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COBALT CONSERVATION THROUGH TECHNOLOGICAL ALTERNATIVES

Committee on Technological Alternatives for Cobalt Conservation

NATIONAL MATERIALS ADVISORY BOARD
Commission on Engineering and Technical Systems
National Research Council

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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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ABSTRACT

Cobalt is an important and perhaps indispensable element used in a variety of critical industrial and military applications - superalloys, cemented carbides, tool steels, magnets, chemicals, paints and driers, and catalysts. The United States depends entirely on foreign sources of supply for primary cobalt making this country very vulnerable to supply disruptions. Currently some 70 percent of the Western World's supplies of cobalt come from Central Africa.

Since the United States is entering a period of increasing materials scarcity and growing dependence on imported materials, several studies have been undertaