a wide spectrum of background experience to help him with these problems. Most of the processing concepts have been tried before. The problems in many cases have been identified. He has some empirically based design rules for specific situations. He has some help from basic science. Because the handling of process streams containing highly erosive particulates on a massive scale and under severe competitive economic restraint has not previously been required -- both the depth of scientific understanding and the availability of data are inadequate. The engineer has 20th Century computational skills and equipment at his disposal; but the plant designer, and even the component designer, can rarely command the time and expertise to carry out the necessary design analysis studies.

A. CRITICAL PROBLEM AREAS

The first problem of the engineer is recognition of the system components which require design attention because of erosion or erosion-accelerated corrosion. The classical aids -- experience, the engineering literature, and common sense -- are all available; but since erosion has not been a widespread engineering problem, the experience, the literature, and the common sense are not "mature." Typical process conditions which alert the engineer to a potential erosion problem are:

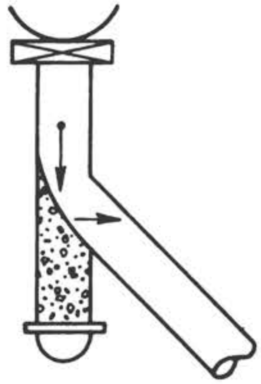
- Situations where changes in direction of flow of a particulate-containing fluid occur:

  Any time a particle carrying fluid changes direction, impact between particles and component parts may occur. The larger the particles and the faster the flow, the more severe the resulting erosion damage problem. Consider two simple examples:

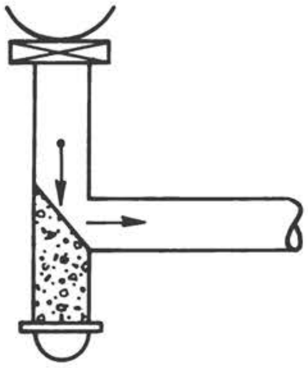
  (1) A pneumatic transfer line is required to lift dolomite particles about 100 feet (30 m). Transport velocities between 50 and 200 fps (15 and 60 mps) are required to convey the stone. A solid loading of 6 lbs (2.2 kg) (of dolomite) per 100 actual cubic feet of transport gas is used. Because of the long lift, expansion joints in the lift line were used. Misalignment by as little as 4 degrees resulted in wearing through an alloy lining with a 1/4 inch (6 cm) wall thickness in less than 50 hours. This situation could have been avoided if the plant designer had been aware that, for the solid size distribution being transported, particle impacts upon a relatively ductile alloy at grazing angles would result in an unacceptable erosion rate. A lift design in which

alignment as well as expansion could be controlled (for example, a welded line with expansion accommodated by a movable surge pot) would remedy the problem.

(2) A lock hopper feeds coal into a gasifier vessel located below and horizontally displaced from the axis of the lock hopper. The designer has the choice of two configurations:



design a



design b

Experience tells the engineer to choose design (b) since even though a slightly higher transport velocity may have to be used, the rebound of particles from the material packs into the blind tee and forms an impact cushion. Particles are then directed principally down the axis of the horizontal transfer pipe. In design (a), particles are directed against the pipe wall causing failure in tens of hours.

These examples, which are simple compared to the particle flow through a valve or a gas turbine, have been cited to indicate the need to make available the experience and the design rules which will assist the design engineer in recognizing trouble spots.

- Situations in which particles will be mechanically scraped over surfaces

The handling of slurry flow, wear on chutes, hopper car walls and floors, etc. are examples of situations in which the engineer can find scraps of information to guide design. In slurry feed service no difficulties are experienced when velocities are limited to the range 3 to 11 fps (0.9 to 3.3 m/s.) and special precautions such as the use of long radius bends or blind T's are used to change the direction of flow. How general are such design rules? Are there situations -- i.e., solids loadings or chemical environment -- which will lead to trouble?

- <u>Pressure "let down" situations in which particle generation, acceleration, and impact, or cavitation damage can occur</u>

  A recent article(1) alerts engineers to some of the dangerous situations and suggests preventive design options. Among the possibilities are the use of chokes instead of orifice plates or valves, appropriate design of the downstream low pressure reservoir, and the selection of specially designed valves streamlined to reduce impingement on vital parts and with valve trim selected to be substantially harder than the flowing particles.

- <u>Situations in which either the particulate loadings, the impact velocities, or the chemical environment are markedly different from past experience -- so that solutions from the past may not prevent future problems</u>

  Power recovery turbine experience in an erosive environment is available. Expander turbines with easily replaceable, inexpensive blading, and with special inlet design to prevent particulate concentration at weak areas of the machine (the highly stressed blade roots, for example) are working in refinery service. Gas velocities in these machines are about half those of a modern gas turbine used for electric power generation. They operate at turbine inlet and metal temperatures several hundred degrees lower. They operate in a chemical environment substantially free of sulfur, alkali metals, chlorine compounds, and low melting ash constituents. The alloys used are less expensive, more susceptible to hot corrosion, less critically loaded, and easier to fabricate. The designer of a power recovery turbine is faced with more severe versions of old problems as well as new problems in many coal processing systems.

The engineer must first recognize where he must exercise his skill through design and specification of materials to achieve a workable and economic system. A few examples have been cited to indicate his difficulties, even in this first step.

To help him, the National Bureau of Standards is carrying out a program sponsored by ERDA-Fossil Energy Research to maintain a centralized failure analysis reporting system covering materials and components used in coal conversion systems. As indicated in Chapter 3, this Failure Analysis and Prevention Program:

(1) analyzes and catalogs pilot plant materials and components failures;

(2) advises pilot plants on failure prevention; and

(3) indicates areas for materials and components research and development.

ERDA-Fossil Energy Research also publishes a Materials and Components Newsletter to disseminate information regarding their programs. This newsletter distributes failure prevention experience.

Many engineering design and construction firms have a background of experience and empirical design rules for dealing with erosion problems and there is a varied and extensive literature (including literature from such diverse sources as the railroad industry on use of sand for braking and the oil industry for coping with sand intrusion into pumps, etc.). In general, the engineering/construction industry in the United States places heavy reliance on customer experience to provide means for combatting erosion. Over the years, major steel and oil companies have determined, primarily on an empirical basis, methods for combatting erosion in equipment such as blast furnaces and catalytic crackers. This experience is transmitted to the engineer/constructor through specifications detailing the kind of material, its configuration and its method of application in installations intended to combat erosion. The engineering contractor then interprets such designs and uses the interpretation to apply erosion-combatting designs to other similar systems. Discussions with two large firms, one active in the basic metals industry and the other in the power, petrochemical and refining industries revealed that neither engineering firm had written guidelines for designing erosion-resistant fluid-solid systems. Both firms had design specialists who would, for example, specify safe velocities to be used in the pneumatic conveying of fine-size solids in metal pipes. Information such as: 30 fps

(9 m/sec) is a safe velocity for catalyst circulation lines in cat crackers, but 60 fps will result in rapid erosive failure was provided, and would be used to specify 30 fps for conveying limestone into a 15 atm pressurized fluidized bed combustion system without any assessment of the differences in the systems.

The Chemical Engineers Handbook, 5th Edition,(2) discusses erosion only in the most general terms, as though it were one type of corrosion. In terms of fluid-solid systems, the handbook states "A large, capable manufacturing industry supplies complete systems" for pneumatic conveying, and makes no attempt to discuss erosion in such systems. Likewise, there is no publication by the American Petroleum Institute on recommended practices in, or standards for the design of, systems handling erosive solids. The API Refinery Practices Committee does consider, in terms of refinery operating safety, problems that arise as a result of catastrophic erosive failure and how these failures were combatted. However, no attempt has been made to assemble and systematically analyze the various erosion problems discussed by the Committee. Apparently, the refiners involved regard their individual problems with erosion and the systematic solution to those problems as information that is proprietary to each refiner. Only in cases involving serious damage or loss of life, where the Occupational Safety and Health Administration procedures would force information into the public domain, is any real information released on specific means used to prevent catastrophic failure, and that is only sporadically available to those who attend the API Refinery Practices Committee sessions.

Neither a centralized compendia of problem situations nor the information needed to quantify the problems is available to the engineer who must first recognize that he has a problem in a particular system or component.

B. EROSION CONTROL STRATEGIES

The engineer, having identified the problem areas, must now devise and evaluate erosion control strategies. He can strive to:

- decrease the number of impacts (through control of particle concentration or through equipment design); and
- decrease the damage done by each impact through control of (a) the kinetic energy of the impacting

particles, (b) the angle of impact, (c) the choice of the material to be impacted, and (d) choice of the operating conditions, pressure, temperature, and chemistry in the local environment.

This section briefly reviews the body of knowledge at the disposal of the engineer to enable him to design workable and economic systems.

1. Decreasing the Number of Impacts

In some systems, particulates are present as contaminants and removing them from the system is a possible erosion control strategy. As one example, coal ash remaining as an impurity in coal gas and airborne particulates present an erosion damage threat to the operation of gas turbines used in combined-cycle electric power generation systems. Gas cleaning to reach an allowable concentration and size distribution of particulates is an engineering option. To engineer this option, the system designer must have available to him:

- the correlations between particle concentrations, size distributions, and component life;
- the performance, operating requirements and costs of alternative gas cleaning systems;
- methods for extrapolating the performance of gas cleaning systems to new process conditions;
- an economic analysis to establish the effect of the tradeoff between gas cleaning and component life on the cost of the ultimate product and the performance (energy efficiency) of the overall system; and
- an understanding of the ceilings on cost and the floors on performance that competitive methods of achieving the same goal place on the process.

As a result of the Environmental Protection Agency's (EPA) recognition of the need for performance and cost data on particulate removal systems, the engineer has available to him the <u>Scrubber Handbook</u>,(3,4) Volume 1 and Volume 2. This study presents the performance and operating experience, and also reviews the state of the art in predicting the performance of various types of commercial gas cleaning systems. A study of these reports and the literature will quickly reveal the large amount of additional effort needed to provide the engineer with effective methods of designing workable systems and predicting their performance and costs.

The situation is much more difficult in the case of the life and performance correlations for various pieces of equipment with particulate loading. Only isolated studies are available. To cite an example -- a simplified theoretical study to attempt to establish the correlation between particle loadings and gas turbine first-stage blade life was made by Westinghouse (under the sponsorship of the Office of Coal Research). This study, which required guesses as to:

(1) the performance of gas cleaning systems (Figure 9-1),

(2) the erosivity of coal ash at temperatures between 1650°F and 2000°F (900°C - 1090°C),

(3) the erosion resistance of turbine alloys (Figures 9-2 and 9-3),

(4) the rebound characteristics of coal ash as a function of angle and velocity of impact (Figure 9-4),

employed a simplified two dimensional gas flow field through the turbine stage (neglecting the cushioning effect of boundary layer development and the particle concentrating effects of secondary flow in the turbine). The study yields the data of Figure 9-5, where the angle of maximum erosion damage as a characteristic of the turbine material was allowed to vary as a parameter. If the "guessed" particulate and material characteristics are correct, and economics and operational restrictions require first stage vane replacement after turbine operation for a minimum of 10,000 hours, then the degree of gas cleaning that must be achieved is defined. This type of study even with guessed data for critical components is not generally available on pumps, valves, fans, and other vital equipment. The engineer requires more such studies along with the erosion data needed to quantify them.

2. Decreasing the Damage Caused by Each Impact

In addition to controlling the particle concentration impacting the hardware, the engineer can design to lower the erosion damage rate. To a first approximation this is accomplished by (1) lowering the kinetic energy of the

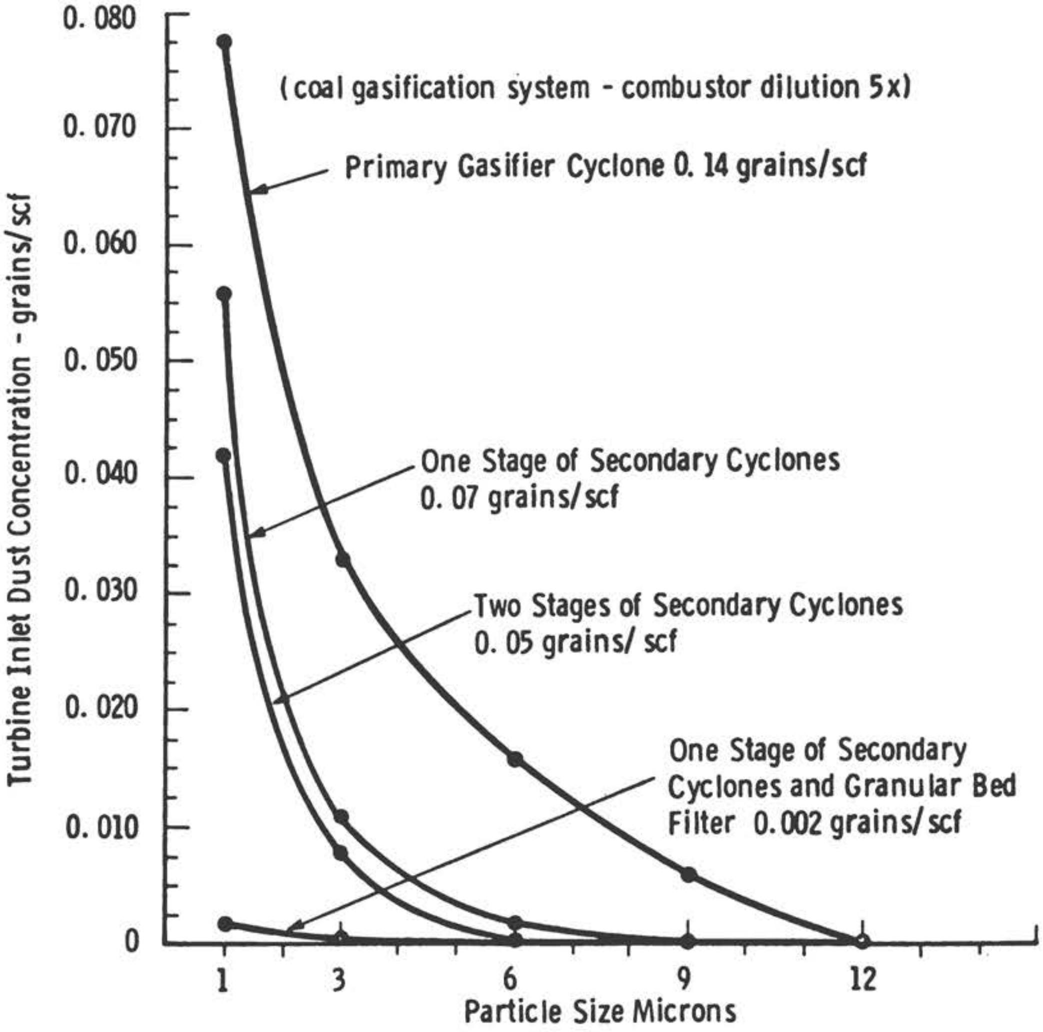


FIGURE 9-1 Particle Size Distributions at the Gas Turbine Inlet Corresponding to Various Particle Cleanup Systems

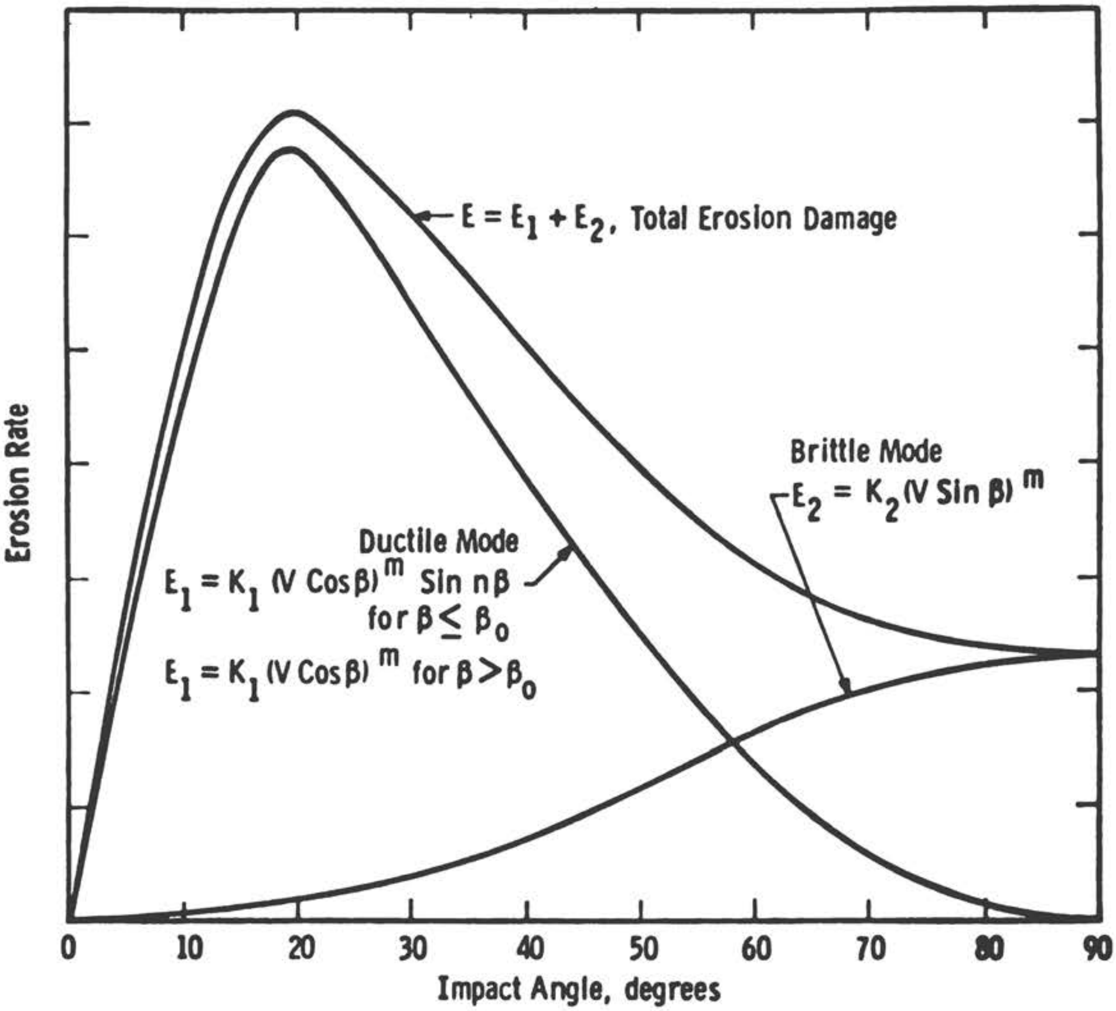


FIGURE 9-2 Erosion Model for Ductile Materials

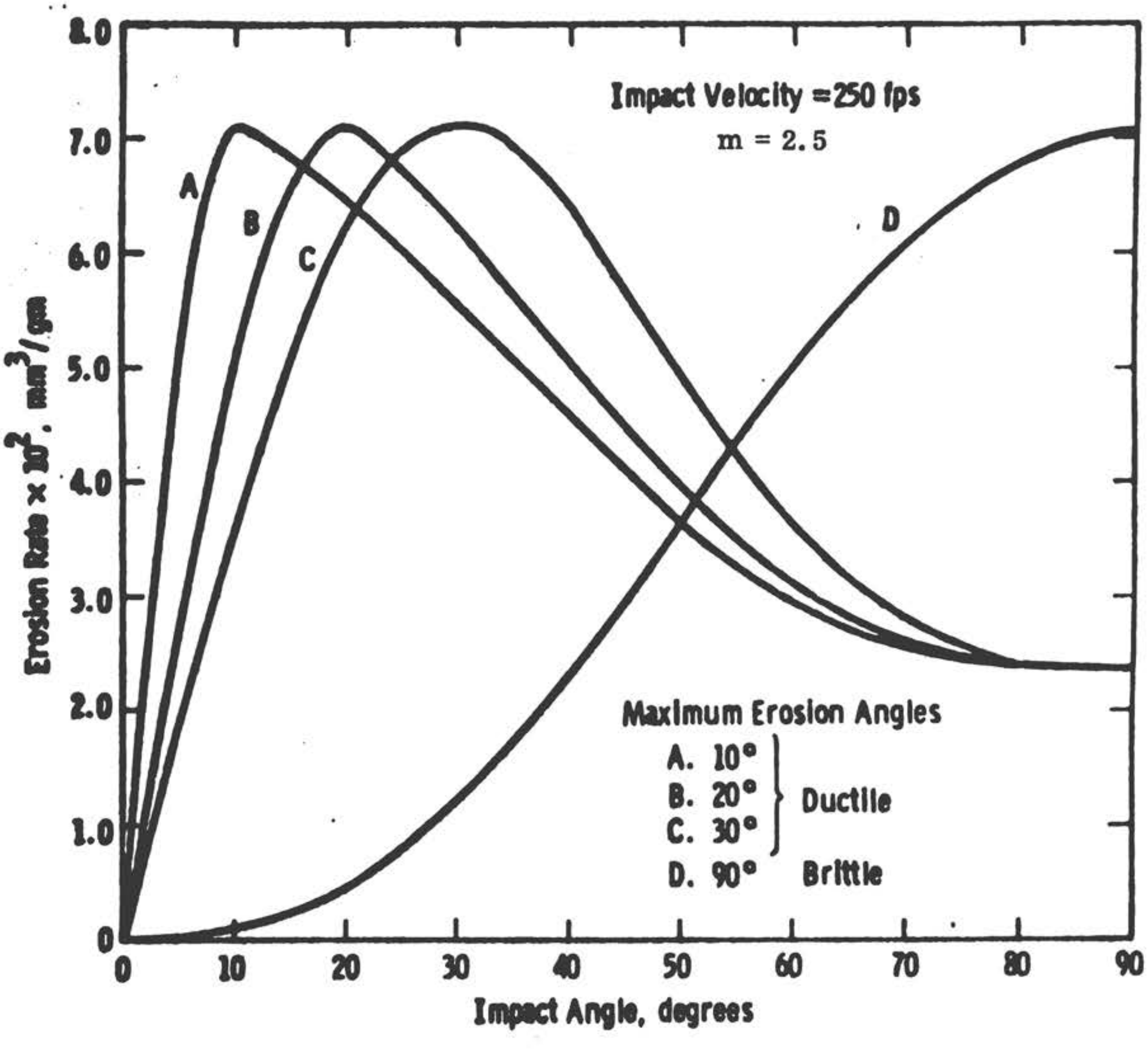


FIGURE 9-3 Erosion Curves Corresponding to Four Angles of Maximum Erosion Damage

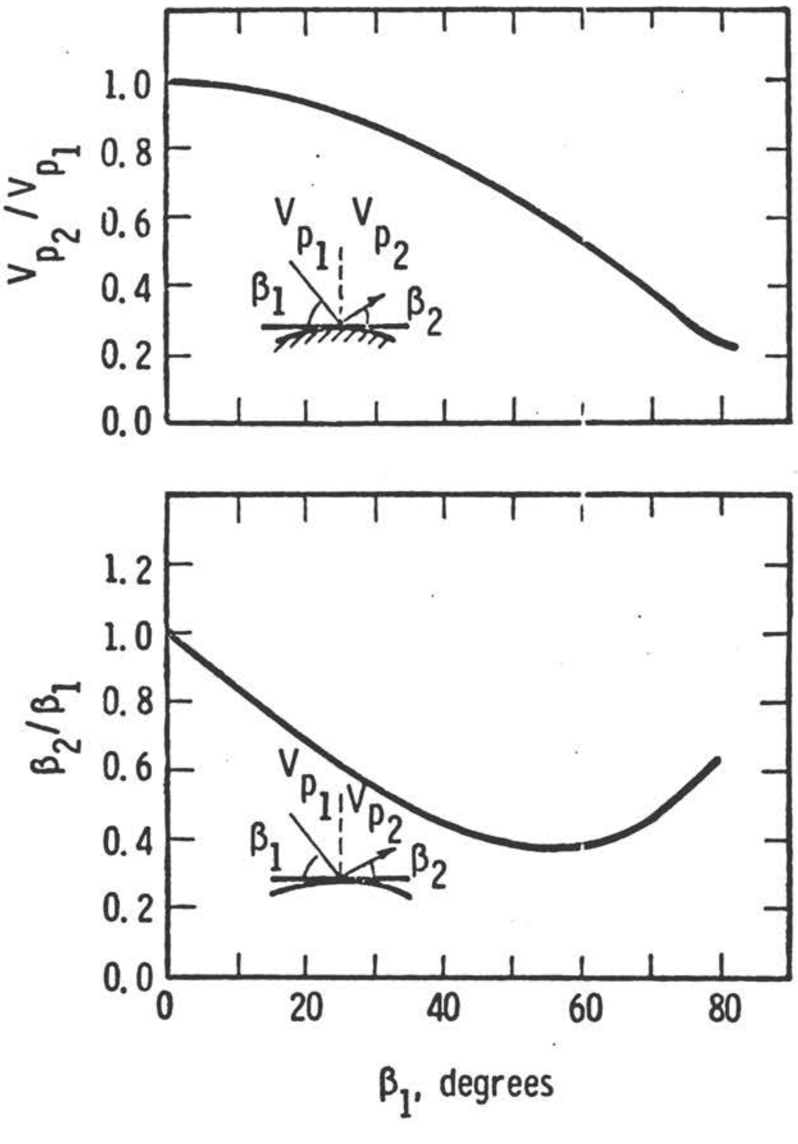


FIGURE 9-4 Particle Rebound Data by Hussein (Data from Ref. 5)

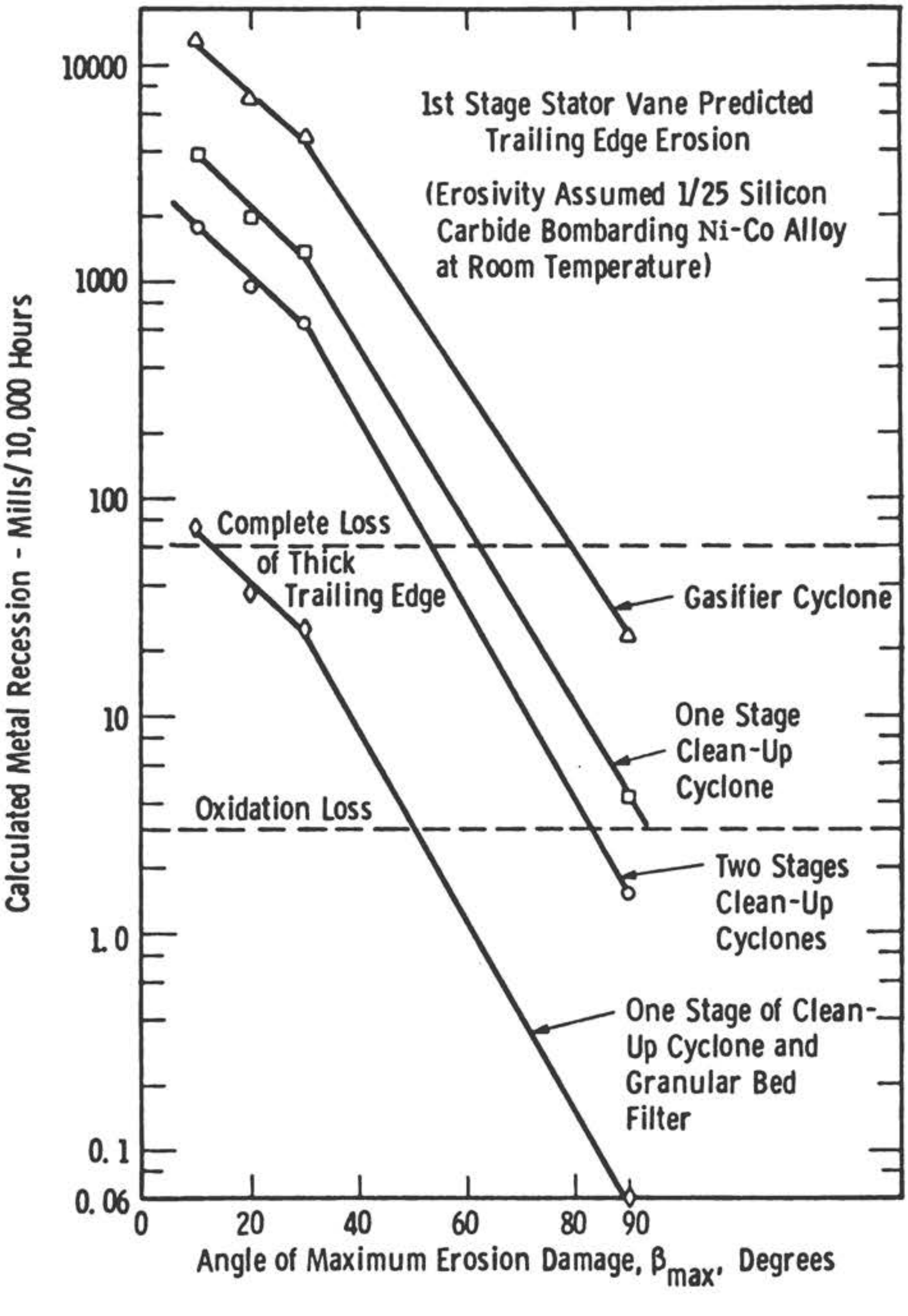


FIGURE 9-5 First-Stage Stator Vane Trailing Edge Erosion

particle before impact, (2) controlling the angle of impact, and (3) choosing the material which absorbs the impact.

Figure 9-6 presents data obtained by Smeltzer and his coworkers[6] showing the erosion damage measured when an aluminum alloy was bombarded at one incidence angle, 37.5° by two different types of particles, silica sand and Arizona road dust. The curve shows the dependence of the erosion damage on the kinetic energy of the particles before impact. Halving the velocity of the particles before impact reduces the kinetic energy and erosion damage per impact to one quarter. Because particle velocity and fluid velocity are related, lowering fluid velocities strongly reduces erosion damage. However, there is a price to pay -- lowering fluid velocities through a pump or pipe decreases capacity. Larger equipment is required to handle the same quantity of material. Capital costs increase. There is also a limit to which velocities can be lowered and still transport particles entrained in the fluid.

Reduction in particle size increases the number of particles per unit mass of particulate matter at the same rate as it decreases the mass of each particle. On this simplified basis, grinding the particles to a finer size distribution is not an effective erosion control technique. (The secondary effects of being able to transport smaller particles at lower velocities, the lower capture efficiency of equipment for small particles, and the aerodynamic braking of fluid boundary layers slowing micron-sized particles, however, will cause reduced erosion damage for distributions of smaller particles in some applications.)

Smeltzer's curve raises the question of the possibility of engineering to achieve particle energies below the threshold at which erosion damage effectively ceases. Table 9-1 tabulates the erosion energy thresholds from Smeltzer's data, and assuming spherical particles of density 2.5 gcm^{-3}, gives calculated values of the maximum velocity which the particle could have before exceeding the threshold.

The erosion damage threshold is on the order of 200 fps (91 m/sec) for these small particles. How does the threshold change as particle size exceeds 20 microns diameter? Large particles may fragment on impact, complicating the situation. The shape and orientation of particles striking the surface and the nature of the exposed surfaces all influence the energy required to remove material. How do the thresholds vary for other impingement angles? How do they vary for other alloys and engineering materials? Hard quantitative data for design use is rare, scattered and difficult to find and often equally difficult to apply. The literature is filled with screening test data that is almost useless for design. Data containing the

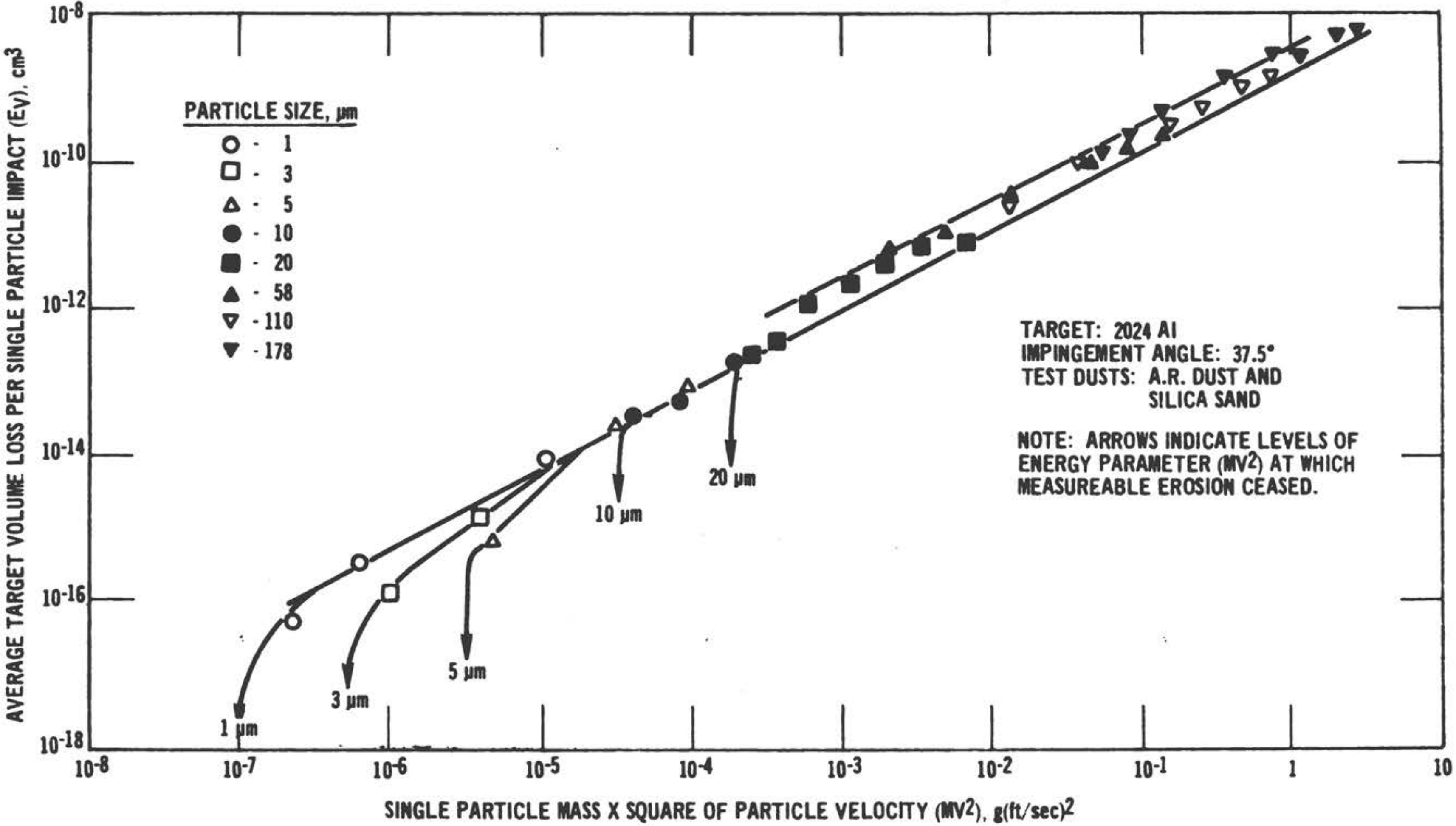


FIGURE 9-6 Erosion Damage Data (According to Smeltzer, et al., Ref. 6)

TABLE 9-1 Erosion Energy Thresholds and Corresponding Maximum Particle Velocities to Avoid Erosion Damage Impacting 2024 Aluminum Alloy at 37.5°

Particle Diameter		Particle Volume $(\pi/6)d^3$	Particle Mass	Threshold mv^2 For Erosion Damage	Maximum Velocity
microns	cm	cm^3	grams	gms $(fps)^2$	fps
1	1×10^{-4}	5×10^{-13}	1.3×10^{-12}	1×10^{-7}	280
3	3×10^{-4}	1.4×10^{-11}	3.5×10^{-11}	5×10^{-6}	120
5	5×10^{-4}	6.5×10^{-11}	1.6×10^{-10}	3×10^{-6}	140
10	10×10^{-4}	5.2×10^{-10}	1.3×10^{-9}	3×10^{-4}	150
20	20×10^{-4}	4.2×10^{-9}	1.0×10^{-8}	2×10^{-3}	140

precautions needed to obtain defined particle-impact velocities and impact angles, on defined surfaces of practical importance, which can be combined with calculations of the angle and velocities of impact in the equipment is needed.

3. Material Selection

Engineers should make an intelligent selection of erosion resistant materials when considering selection or design of components expected to experience erosive conditions.

With an appreciation of the limitations both in reliability of erosion properties and the cost, materials can be selected specifically for their erosion resistance. For instance, the effective lives of centrifugal slurry pumps have been increased by several hundred percent by attaching ceramic erosion plates to critical areas of the impellers. In this example, the significant cost of the ceramic inserts was compensated by a significant reduction in cost downtime for pump repair.

The materials selection process involves location of anticipated excessive erosion areas in the system and estimation of impingement angle, surface temperature, and particle velocity. Temperature and impingement angle can be used as the criteria to narrow the materials selection process. Generally, high temperature [above 100°F (38°C)] and high impingement angle requires ceramics, and intermediate temperature [to 800°F (425°C)] and low impingement angle requires metal alloys. Elastomers are appropriate for high impingement angle and moderate temperature [below 300°F (150°C)].

Abrasion- and wear-resistant alloys can be classified as indicated in Table 9-2.

TABLE 9-2 Classification of Erosion-Wear Alloys

This classification can be further reduced to two basic types of alloys: (1) alloys with hard particles in a tough matrix, which include tungsten carbide composites, high-chromium irons, cobalt-base alloys, and nickel-base alloys, and (2) work-hardening steels, which include both martensitic and austenitic steels. Most frequently, these products are used in the form of hard-facing deposits on a more economical or otherwise required engineering substrate, although other forms such as fabrications from wrought products, castings, or powder metallurgy inserts are also employed to reduce erosion, abrasion, and wear in localized areas.

For a variety of materials, erosion resistance appears to increase with increasing hardness. This is not true, however, within a given class of materials. In metal alloy systems, microstructure and toughness can be important properties to consider for erosion resistance. For many steel alloys for instance, erosion resistance is little influenced by different bulk hardness levels achieved in a given alloy. An example of this effect was shown in Figure 5-6 where erosion resistance of tool steel is shown essentially constant over a fourfold range of hardness. Generally, erosion resistance increases with increasing carbide content. Microstructure is important in steels and cast irons. For a given carbon level, erosion resistance tends to increase as one goes from bainitic to pearlitic to austenitic to martensitic structures. However, when corrosion is involved or when toughness may be a factor (large particles, high impact velocity) austenitic materials often outperform martensitic steels. For those alloys which depend on structure for hardness, those with a fine, well dispersed carbide in a high yield strength matrix perform best. The erosion process tends to remove hard particles from a softer matrix. The higher the ferrite content of pearlite, the lower the resistance to erosion. Chromium and molybdenum increase the matrix strength and, therefore, improve erosion resistance. Although hard, tough structural alloys often can provide sufficient erosion resistance for energy systems, there is a growing list of special alloys being selected for aggressive environments found in developing energy systems such as coal gasification plants. A partial listing of alloys being considered for coal gasification applications is shown in Table 9-3. These alloys combine significant corrosion resistance with erosion resistance.

The effect of elevated temperature on erosion characteristics of engineering alloys is not well understood. It is known that many alloy systems, notably austenitic steels, show an increase in erosion resistance as temperature increases to a point where loss in yield

TABLE 9-3 Candidate Metallic Materials for Application in Coal Gasification Plants

Designation	Classification	Nominal Composition - Percent							Application
		C	Mn	Si	Cr	Ni	Mo	Other	
Ni-Hard*	Alloy White Iron	3.30	0.50	0.50	2.50	4.50	-		Wear parts for pumps, valves, feeders
Ni-Hard IV*	Alloy White Iron	3.20	0.50	1.75	8.50	6.00	-		
15 Cr-3 Mo	Alloy White Iron	4.00	0.85	0.50	15.00	-	2.75		
Stellite 12**	Hard Facing Alloy	1.80	-	-	29.00	-	-	(59.0 Co (9.0 W	
A-285	Carbon Plate Steel	0.20	0.70	-	-	-	-		Shells, heads, ducts
A-204	C-Mo Plate Steel	0.25	-	0.25	-	-	0.50		
A-302	Mn-Mo Plate Steel	0.25	1.00	-	-	-	0.50		
A-387 (Grade D)	Cr-Mo Plate Steel	0.15	0.40	0.40	2.25	-	1.00		
A-516	C-Si Plate Steel	0.27	0.70	0.25	-	-	-		
A-533	Mn-Mo-Ni Plate Steel	0.25	1.25	0.25	-	0.85	0.50		
310	25/20 Stainless Steel	0.20	1.00	1.00	25.00	20.00	-		Exposed internals and penetrations, high temperature cyclones
Alloy 800	Wrought Heat-Resistant Alloy	0.04	0.75	0.35	20.00	32.00	-	Bal Fe	
Alloy 600	Wrought Heat-Resistant Alloy	0.04	0.20	0.20	16.00	72.00	-	Bal Fe	
Inconel 601*	Wrought Heat-Resistant Alloy	0.05	0.50	0.40	22.00	60.00	-	(1.35 Al (Bal Fe	
HK-40	Cast Heat-Resistant Alloy	0.40	1.00	1.00	25.00	20.00	-	Bal Fe	
HP	Cast Heat-Resistant Alloy	0.40	1.00	1.00	25.00	35.00	-	Bal Fe	
Supertherm***	Cast Heat-Resistant Alloy	0.50	0.30	1.70	26.00	35.00		(5.00 W (15.00 Co (Bal Fe	
50 Ni-50 Cr	Wrought Heat-Resistant Alloy	-	-	-	50.00	Bal	-		
	Kanthal Type				15-25			(3-6 Al (Bal Fe	
Alloy 400	Formerly Monel	0.12	0.90	0.15	-	Bal	-	31.5 Cu	Shell liner

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* Trademark of the International Nickel Company, Inc.

** Trademark of the Stellite Division of Cabot Corporation.

*** Trademark of Engineered Products Division of Abex, Inc.

NOTE: Data from A. M. Hall, Battelle Columbus Laboratories, Columbus, Ohio.

properties accelerates. The ductility gained at elevated temperatures can reduce erosion through increased fracture toughness; however, while benefits may be gained from the standpoint of erosion, the concomitant reduction in strength may not satisfy the overall structural requirements.

The use of erosion resistant coating is growing as the size of components requiring both structural strength and erosion resistance increases. One major factor in this trend is economic. Many special alloys and ceramic materials whose cost per pound is high can be just as effective when used as a coating on a much less expensive structural steel. Coating systems include hard facing, plasma spray and electroplating. The bond between the coating and substrate is essential to the success of the coating. Therefore, selection of the coating requires not only consideration of the corrosion/erosion resistance of the coating material but also the compatability or "match" between the coating and substrate.

Because hard-facing is frequently used, the following are a description of typical erosion/wear alloys applied by the many hard-facing techniques.

a. Tungsten Carbide Composites. Tungsten carbide is about 4-weight percent carbon with the balance tungsten. It is one of the most abrasion-resistant materials and is a widely used "hard" particle. Other carbides, oxides, borides, and nitrides are also used in composites, but tungsten carbide generally performs better and is preferred. Tungsten carbide is generally sold as a "tube rod" composed of about 60 percent by weight of carbide with the balance being the sheath--usually steel. The sheath of the rod is melted onto a substrate and when solidified holds the hard carbide particles in place to protect the base from erosion.

Small carbide particles in the tube rods are utilized when smooth surfaces and improved impact resistance are desired. Conversely, larger particles yield a rougher surface, better abrasion resistance, but less impact resistance. (Impact often results in fracture and subsequent loss of the carbides).

Modification of the basic tungsten carbide in steel tubes by substituting either nickel- or cobalt-base tubes for the steel is a technique frequently used to improve the aqueous corrosion or high temperature oxidation resistance of the deposit.

b. High-Chromium Irons. A multitude of high-alloy, high-chromium wires and rods are commercially available and optimum selection is often difficult. These materials nominally contain 2 to 6 percent by weight carbon and 14- to 31-weight percent chromium. Other alloying elements like silicon, manganese, molybdenum, nickel or cobalt are added to enhance specific characteristics like fluidity, toughness or corrosion resistance. These alloys are recommended to avoid severe abrasion but light impact applications such as in moving or grinding earth related materials.

c. Cobalt- and Nickel-Based Alloys. These materials are typically highly alloyed with a combination of several of these: carbon, chromium, tungsten, silicon, molybdenum, manganese, and boron. The alloys are characterized by their resistance to combination environments of temperature, corrosion, abrasion, erosion or metal-to-metal wear. Hard chromium carbides (Cr_7C_3) and/or tungsten-molybdenum rich carbides (M_6C) form in a tough corrosion-resistant matrix as the deposits solidify from the molten state on deposition.

Nickel-base alloys followed cobalt-base alloys in development and were developed basically as a cheaper substitute. Frequently, nickel-base alloys contain boron and silicon to reduce the melting temperature, to impart a fluxing action, and to make deposition easier.

d. Work Hardenable Alloys. These products are used for severe impact and light to moderate abrasion or erosion applications at low temperatures. Nickel, chromium and/or manganese are alloyed with iron to provide an alloy which work-hardens with impact during service. Thus, a tough hard surface is combined in one product. Typical applications are in shovels and material handling equipment.

C. MATERIAL LIMITATIONS AND UNKNOWNS

The above "rule-of-thumb" guidelines are useful and have been successfully employed to alleviate and solve engineering erosion and wear problems, but there are significant limitations to this state of the art.

Much of the erosion data and expertise are founded on room and near room temperature experience. Elevated temperature experience, especially in hostile environments, is not currently available. Resistance to deformation (hardness) is a key variable in some erosion-wear equations and it is known that softening of materials occurs at variable temperature conditions so that materials which are hard at room temperature may become quite soft and susceptible to erosion at even moderate temperatures. Recent data from EPRI studies support the corollary that some comparatively soft materials at room temperature remain comparatively hard and more erosion resistant at higher temperatures, as illustrated in Figure 9-7.

Elevated temperature classification, even on an empirical basis, of existing engineering erosion resistant materials is poorly documented. This is required, at least on a limited basis, before successful modeling can be accomplished to predict a wide variety of condition-dependent materials.

Many of the wear/erosion resistant alloys (castings and hard-facings) used today were developed seventy years ago as were the specifications which govern their compositions. With respect to compositional ranges of alloys, the industry is operating under the melting, refining, and application technology which is little changed since 1900. Little has been done to better define and optimize the major element ranges (chromium often has a 4-weight percent range for example). The same is true to a greater extent of the permissible ranges of minor elements; those elements are commonly present as unintentional addition up to perhaps 3- to 4-weight percent. Modern melting techniques and associated control capabilities allow major elements to be controlled at least to the 2-weight percent level and minor elements to the 1 w/o range and, in some instances, to 0.5 w/o ranges.

Tighter composition ranges would mean higher costs, but improved service and reliability might well justify closer controls. Metallurgical form, morphology, and structure of commercially available alloys can, and do, vary significantly depending upon a) the composition of the particular batch as alluded to above, b) dilution and technique of application in the instance of hard-facing and c) solidification and cooling rates of hard-facings and castings. Little has been done to establish the relation of these inherent variables to service capability and reliability.

Further, alloy systems are typically modified by high-temperature exposure, i.e., phases stable at room temperature are metastable at higher temperatures. In many instances these changes are ill-defined.

Cost and availability of erosion resistant materials are considerations if energy-producing systems are to be cost effective. Traditional erosion-resistant materials contain significant amounts of chromium, tungsten, and cobalt which will be in short supply at the same time that the demand for existing alloys increases in proportion to the nation's energy requirements and other applications of the scarce materials increase. These are nondomestic elements and recently have experienced sky-rocketing price increases. The ability to substitute other more readily

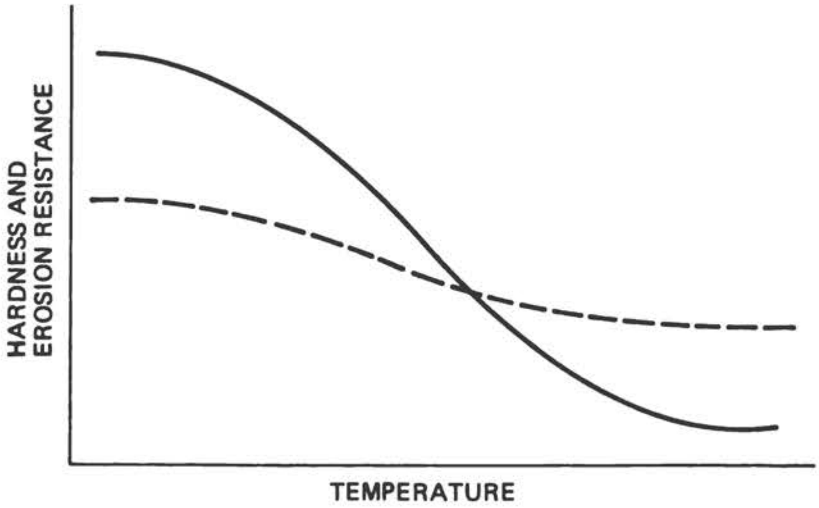

FIGURE 9-7 Schematic of Hardness and Erosion Resistance of Two Classes of Materials as a Function of Temperature

available constituents (nitrides and/or borides for carbides; iron, nickel or manganese for cobalt; and molybdenum for tungsten) is unknown and requires attention if even the current level of erosion resistant capability is to be maintained. Finally, the market for and application techniques of current erosion-resistant alloys requires evaluation.

Powder metallurgy and especially moderate cost expendable powder metallurgy inserts offer promise of an efficient method of alleviating costly downtime in energy producing systems. Powder metallurgy inserts and components can be manufactured from alloys which can be neither successfully cast in significant cross sections nor laid down by hard-facing procedures. This is a fruitful, but poorly developed, area of endeavor.

Method technology has grown consistently in the hard-facing and surface technology areas: examples are plasma spraying, vapor deposition, diffusion bonding, and submerged arc application.

Laser technology has developed sufficiently so that it should be considered as an additional tool for precise surface modification to improve erosion and as a method for joining erosion-resistant materials to substrates. This is a concept which requires reduction to practice.

D. CERAMIC MATERIALS

Severe conditions in energy systems such as gasifiers in coal gasification plants require large sections of ceramic materials. This is a complete departure from metal alloy systems or coatings in that the material is selected for its resistance to high-temperature [over 1800°F (980°C)] corrosion and its very high hardness. Materials like these having engineering applications include aluminum oxide (hot pressed, high density), silicon nitride, silicon carbide, zirconium dioxide, and magnesium oxide. There are many more combinations of oxides, carbides, borides, and nitrides having various binders and sintering systems. These materials are used in preformed sections which are fitted together and mounted on structural metal frames or holders. They are also used as wear plates to be mounted in critical high-erosion zones of components. Selection and application requires consideration of temperature, gaseous environment, thermal expansion properties of the mounting system, and cost of forming. Shaping can only be done by grinding and this is prohibitively expensive for large components. The use of ceramics in structural applications, specifically for gas turbines, is described in a recent National Materials

Advisory Board Report(7). This report adequately covers design consideration.

E. REPLACEMENT TECHNOLOGY

Finally, the engineer should consider the problem of maintenance and replacement of components subject to erosion. Parts such as valve seats, wear plates, etc. can be incorporated into a design so that they are easily replaceable. Since there is no universal completely erosion-resistant engineering material one must learn to live with and accommodate to the fact of erosion as a cumulative damage process.

F. SUMMARY

At the present time the engineer, faced with design and operation of systems in which erosion, corrosion, and deposition are major concerns, is supported by a largely empirically based technology. Many of the process conditions -- high-temperature corrosive environments -- are new and there is no relevant background of experience to draw on. Carrying out an integrated development program with an adequate parallel technology development program offers the most cost-effective method of insuring that demonstration plants demonstrate solutions rather than problems. Extension of basic understanding of material removal mechanisms from alloys and ceramics, extension of understanding of fabrication and application processes and extension of design capability in parallel with building and operating plants are needed.

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APPENDIX

EROSION/CORROSION RESEARCH PROJECTS

Active projects on erosion/corrosion identified during the tenure of the Committee are compiled in Tables A-I through A-III. The listings include not only efforts arising from energy conversion activities, but also work in other areas which have some bearing on ERDA's concerns with erosion/corrosion. The work identified undoubtedly does not include all that is under way or completed within the last few years, particularly that which is performed as part of a system development. However, the compilation was useful in indicating the scope of many programs of interest to the Energy Research and Development Administration, the Department of Defense, the National Aeronautics and Space Administration, the National Science Foundation, the Department of the Interior, the Department of Commerce, as well as organizations outside the government, such as the Electric Power Research Institute.

The compilation is arranged in three tables, covering erosive temperature regimes, as follows:

Table A-I:	Erosion/Corrosion: Room Temperature To 390°F (200°C)
Table A-II:	Erosion/Corrosion: At Temperatures Between 390°F (200°C) And 1110°F (600°C)
Table A-III:	Erosion/Corrosion: At Temperatures Over 1110°F (600°C)

TABLE A-I. Erosion/Corrosion: Room Temperature To 390°F (200°C)

In this temperature regime, energy conversion programs reflect an interest in developing understanding of mechanisms of erosion and wear relating to coal-handling equipment. Studies are conducted in laboratory and plant environments on metals, coatings, and ceramics. In particular, improved valve materials, coatings and designs are sought. DOD interest is in developing improved materials and coatings for missiles and aircraft components subject to erosive wear by dust, rain, and ice. Mechanisms of erosion studies are prominent. Components of interest include radomes, infrared (IR) domes, IR windows, nose tips of missiles, leading edges of aircraft structures, turbine fans, turbine compressors, and helicopter rotors. Behavior of ceramics and plastic composites are of particular concern. Studies of cavitation erosion in high performance propellers, machinery, and structures of high-speed craft such as hydrofoils are of interest for marine applications.

TABLE A-II. Erosion/Corrosion: At Temperatures Between 390°F (200°C) And 1110°F (600°C)

In this temperature regime, energy conversion interests are related largely to steam turbine systems and coal gasification system valves controlling movement of coal slurries and chars. Particular problems include erosion in cooling channels caused by high velocity water in water-cooled turbines. Spalling of oxides in steam turbines is a problem. Geothermal brines involve erosive problems because of solid particulates. Metals, ceramics, and coatings are evaluated.

TABLE A-III. Erosion/Corrosion: At Temperatures Over 1110°F (600°C)

High-temperature erosion/corrosion interactions become significant in investigations shown in Table A-III. The systems studied include mechanisms of erosion/corrosion in coal conversion, high-temperature gas turbines, MHD systems, and military-oriented applications, such as re-entry vehicles and gun barrels. In coal conversion systems, components considered are primarily valving, transfer lines, cyclones, heat exchangers, boilers, combustors, and gasifiers. Material development and evaluation of components are considered relative to resistance to combustion products of liquid and gaseous fuels.

In high-temperature gas turbines, particular emphasis on material resistance to oxidation-sulfidation reactions is noted in addition to high temperature particulate erosion. Materials development and evaluation primarily involves superalloys and ceramics. Rotors, stators, combustors, and regenerator/recuperator materials show the greatest erosion/corrosion problems.

TABLE A-I. Erosion/Corrosion: Room Temperature To 390°F (200°C)

PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To conduct an experimental investigation of mechanisms of wear and erosion.	Plastic deformation associated with erosion (single and multiple particle impact) of metals (copper and stainless steels) will be evaluated by electron microscopy. Effects of work-hardening and microstructure will be assessed. Apparatus is being built allowing accurate measurement of particle velocity and impact angle. Longer range plans include evaluation of erosion-induced substructure and erosion of ceramics.	Mechanism studies	Argonne National Laboratory	ERDA
To develop NDI techniques for coatings in-situ in large scale plants.	Wear and process resistant coatings are investigated by NDI techniques to enable in-situ inspection of them.	General purpose	Oak Ridge National Laboratory	ERDA
To develop understanding of the metallurgical properties of surfaces used in weapons development and the generation of desired surface properties by choice of materials, surface modification, and the forming of new surfaces.	Studies are made of surface-surface contact deformation and adhesion using carefully controlled environmental conditions and sensitive measurement techniques appropriate to applications in friction and wear, electrical contacts, and friction bonding. Electrical contact arcing studies involve the effects of voltage on contact erosion, and material transfer between arcing contacts.	Weapons development	Sandia Laboratories	ERDA (Division of Military Applications)
To investigate erosion at room temperature of nominally brittle materials.	Single crystals and polycrystals of MgO, Si, and W will be impacted by solid spherical particles of hardened steel and Al_2O_3. Single impact studies will be undertaken using particles with diameters from 1 to 3,000 microns impacted at velocities to 200 m/s. Mechanisms involved in nucleation and growth of cracks will be investigated.	Mechanisms of erosion	University of Kentucky, School of Engineering	NSF DMR75-10347
To examine the mechanism of erosion of metals by cavitation and the influence of metallurgical structures on erosion rates.	Influence of sample thickness on the depth and magnitude of the residual stresses will be measured. Size of bubbles created at 10-30KHz will be determined. Relationship between applied and residual stresses will be determined.	Cavitation mechanisms study	State University of New York Stony Brook, NY	NSF DMR72-03227A01

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR NO.
To investigate mechanisms of solid particle erosion on single crystals of ceramics and metals.	Spherical and oriented cubical particles will be impacted on crystal surfaces at velocities up to 3 x 10 to the fourth power cm/sec. Variables to be studied include particle size and velocity, angle of impingement, and crystallographic orientation of the target surface. The size and shape of particles before and after impact will be examined to determine if eroding particles are damaged by impact. A comparison of various erosion theories will be initiated.	Basic study to provide guidelines for designers of materials used in energy systems such as coal gasifiers and magnetohydrodynamic generators	Pennsylvania State University, School of Earth and Mineral Sciences	NSF DMR76-02733
To develop chemical vapor deposition (CVD) techniques for coating ferrous ball valve seats with erosion resistant materials.	Procedures have been developed to coat ball valve seats with CVD tungsten. Laboratory erosion rates are less than that of Stellite 6B. Ball valve seats will be tested in-situ in a coal gasification plant. Titanium nitride and titanium carbide coatings are being developed and evaluated.	Valve materials for coal gasification units requiring resistance to wear, abrasion, erosion, and shock	Rolla Research Center	Bureau of Mines
To develop feasible designs for large valves for service with lock hopper systems for admission of coal into and release of char from full scale coal gasification reactors.	Studies include evaluation of bearing designs and materials resistant to wear and abrasion in a valve handling pulverized coal and char.	Coal gasification reactors	Rockwell International Company, Flow Control Division, Pittsburgh, PA	Rockwell International Company
To mitigate erosive effects of rain and sand on naval aircraft.	Abrasion-resistant coatings are evaluated by whirling arm tests in a rain field. Teflon-filled polyurethane coatings and elastomeric polyurethanes are being studied.	Rotor blades made from fiberglass reinforced resin matrix composites; radomes; metal leading edges of aircraft	Naval Air Development Center	NAVAIR
To develop capability for research on rain erosion damage and for qualification of materials.	A rotating arm apparatus has been designed and fabricated. Impact fracture velocity, erosion incubation times, and erosion rate dependency on rain intensity, velocity, and impact angle will be established for predicting the behavior of radomes, metal coatings, elastomers, paint, or metals.	Aircraft and missile radomes, leading edges, and structures	Naval Air Development Center	NAVAIR
To develop erosion-resistant coatings for gas turbine components	Resistance of coatings to erosion by sand is evaluated on a T58 turbine engine first stage compressor rotor. Coatings include $Ni-Cr_3C_2$, Al Seal, Sermetel W, and Chromalloy A-12.	Turbine fan and compressor blading	Naval Air Propulsion Test Center	NAVAIR

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To develop resin matrix composites with inherent resistance to impacts by heavy particles (gravel, metal) as well as light particles (water, sand).	Composites containing reinforcements in three directions will be evaluated for resistance to impact using steel indenters. Materials to be studied include fiberglass and carbon fiber reinforced resins.	Composite airframe structures	Fiber Materials, Inc.	NAVAIR
To develop understanding of response to impact of polymeric materials, including composites and polyurethane coatings.	Emphasis is on studying reactions of polymethyl methacrylate, polycarbonate, and epoxy to impact by steel balls. Response is evaluated in terms of breaking of material and densification in the impacted area.	Radomes and composite airframe structures	General Electric Company (Schenectady, NY)	NAVAIR N00017-75-C-0320
To develop wear, erosion, and corrosion resistant coatings for titanium alloys.	Chromium-molybdenum coating systems are being developed for application to Ti-8Al-1V-1Mo, Ti-6Al-4V, and Ti-6Al-6V-2Sn. Deposition techniques include electroplating and sputtering. Coatings containing 1 and 3% Mo are impinged by a high velocity stream of 27 micron aluminum oxide particles to evaluate erosion behavior.	Aircraft components, including gas turbines	Pratt & Whitney, Florida Division	NAVAIR N00019-76-C-0342
To develop evaluation procedures and predictive capability for the impact performance of composite materials. Material/structural response and localized damage mechanisms will be studied.	An experimental/analytical approach will be mounted to investigate the impact performance of homogeneous and advanced composite materials. Penetrability of penetrators made of Al, 6Al-4V-Ti, epoxy, and aluminum reinforced with alumina fibers have been evaluated. Ceramic face/fiber reinforced plates for armor are being evaluated.	Armor	Naval Research Laboratory	Naval Research Laboratory
To perform particle erosion tests in the Naval Surface Weapons Center Ballistic ranges in support of nosetips erosion studies.	Tests will be performed in the 1000-ft. hyper-ballistics range. Erosion data will be obtained by flying models through rain or dust and optically observing the damage in flight.	Nosetips of re-entry bodies	Naval Surface Weapons Center, Silver Spring, Md.	Navy Strategic Systems Project Office

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To investigate fracture-related impact damage, such as brittle-to-ductile transition, fracture toughness, strength.	Materials include alumina, silicon carbide, silicon nitride, spinel, silicon, zinc selenide, magnesium oxide. Tungsten carbide, steels, and aluminum impacter spheres will be employed with velocities of 3 and 600 meters per second.	Ceramic components such as missile domes	National Bureau of Standards	ONR 032-535
To develop understanding of ceramic materials behavior under particle impact loading. Analytical prediction, particularly of incubation stage.	Target materials include lithium fluoride and magnesium oxide. Liquid droplets of well-defined diameter and velocity will be used.	IR windows, nose tips, radomes, high temperature blading, bearings	Battelle Columbus Laboratories	ONR 032-64
To determine the mechanisms of pitting of aluminum alloys in seawater at flow velocities typical of surface effect ships.	Aluminum alloys are exposed to seawater at flow velocities from 0 to 60 knots with controlled Reynolds numbers. A model for pitting is to be established relating oxygen content, velocity and boundary layer turbulence to critical pitting potential, pitting behavior, and pit morphology.	Navy surface effect ships	Bell Aerospace Company, Division of Textron Inc.	ONR N00014-75-C-1087
To conduct theoretical and experimental studies on the dynamics of cavitation damage and on the effect of dilute polymer solutions on inhibiting cavitation.	Experiments will be carried out to study the pressure behavior across a flat plate and to measure polymer relaxation times.	Navy ship and machinery elements such as propellers, shafting, rudders, struts, hydrofoils	University of California, School of Engineering, San Diego, California	ONR N000-14-69-A-0200-6004
To achieve fundamental understanding of the cavitation erosion process.	Emphasis is on establishment of scaling laws for modeling cavitation erosion intensity; study of role of physical properties of liquid on cavitation erosion; investigation of the adhesion failure of protective coatings due to cavitation erosion; and study of wear particles produced by cavitation erosion in lubricating oils.	High speed Navy craft such as hydrofoils, supercavitating propellers and high performance machinery	Catholic University of America, School of Engineering and Architecture	ONR N00014-67-A-0377-008
To develop an understanding of fracture mechanisms under particle impact loading.	Quantitative fractography is used to characterize impact damage and subsequent fractures in polycrystalline ceramics under indentation loading. Si_3N_4, SiC, and glass are compared.	IR domes, radomes, turbine parts, bearings	Ceramic Finishing Company	ONR 032-545

PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR NO.
To improve understanding of the mechanism of cavitation erosion and the ability to predict field experience from laboratory data.	Theoretical and experimental investigations are carried out. Emphasis is on investigation of scaling laws for cavitation erosion, study of the role of physical properties of liquids in cavitation erosion, and the concept of erosion strength as a scaling parameter.	High speed naval craft, hydrofoils, supercavitating propellers, high performance machinery	Daedlean Associates Woodbine, Maryland	ONR NR062-436
To investigate damage on crystalline inorganic materials caused by rain, ice crystals, and airborne dust at high impact velocities. Erosion mechanisms will be studied.	Calcium fluoride, magnesium oxide, silicon, germanium and sapphire will be exposed to single and overlapping water drop impingement with an air gun.	Infrared sensor windows, infrared laser windows, and radomes of missiles and aircraft	Effects Technology, Inc., Santa Barbara, California	ONR 032-565
To define lifetime and performance limitations such as erosion damage to aid development of materials capable of resisting exposure to erosive environments. To establish erosive models for multiple solid particle impacts on brittle materials.	Hot pressed silicon nitride, reaction sintered silicon nitride and hot pressed magnesium fluoride will be studied after impact by controlled numbers (one to ten thousand) of particles.	Gas turbine components, radomes and IR domes	Solar Division, International Harvester Company	ONR 032-542
To develop methods of predicting the occurrence and intensity of cavitation erosion in full scale marine systems from laboratory tests.	Experimental investigation will be conducted to develop and validate laboratory methods of predicting cavitation damage in prototype systems. Effort will include development of pulse-counting techniques for correlation with damage measured in a vibratory test facility in water over a range of pressures and temperatures.	Navy high speed craft such as hydrofoils. Supercavitating propellers and high performance machinery	University of Michigan, School of Engineering	ONR N00014-76-C-0697
To determine the response of plasma spray coated steel to cavitation erosion in the marine environment, and to correlate this response with coating characteristics and the dynamics of the cavitation process.	Steel is plasma sprayed with aluminum and alumina under a variety of conditions. Coatings are characterized and cavitation response measured using a vibratory probe in distilled water, saline solutions, and seawater.	High speed Navy craft	State University of New York, Stony Brook, NY	ONR N000-14-75-C-1018
To develop an understanding of the onset and extent of brittle fracture and plastic deformation of brittle ceramics under single particle impact tests.	Materials removal caused by high impedance (WC) projectiles will be studied in the plastic regime. Glass or sapphire spheres will be impacted on ZnSe, ZnS, and MgO targets. Nylon spheres will be impacted on ZnS, MgO Si_3N_4, SiC.	IR domes, radomes, turbine parts, bearings	Rockwell International Science Center, Thousand Oaks, California	ONR 032-552

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR NO.
To understand materials behavior under particle impact loading in order to predict erosion rates, establish material development guidelines, predict performance under expected environments and define failure conditions.	Understanding is being advanced especially in the transition from low-velocity, rain-erosion processes to hypervelocity re-entry conditions. Delineation of velocity conditions under which static linear formulations become inadequate and the sensitivity of damage to microscopic and microstructural materials parameters are defined. The relation between single and multiple impact phenomena will be investigated.	Ceramic materials in IR windows, nose tips, heat shields and turbine blades which are particle impact loaded	Prototype Development Associates, Santa Ana, California	ONR N00014-75-C-1036
To improve the environmental durability of IR and radar domes in operating environments imposing severe conditions such as mechanical and thermal loading, and impact erosion.	Efforts are underway to improve the environmental durability of magnesia. Sputtered coatings of spinel (Mg Al_2O_4) and fosterite (Mg_2SiO_4) on magnesia are to be run in a high-humidity chamber. These materials and silicon nitride coated magnesia will be evaluated for rain erosion resistance. CVD coatings will also be assessed.	Missile radomes	Raytheon Company	ONR NR-008-002
To develop an understanding of the dynamic materials properties that govern erosion resistance of brittle materials and to infer how these properties are influenced by microstructural features.	Materials include alkali halides, ZnSe, MgF_2, and Si_3N_4. Plate impact fracture tests will be performed and compared with computational results. Micro-fracture features will be qualitatively assessed and correlated with computed stress histories. Subsurface fracture under particle impact sites will be compared with computationally simulated results.	Ceramic components such as IR windows, nose tips, radomes	Stanford Research Institute	ONR 032-563
To develop improved ceramic radome materials.	Supersonic rain erosion sled testing is conducted on fused silica, Si_3N_4, Sialon and ablative plastic cones for studying materials properties effects.	Radomes, rain caps	AMMRC MICOM	Army Materials and Mechanics Research Center

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To evaluate material samples and coatings required for improved high performance rain resistant radomes which are easier to mass produce than slip cast fused silica.	Samples eroded in sled tests will be examined. Slip cast fused silica specimens of various densities will be tested. The potential of new radome materials including laminates, composites, and coatings will be studied. Quasi-theoretical relations will be developed for use in design and selection of materials.	Radomes	Tennessee Technological University, Department of Engineering Science	U. S. Army Missile RD&E Lab., Redstone Arsenal
To study strengthening mechanisms in ceramics requiring resistance to rain and dust in IR windows and radomes (i.e. sapphire and alkaline earth halides).	Studies are made of the role of dislocation dipoles and loops in the work hardening and recovery of sapphire; the effectiveness of dopants in hardening of sapphire; the precipitation hardening of sapphire; and the relationship between crystal structure and deformation in spinels.	Missile IR windows and domes	Case Western Reserve University	DARCOM Army Research Office
To investigate the erosion processes in small turbomachinery in order to develop a quantitative model which will facilitate the prediction of erosion in future advanced turbomachinery.	Factors affecting ductile erosion, such as angle of impingement, particle velocity, size, shape and strength will be investigated experimentally. Work will be performed to examine effects of target material size, velocity dependence due to the angle of impingement and aerodynamic effect of temperature on erosion of alloys for compressors and turbines.	Helicopter gas turbine engines and filtration devices for gas turbine driven generator sets	University of Cincinnati	DARCOM Army Research Office
To produce erosion resistant coatings on leading edges of helicopter blades.	Titanium boride coatings on titanium alloys are optimized using sand blast and rotating arm rain testing for application to leading edge protection.	Helicopter rotor blades	Solar Division, International Harvester Company	AVSCOM (Army)
To investigate means of removing sand and dust-laden scavenge air from an integral engine inlet particle separator, thereby improving engine reliability and maintainability.	A parametric analysis is conducted of several separator scavenge systems to evaluate the efficiency and reliability. The selected system will be designed, fabricated and tested.	Aircraft gas turbine engines	AVCO-Lycoming	AVSCOM Air Mobility Research and Development Laboratory, Ft. Eustis

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To develop, fabricate, and environmentally test rotor blade leading edge elastomeric erosion protection strip.	Materials for erosion protection are reviewed, fabricated into specimens, and environmentally tested. A polyurethane erosion protection strip has been selected.	Leading edges of composite helicopter rotor blades	Hughes Helicopters, Culver City, Calif.	AVSCOM Air Mobility Laboratory Ft. Eustis
To evaluate threat to re-entry vehicles by hydrometeor erosion. To evaluate the ability of satellite instruments to estimate characteristics of ice clouds.	Radiative transfer in ice clouds will be studied. Numerical cloud models will be used to improve satellite estimation of cloud ice content.	Re-entry vehicles	Utah University	Air Force Geophysics Laboratory Hanscom AFB, Bedford, Mass.
To assess the effect of clouds and hydrometeors on aerospace vehicle erosion.	Numerical processing and analysis procedures are developed for airborne cloud physics instrumentation. Computer programs are developed to permit analysis of particle distributions, liquid water content, and other pertinent cloud physical parameters.	Aerospace Vehicles	Digital Programming Service, Waltham, Massachusetts	USAF Geophysics Laboratory Hanscom AFB, Bedford, Mass.
To investigate hypersonic ice erosion of re-entry vehicles.	Carbon-carbon nose tip materials and carbon-phenolic heat shield materials are investigated in ballistic ranges for hypersonic multiple impingement ice erosion and in single particle impacts for modeling tests. Analytical model of charlayer influence on erosion behavior is being developed. Single vs. multiple impact is being studied.	Re-entry vehicles	AVCO Corporation	USAF Materials Laboratory F33615-74-C-5149
To investigate rain erosion effects on IR window materials.	Chalcogenide materials such as ZnS, ZnSe, GaAs, and Ge are being impacted with single water drops and multiple drops for determination of cracking/fracture mechanisms which result in transmission loss through these windows. SEM and other microscopy are being extensively utilized with computer simulation of impact loading.	Aircraft and missile infrared windows	Bell Aerospace Company, Division of Textron Inc.	USAF Materials Laboratory F33615-76-C-5125

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To investigate supersonic rain erosion performance of ceramic materials and thermal protection materials.	Monolithic ceramics, carbon-carbon and quartz silica composites are exposed to multiple rain at velocities up to 5500 fps. Influence of impingement angle, velocity, heating, and influence of materials construction variables on erosion behavior are determined.	Missile radomes	USAF Materials Laboratory In-house Holloman Rocket Sled	USAF Materials Laboratory
To define mechanisms of erosion in re-entry materials.	Mechanisms of erosion in re-entry vehicle nose tip materials are determined by single impact tests. A comprehensive model which attempts to isolate individual environmental and materials parameter influences is being developed. Dynamic materials property tests and dynamic penetration tests are used.	Re-entry vehicles	Effects Technology, Inc., Santa Barbara, California	USAF/SAMSO
To develop antistatic, thermal flash resistant, rain erosion resistant polymeric coatings.	Polyurethane and fluorocarbon elastomeric coatings for aircraft radomes are being optimized using rotating arm rain erosion testing. Thermonuclear flash resistance, antistatic properties, radar transmission are also required.	Aircraft radomes	AVCO Corporation	USAF Materials Laboratory F33615-76-C-5210

TABLE A-II. Erosion/Corrosion: At Temperatures Between 390°F (200°C) And 1110°F (600°C)

PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To determine erosion effects on materials for use in geothermal systems.	Metal carbides, Stellites, AlN, Si_3N_4, SiC, MP35N cobalt base alloy; vapor-liquid-erosive environment containing fine solid particulates.	Turbine blades, nozzles	Lawrence Livermore Laboratory	ERDA
To develop and test hardsurfacing techniques for use of mechanical interfaces which require low friction movement without self-welding in a sodium or inert gas environment.	Design data on performance of metal-metal contact interfaces are required in LMFBR applications. The liquid sodium environment has potential of reducing lubricative oxide scales allowing metal-to-metal contact with resultant friction, wear, and welding. Candidate interface designs are tested in sodium, air, argon, and sodium vapor, for performance of hardsurfacing materials. Test data are reduced to design form and recorded in the <u>Nuclear Systems Materials Handbook.</u>	Nuclear reactors (LMFBR program)	(1) Westinghouse Advanced Reactor Division (2) Hanford Engineering Development Laboratory (3) Liquid Metal Engineering Center	ERDA Reactor Development and Demonstration Division
To survey the status of titanium technology and utilization for steam turbine blading. To collect information on development, operation, and payoff.	Titanium blading is of interest to steam turbine companies, and has reached production status in some organizations. The erosion resistance of titanium in wet steam appears better than 12 chromium steel and nearly as good as Stellite shielding in some tests.	Steam turbines	Battelle Columbus Laboratories	EPRI TPS76-641
To summarize the occurrence and control of steam grown oxide scale exfoliation from superheater and reheater tube steels.	A general description of growth rates, mechanisms and morphologies of oxide films on principal power generation steels will be made. The spalling processes will be described and the operational failures and problems arising will be reported. A theoretical development will be presented describing the spalling process and the probability of tube blocking or turbine erosion.	Steam turbines, superheater and reheater tubes	British Electricity International Ltd.	EPRI TPS76-655
To evaluate jet impingement erosion caused by high velocity water in cooling channels.	Study is concerned with the parameters of velocity, angle of impingement, and to a lesser extent with materials including ceramics.	Water-cooled ultra-high temperature turbines	General Electric (Schenectady, NY)	EPRI RP 234-2, and ERDA E(49-18)

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To study wet steam flows, including liquid film behavior.	Studies will be made of steam flow past inserted profiles upon which thin liquid films are generated, including problems of film stability and the spectra and trajectory of downstream liquid droplets.	Steam turbine erosion	University of Michigan, School of Engineering	NSF ENG75-21315
To develop wear, abrasion, and shock-resistant hard coatings to protect valves that control coal slurries and char removal in the coal gasification process.	In the coal gasification (Synthane) process, coal slurry and char must pass through valves at ambient temperatures for the slurry and at up to 180°F for the chars at pressures up to 900 psi. An investigation is underway to develop a method for plating commercial valve components with TiB_2 and for testing coated components in a simulated gasifier environment.	Valves in coal gasification systems	College Park Station, Maryland	Bureau of Mines
To compare material erosion by solid and liquid particles in turbines.	Materials and coatings are tested at temperatures from 70°F to 1000°F by impingement of aluminum oxide abrasives. AISI 403 is used to check the effects of particle size, velocity and concentration. In liquid particle tests, comparison is made of material erosion under laboratory conditions simulating actual use.	Materials for turbine construction	Carrier Corporation	Internal
To obtain materials resistant to high velocity seawater.	Metal alloys, such as copper-nickel alloys are evaluated in high velocity seawater. Interest is in velocities up to 120 feet per second.	High performance marine vehicles and associated subsystems, such as propellers and appendages of high performance boats	Naval Ship Engineering Center	NAVSEA

TABLE A-III. Erosion/Corrosion: At Temperatures Over 1110°F (600°C)

PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To develop wear-resistant valve materials. To improve the understanding of erosion and abrasion in coal gasifiers and to screen a large number of existing and experimental materials for their erosion and abrasion resistance. To demonstrate that best materials can be made into hardware which will reliably function in gasifier valve applications.	Efforts divided into three subtasks: erosion testing, abrasion testing, and experimental hardware manufacturing and testing. Erosion testing is done at room temperatures and at elevated temperatures under conditions simulating environments expected in specific gasifier areas. Samples are blasted with a gas-propelled stream of fine alumina powder at temperatures to 800°C. A relative erosion resistance index is compared to Stellite 6B. Three-body abrasion testing is done on a friction and wear testing machine. Valve parts of experimental materials are tested in pilot plant service. Over 100 materials have been erosion tested at room temperature and 700°C.	Project is directed particularly towards valves for lock hoppers operating at temperatures up to 250°C, for char removal service at 315°C, for advanced design lock systems that will withstand temperatures up to 1000°C, for pressure letdown functions, and other requirements which may arise in the course of gasifier operating tests.	Bureau of Mines, Albany, NY	ERDA
To develop test methods for evaluating metal erosion under conditions of elevated temperatures and reactive environments.	Two different erosion tests have been developed. A commercial small nozzle erosion tested was modified to operate to 500°C. A second unit produces a gas-particle stream at temperatures to 1000°C. Several steels and nickel base alloys have been evaluated.	Coal gasification environments	National Bureau of Standards	NBS/ERDA
To develop tests and data to evaluate durability and reliability of ceramic materials proposed for use in coal gasification plants. Studies will be made of fracture, strength, deformation, erosive wear and chemical degradation reactions which affect these properties.	Multiple particle impact tests are conducted in flowing gas streams to characterize the erosive wear behavior of castable refractories. A high temperature erosion apparatus has been constructed capable of reaching 1000°C with particle velocities ranging from 10 to 100 m/s. Coal gasification environments can be duplicated.	Coal gasification plants	National Bureau of Standards	ERDA

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To study erosion damage mechanisms.	Erosion damage mechanisms, including effects of microstructure, are being studied in oxide ceramics (Al_2O_3, Al_2O_3-MgO) and in face-centered cubic metals under sliding contact. Subsurface damage will be evaluated by electron microscopy. Tests will also be conducted in corrosive environments with ceramics of complex microstructure (e.g., refractory oxide brick).	Mechanism study	Oak Ridge National Laboratory	ERDA
To develop a technically sound basis for understanding and dealing with erosive wear in coal conversion plants. The erosion program is divided into experimental and analytical efforts. The experimental effort is designed to provide meaningful data on erosive wear as input into the analytical model for use in materials selection and plant design.	Experimental effort will build upon the more empirical screening tests performed by MPC/IITRI. Emphasis will be placed on more carefully isolating and controlling the primary variables. Tests are planned on the low alloy steels at lower temperatures as well as the more corrosion resistant alloys at higher temperatures. The analytical modeling effort will develop models that can predict comparative erosion rates for metals and ceramics.	Coal conversion applications	Argonne National Laboratory	ERDA
To evaluate: (1) the potential of coatings to solve erosion/corrosion problems; (2) the current commercial capability for supplying coatings; and (3) the potential of commercially available refractories for use as an inlay in transfer lines.	Ceramic coatings and inlay refractories are being evaluated for use in coal plant components under highly erosive/corrosive conditions. Coatings include oxides, carbides, nitrides, and borides on substrates of carbon steel, stainless steels, and high nickel alloys. Several coating techniques are under evaluation, particularly plasma-spraying of various oxides.	Pilot or demonstration plant components such as transfer lines, cyclones and pump casings for coal conversion plants	Argonne National Laboratory	ERDA
To establish engineering durability data on candidate heat-exchanger and superheater tube materials for service in an atmospheric fluidized bed coal combustor containing limestone as a sulfur sorbent. To conduct erosion/corrosion experiments on candidate materials.	Metal temperatures will be in the range 1100-1800°F. Materials include alloy steels, stainless steels, and superalloys, bare and coated. In-bed gas and particle velocity, and particle size will be measured in a 24-inch diameter atmospheric fluidized bed unit.	Heat exchanger and superheater tube materials for a fluidized bed coal combustor	Battelle Columbus Laboratories	ERDA

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To test, identify, and evaluate commercial and advanced experimental materials and coatings under design conditions simulating advanced fuel power cycle combinations.	Preliminary evaluation is carried out in the KDL Solid Fuel Fired Test Furnace using coal feedstocks of economic significance. Optimized materials will be evaluated in operating boilers. Preliminary selection of alloys and coatings include materials whose predicted 100,000 hour creep strength is favorable for 1300-1800°F advanced power cycles. Metals, coatings, and ceramics will be studied.	Boiler tubes for advanced power cycles employing coal feedstocks	Combustion Engineering Power Systems	ERDA
To remove particulates from coal-derived hot gases, in connection with fluidized bed processes. The objective is to protect gas turbines from the erosive and corrosive effects of particles in combusted gases exiting from a fluidized coal-dolomite bed.	Most stringent effects are associated with alkali metal corrosion. Particles under 2 microns are not erosive, but corrosive effects are observed when particles are deposited. Particles larger than 5 microns are erosive, but can be removed by separators.	Gas turbines for power generation	General Electric (Schenectady, NY)	ERDA E(49-18)-2357
To provide an engineering data base on performance of gas turbine nozzle and bucket materials in combustion environments of coal-derived low BTU gas and liquid fuels.	Initial tests will define problems encountered when burning liquid and low BTU gas at 1950°F. Evaluation will be made of corrosive effects and the likelihood of ash plugging cooling holes. In screening tests, 21 materials will be evaluated at 1600°F and 1800°F in small burner test stands using diesel oils doped with several ratios of Na and K.	Gas turbines using low BTU coal-derived fuels	General Electric (Schenectady, NY)	ERDA
To provide 1000 hours engineering data on the corrosion/erosion deterioration of gas turbine materials exposed to the exhaust gas from a pressurized fluidized bed combustor. Estimates of part lives will be made.	Up to 7000 hours of materials screening for corrosion will be accomplished in small burner rigs at 1600°F and 1000 hours of materials testing for corrosion/erosion will be accomplished in a turbine test passage installed in the ERE miniplant. Four candidate turbine bucket and vane materials will be evaluated in atmospheres representative of a pressurized fluidized bed coal combustor.	Gas turbines for use in exhaust gas of a pressurized fluidized bed coal combustor.	General Electric (Schenectady, NY)	ERDA

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To develop improved performance, cost effective metal and ceramic materials for use in the elevated temperature components of coal gasification systems. To generate material design criteria by determining the effects of composition, microstructure, surface conditions and environment variables on the combined erosion-corrosion behavior of metals and ceramics in simulated coal gasifier environments.	Have developed a test device to accurately simulate all elements of the environment within a coal gasifier, except the operating pressure. Have refined analytical expressions for predicting erosion rates of metals and determined effects of elevated temperatures on the erosion rate of 310 stainless steel to 1000°C for a number of impingement angles and velocities of 100 to 200 feet per second in neutral gas. Have determined the composition and morphology of sulfide scales formed on 310 stainless steel. Have determined the effect of markedly different metallic microstructures of the same hardness on erosion resistance at room temperature. Have determined the effect of fabrication of SiC and Si_3N_4 on their erosion resistance at room temperature.	Coal gasifiers	Lawrence Berkley Laboratory	ERDA
To determine the mechanisms of erosion/corrosion in elevated temperature alloys subjected to high temperature, erosive, reactive gas environments.	Studies are made of the role of alloying elements in resisting deterioration in gasifier environments and the design of low cost alloys to resist degradation while retaining sufficient high temperature strength. An erosion/corrosion test device has been constructed to simulate temperatures up to 1200°C, reactive gases (H_2, H_2S, CO, CH_4, etc.) and gas/particle flows obtained in coal gasification (100-500 fps).	Coal gasification systems and direct coal-fired turbine power plants	Lawrence Berkeley Laboratory	ERDA
To develop topping cycle technology for coal fueled electric power plants.	Si_3N_4, SiC resistance to flyash debris.	Helical expander rotors	Lawrence Livermore Laboratory	ERDA

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To provide information on materials available for use in coal gasification plants. Screening tests are conducted in the laboratory simultaneously with exposure tests in pilot plants as they become available.	Materials to be tested include metals and refractories. Effects of surface treatments will be measured. In a high pressure container, erodents such as char, dolomite, and ash impinge through tubes on specimens mounted on a rotating table. Tests up to 1000 hours at 1800°F are conducted on materials including stainless steels, nickel alloys, cobalt alloys, ceramic castables and brick.	Coal gasification plants	Metal Properties Council, IITRI, SWRI	ERDA
To evaluate corrosion and erosion of turbine materials in an environment simulating the CPU-400 combustor operating on coal. To assist the Combustion Power Company in the analysis of the environment in the CPU-400 combustor, particularly in the area of vapor and particulate phases.	After the environment has been characterized, short and long term tests will be conducted to determine indices for fouling, erosion and corrosion, and for specifically pinpointing problem areas that limit the life of high temperature turbine materials in the environment produced by a coal and dolomite fired fluidized bed combustor operating at 0.4 MPa.	Combustion Power Co. CPU-400 combustor operating on coal	Solar Division, International Harvester Company	OCR/ERDA Subcontract from Combustion Power Company
To obtain fireside corrosion data on heat exchanger materials exposed in the Exxon Pressurized Fluidized Bed Coal Combustor. To formulate recommendations and specifications on alloys for in- and above-bed heat exchanger materials in the fireside environment.	Materials to be evaluated include alloy steels, stainless steels, and superalloys. Specimens will be exposed in the Exxon Pressurized Fluidized Bed Coal Combustor at temperatures of 1050°F to 1600°F. Welded joints will be evaluated. Specific coals will be used with a dolomite sorbent. Selected laboratory tests will be carried out in a fluidized bed environmental simulator.	Heat exchanger and turbine materials for a coal-fired fluidized bed combustion environment	Westinghouse Electric Company	ERDA
To develop improved letdown (pressure reduction) valve materials and insights on how best to use these improved materials in coal liquefaction plants.	The erosion test consists of driving a heated slurry of unfiltered Wilsonville SRC product in anthracene oil against the specimen. Erosive wear tests were conducted on eight ceramic materials including AlN, Al_2O_3, B_4C, SiC, Si_3N_4, TaC, TiC, and ZrB_2.	Letdown valves for coal liquefaction systems	Battelle Columbus Laboratories	EPRI RP458

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR NO.
To determine the effect of alloy variables on the resistance of a material to attack in a high temperature gaseous environment in which both erosion by particulates and corrosion may occur. Design criteria will be established and new systems designed.	Project is concerned with relatively low velocity particles (to 75 feet per second), characteristic of coal fired boilers, fluidized bed combustors or gasifiers, and with oxidizing and reducing atmospheres. Metallic materials are being exposed to laboratory environments including erosion in an inert atmosphere, corrosion in oxidizing and reducing atmospheres.	Coal fired boilers, fluidized bed combustor gasifiers	Battelle Columbus Laboratories/Stellite Division, Cabot Corporation	EPRI 589
To provide an optimized high pressure letdown valve for the coal liquefaction process by developing a design solution for the erosion problem.	A letdown valve will be designed and fabricated for installation in a functioning coal liquefaction system. After preliminary bench testing to verify the operating principle, the valve will be evaluated in a coal liquefaction plant.	Coal liquefaction letdown valves	Consolidated Controls Corporation	EPRI RP77
To develop alloys with superior resistance to (1) fireside corrosion and (2) steamside exfoliation scale, for use as reheater and superheater tubing in coal-fired boilers.	The relative performance of promising material is being determined under the most adverse conditions occurring on the fireside of heat transfer surfaces. In the 560°C to 700°C range aggressive liquid phase attack occurs by complex alkali iron sulfate salts produced by ash deposits from sulfur-containing flue gas, with aggravated effects due to chlorine and carbon. A variety of metals and coating systems are being exposed to simulated fuel-ash/flue gas mixtures for selected times and temperatures. For steamside corrosion, knowledge is being obtained of scale exfoliation as affected by thermal stress and elastic strain. The effects of surface preconditioning treatments on scale formation and exfoliation behavior are studied. Pretreatments include diffusion coatings, conversion coatings, preformed oxides and shot peening.	Coal-fired boiler superheater and reheater tubes	Foster Wheeler Energy Corporation	EPRI RP644

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To evaluate erosive/corrosive effects arising from combustion of low grade liquid and gaseous fuels derived from coal.	Cascade tests are planned to evaluate erosive/corrosive effects on materials for periods ranging to several thousand hours. Fuels contain erosive ash and corrosive alkali metals.	Power generation equipment	General Electric (Schenectady, NY)	EPRI Contract: RP234-2 (1975) ERDA Contracts: E(49-18)-1806 E(49-18)-1765
To determine the susceptibility of silicon carbide to accelerated attack in coal combustion atmospheres containing fused coal ash.	Two grades of silicon carbide (carborundum KT and Super KT) are exposed to simulated coal combustion atmospheres for 50 and 288 hours. Samples are coated with acid and basic coal ash and exposed to temperatures reaching 1450°C.	Coal combustion atmospheres containing fused ash	Lockheed Palo Alto Research Laboratory	EPRI TPS76-523
To diagnose causes of accelerated corrosion failures in operating systems, to design simulator experiments for materials selection for new systems, and to control the operating conditions of systems to avoid accelerated high temperature corrosion.	Corrosion chemistry will be studied in low oxygen activity atmospheres characteristic of gasified or incompletely combusted coal. Effect of oxygen, sulfur, carbon, and hydrogen on metal alloys will be defined.	Gasified or incompletely combusted coal environments	Lockheed Palo Alto Research Laboratory/Ohio State University	EPRI RP716
To study the effect of erosion on the hot corrosion of superalloys, and in particular those alloys similar to candidate corrosion-resistant alloys, with the aim of establishing principles that will permit the design of resistant alloys and coatings in later program stages.	Solid particles will be injected into a dynamic combustor capable of developing gas velocities at 1600°F of 1000 ft/sec. The combustor will provide for injecting contaminants such as Na_2SO_4 or Na_2SO_4-NaCl. Materials to be examined include nickel and cobalt alloys and Si_3N_4.	Gas turbines operated as part of coal gasification or advanced coal combustion systems	Pratt and Whitney Aircraft	EPRI RP543

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To develop improved refractories resistant to erosion and salt attack for gasification and combustion systems.	The temperature regime will include both dry ash gasifiers (up to 2200°F) and slagging gasifiers (up to 3200°F). For erosion/corrosion applications, various grades of alumina, chromia-alumina, fireclay, and SiC refractories are being evaluated in large fluidized bed and pneumatic transport line test facilities at temperatures up to 2200°F using dead-burned dolomite particles. The slagging resistance of refractories is being determined with drip and gradient slag tests under reducing and oxidizing conditions at temperatures between 2650°F and 3150°F. High purity alumina, alumina-chromia, magnesia-chromia, SiC shapes, and a phosphate bonded alumina-chromia castable are being evaluated.	Coal gasification systems including slagging and non-slagging systems with fixed, fluidized or entrained bed reactors	Westinghouse Research Laboratories	EPRI RP625
To investigate mechanisms of corrosion of refractory ceramics in hot gases such as hydrogen and steam.	Corrosion mechanisms, in tests to 1200°C, will be correlated with differences in microstructure, with particular emphasis on second phase composition and distribution.	Coal gasification systems	University of California, School of Engineering, Berkeley	NSF DMR75-03611
To investigate kinetics of deterioration of oxides, carbides, and nitrides in coal conversion process environments.	Mechanisms of corrosion will be studied by microstructural examination coupled with weight loss studies as a function of time in high temperature/high pressure environments.	Coal conversion processes	University of Utah	NSF DMR75-02893
To investigate ceramic materials' problems in coal fired, open cycle MHD.	Studies will be made of attack of slag-seed mixtures on air preheater materials and slag-seed corrosion of electrode materials	Coal-fired, open cycle MHD power generation	University of Utah	NSF AER72-03512 A03
To improve the understanding of erosion and abrasion and to screen a large number of existing experimental materials for their erosion or abrasion resistance.	Screening is done on laboratory machines which duplicate conditions in lock hopper valves and pressure letdown valves. Data from over 1700 erosion tests have been accumulated on commercial and experimental materials, including metals, commercial refractories, carbides, and nitrides.	Coal gasification plant valves, including advanced design lock hopper valves operable at 1000°C, and pressure letdown functions	Albany Metallurgy Research Center	Bureau of Mines

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To develop ceramic materials that will protect metal from high temperatures and the erosive and corrosive atmosphere encountered in coal gasification processes.	Commercial refractory castables and brick are exposed to either H_2O, H_2, CO and a simulated coal gasification atmosphere at 1000 psi and 1000°C for period of 250-1000 hours. Physical properties of the materials, including erosion resistance are measured before and after exposure.	Coal gasification processes	Bureau of Mines, Tuscaloosa Research Center, Tuscaloosa, Ala.	Bureau of Mines
To perform research and development and provide standards service on construction materials for conversion processes and on process chemistry. Durability and reliability of construction materials shall be studied for conversion systems.	Attention is devoted to problems of developing accurate methods of measurements of wear, corrosion and fracture under severe environmental conditions encountered in service. Methodology is developed for measuring chemical and physical properties related to performance of materials for use in energy conversion systems. Crucial aspects of the chemistry of coal conversion shall be studied to allow optimization of coal conversion processes.	Coal conversion processes	National Bureau of Standards, Inorganic Materials Division Project Title: "Reliability of Materials for Coal Gasification"	Department of Commerce
To provide theoretical understanding of the contact of turbine blades with housings to permit design of blade tip seals.	The study analyses frictional wear, deformational and thermo-elastic effects in high speed (1500 fps) contact of solid materials in realistic geometrics.	Gas turbine and jet engine blade tip seals	Northwestern University, School of Engineering	NASA
To screen candidates for use as structural materials in a coal gasifier.	A test apparatus was employed which simulated the temperature, gaseous environment and particle impingment conditions of a fluidized bed coal gasifier producing low BTU gas. Significant parameters: temperature - 1800°F, particles - coal char, impingement velocity - 125 fps. Candidate materials included metallics, ceramics, and coated metallics tested for 100 hours.	Fluidized bed coal gasifiers	Solar Division, International Harvester Company	Argonne National Laboratory

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To develop coatings protecting superalloys against oxidation-sulfidation for 20,000 hours life.	For land-based applications, erosive particles such as sand can be filtered out. Carbon, such as that arising from incomplete combustion, results in local reducing conditions which interfered with formulation of protective oxides on superalloys. Effects of high velocity gases on oxidation-sulfidation processes will be studied.	Utility installations burning corrosive distillate fuels	General Electric (Schenectady, NY)	Internal
To determine the response of selected ceramic materials to a combination of the corrosive atmosphere of combustion product gases, high temperatures, and the erosive action of high-velocity coal ash particles.	A burner, operating on liquid hydrocarbon fuel, is to be directed by means of a 25 mm diameter nozzle onto the surface of test samples of selected commercial ceramics. Coal ash is to be introduced into the nozzle, heated and accelerated by the hot stream. Samples are to be moved into and out of the gas stream after burner and ash conditions have been set and stabilized.	Mechanisms of corrosive/erosive attack by combustion gases containing coal ash.	Solar Division, International Harvester Company	Lawrence Livermore Laboratory, University of California
To evaluate commercial practices with respect to abrasion resistance at elevated temperatures. To study mechanism of abrasion and its relation to hot hardness.	Resistance of commercial refractory materials to abrasion at high temperatures is a major concern in coal gasification processes, MHD conversion, and blast furnace operations. Abrasion resistance is determined by a self-abrasion technique. Hot hardness and impact resistance are also evaluated.	Coal gasification processes, MHD conversion, and blast furnace operations	University of Illinois, Department of Ceramic Engineering	Refractories Institute
To screen a large number of metallic and ceramic materials for erosion-corrosion in a simulated coal gasifier environment.	Same as previous entry for Solar (sponsored by Argonne National Laboratory) except that the number of testing hours is 1000.	Fluidized bed coal gasifiers	Solar Division, International Harvester Company	Union Carbide Corp., Nuclear Division
To control refractory erosion/corrosion in process vessels.	Work involves research/engineering/design and evaluation of vendor-supplied materials in order to (1) develop satisfactory refractories for new larger blast furnace units; (2) overcome problems associated with argon/oxygen degassing process for stainless steels; (3) improve refractories for continuous casting.	Steel production	U.S. Steel Research Center, Monroeville, Pa.	Internal

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To establish allowable particulate and chemical contaminant levels for reliable operation of gas turbines on coal gas.	Cooled turbine alloys - combusted coal gas containing alkali metal compounds; sulfur oxides; and hydrogen chloride; and micron, and submicron ash particles.	Gas turbines	Westinghouse Research and Development Center	Westinghouse Electric Corp.
To improve marine gas turbines by evaluating alloys, ceramics and coatings promising improved resistance to hot corrosion attack in marine environments.	Investigations are made on the effects of erosion by sea salt and carbon particles on the life of superalloys and coatings in turbines. Also hot corrosion resistance of MCrAlY and ceramic coatings are evaluated in burner rigs.	Gas turbines for Navy shipboard propulsion	Naval Ship Engineering Center	NAVSEA
To develop erosion-resistant materials for re-entry vehicles.	Re-entry vehicle nose tips are eroded as a consequence of hypersonic re-entry through ice, snow, and clouds. Refractory materials are of interest, i.e., carbide/carbide-graphite composite structures.	Nose tips of re-entry vehicles	Naval Surface Weapons Center, White Oak, Md.	NAVSEA
To develop oxidation and erosion-resistant seals for gas turbines.	Seals, which mate against rotating superalloy turbine blades must resist thermal shock, abrasion, and erosion, at temperatures to 3000°F. A graded ceramic-metal composite consisting of Y_2O_3stabilized ZrO_2 and Nichrome is being developed and evaluated.	Gas turbine blade seals	Pratt and Whitney Aircraft	Naval Air Propulsion Test N00140-C-0586
To perform coupled analysis of the heat-transfer rates, shape change, in-depth conduction, and particle erosion effects on nose tips of maneuvering re-entry vehicles.	Existing computer codes will be converted by the contractor for use in the Naval Surface Weapons Center, White Oak, Md.	Re-entry vehicles	Prototype Development Associates, Santa Ana, Calif.	Naval Surface Weapons Center White Oak, Md.
To determine the increase in thermal input into a nose tip and to isolate sources of this input, when an erosive field is encountered at high speeds	All possible heat augmentation sources will be evaluated. A theoretical approach will be utilized to account for heating levels resulting from erosive fields. Results will be experimentally verified and used to calculate the total recession of nose-tip material during re-entry flight through an erosive atmosphere.	Re-entry nose tips	Science Applications, Inc., El Segundo, Calif.	Naval Surface Weapons Center, White Oak, Md. N60921-74-C-0357

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To develop an understanding of the impact damage and erosion of carbon-carbon composites.	Damage patterns are studied in carbon-carbon composites after projectile impacts and static penetration. Impact tests are done in a steep temperature gradient.	Re-entry vehicle nose cones and launch vehicle rocket nozzles	Rockwell International Science Center, Thousand Oaks, California	ONR 023-570
To identify the extent of chemical reaction between propellant gases and gun steel, to determine the most erosive conditions of propellant gases, and to determine if surface cracking is due to solution of gases.	A ballistic compressor is under construction capable of producing gun chamber P-V-T conditions. The extent of chemical reaction or solution of constituent gases with gun steel is being determined.	Gun barrels	DARCOM Materials and Mechanics Research Center Watertown, Mass	Army Materials and Mechanics Research Center
To obtain details of the erosion mechanisms from near surface characterization of eroded steel. To search for a theoretical technique which would enlarge the knowledge of chemisorption, a process occurring in gun tube erosion.	Eroded surfaces will be simulated by exposing gun steel to various pure gases and burning propellants. Measurements will be made of oxygen, nitrogen, and carbon depth profiles and correlations will be sought between these profiles and ballistic parameters, as well as steel surface conditions.	Gun barrels	Aberdeen Proving Ground ARRADCOM Ballistic Research Laboratories	ARRADCOM
To measure the amount of erosion wear from a real gun bore surface by observing the loss of radioactive isotope from that surface.	A 20 mm gun barrel will be modified by drilling 3 holes into the barrel at different locations. A proton beam will bombard the three spots through the holes. The barrel will be fired and the loss of intensity of gamma-radiation will be correlated with wear loss.	Gun barrels	Aberdeen Proving Ground ARRADCOM BRL Applied Mathematics and Science Laboratory	ARRADCOM
To formulate and test a mechanism of gun barrel erosion based on formation of a melted layer on the barrel surface.	A finite element heat transfer code is used to calculate the temperature profile in a gun barrel. The code is used to calculate base temperatures for weapons in which the rate of erosion limits barrel life. Investigation will be made to determine if a melted layer forms and how deep the melted layer is compared to measured rates of erosion.	Gun barrels	Aberdeen Proving Ground ARRADCOM Ballistic Research Laboratories	ARRADCOM Ballistic Research Laboratories

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To refine techniques used to measure the response of projectiles during normal and oblique penetration of armor. To describe and test relationship between penetrator erosion and material property.	Impact experiments will be performed using tungsten alloy rods with different amounts of swaging to determing the extent to which response measurements can be related to effectiveness of the penetrators against rolled homogeneous armor. Selected metals will be used to reveal how material properties influence heat. Observations on recovered penetrators will establish nature of shear in terms of properties under investigation.	Projectile impact and erosion	ARRADCOM Ballistic Research Labs., Terminal Effects Div.	ARRADCOM Ballistic Research Labs., Aberdeen Proving Ground
To study the load carrying and wear characteristics of rotating band materials at velocities similar to projectiles for the first few inches of travel.	The wear characteristics of gilding metal and iron are determined. The test rig is a pin-on disk wear testing machine employing a large diameter gun-steel disk revolving at high speed and a small pin of the test material.	Projectile rotating bands	Armcom Research Directorate, Watervliet Arsenal	Armcom Benet Weapons Lab., Watervliet, Arsenal
To measure the amount of erosion wear from a gun bore surface by observing the loss of radioactive isotope from that surface.	The radioactive isotope Co^{56} will be produced in the bore surface. A proton beam will be used to produce this isotope from Fe^{56}. Loss of material from the surface will be measured by monitoring the loss of gamma ray activity as the gun is fired.	Gun barrels	DARCOM Ballistic Modeling Div. Aberdeen Proving Ground	DARCOM Ballistic Research Laboratory
To develop a 10KW turboalternator for higher temperature operation and 6000 hours between overhauls.	Substitution of Si_3N_4 guide vanes for superalloys; oxidizing environment, dust ingestion.	Mobile power supply systems	Solar Division, International Harvester Company	MERADCOM

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To increase wear lives of cannon tubes.	Tubes are plated or lined with various materials and fired. The effects of wear and erosion are observed and evaluated. The 105 mm M68 tube is used. Cobalt-alumina, cobalt, and chromium coatings have been evaluated.	Gun tubes	Watervliet Arsenal	Watervliet Arsenal
To improve the oxidation characteristics of a sintered powder, rub-tolerant, turbine shroud material.	Porosity and bonding strength of the powder will be varied. Products will be subjected to rig tests including erosion, oxidation rub tolerance, and strength.	Gas turbine shrouds	Union Carbide Corp., Cleveland Ohio	USAF Aero Propulsion Lab.
To evaluate the particle acceleration performance of two Arnold Engineering Development Center facilities designed to provide a combined ablation-erosion environment.	Flows produced in the heat facility direct-injection nozzle will be used as a test bed for particle diagnostic techniques at high densities. The initial effort will be concentrated on laser velocimetry.	Ablation-erosion environment	ARO, Inc. Arnold AFS	Arnold Engineering Development Center
To develop a combined ablation-erosion arc facility and associated diagnostic techniques.	Major areas of interest include nozzle research, arc facility calibration, and operation of an arc heater with a liquified gas supply. A dust injector has been designed.	Ablative-erosive re-entry vehicle environments	ARO Inc., Arnold AFS	Arnold Engineering Development Center
To collect and analyze range test data on erosion, ablation under re-entry conditions. Experimental heating rates and heating rate distributions will be determined.	A data collection system is to be established based on computer programs. Predicted surface temperatures will be compared with experimental data. Machine sketches will be made of the geometric and isothermal contours of the nosetips, to compare thermal with geometric features.	Re-entry nosetips	ARO Inc. Arnold AFS	Arnold Engineering Development Center
To develop a basic mechanics model of composite materials based on constituent properties in order to predict failure and damage under dynamic loading, including erosion resulting from high-speed particle impact.	Extension will be made of the thermodynamic theory of elastic-plastic wave propagation at finite deformation to predict stress and deformation fields in carbon-carbon composites. Extension will be made of present continuum theory to predict failure modes and damage.	Rocket nozzles and hypersonic vehicles	University of California, La Jolla, Calif.	AFOSR

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PROGRAM OBJECTIVE	MATERIAL/ENVIRONMENT	APPLICATIONS	PERFORMING ACTIVITY	SPONSOR/NO.
To determine the basic mechanism of erosive burning by formulating a theoretical model describing the important chemical and physical phenomena. Results will be verified in erosive burning experiments.	Composite propellant test samples will be fed into the combustion zone. A range of chamber pressures, gas velocities, mass fluxes, and pressure gradients will be tested. Design of the experiment is guided by a computer simulation of the physical processes.	Rocket weapons	Pennsylvania State University	AFOSR
To develop and verify an accurate method of predicting propellant burn rates in erosive environments.	An existing, two dimensional, multispecies, lamina/turbulent shear layer computer program will be modified to include boundary layer effects with mass injection and surface roughness. A simple flame sheet analysis of the combustion process will be utilized.	Rocket weapon systems subject to erosive burning	Aeronautical Research Associates of Princeton, Princeton, N.J.	AFOSR
To develop and verify an accurate method of predicting propellant burn rates in erosive environments.	Specially formulated propellant samples are burned in an erosive environment. High speed photography is used to study burn rates. A theoretical model of the erosive burning process is being developed and programmed.	Rocket Weapons	Atlantic Research Corp., Alexandria Va.	AFOSR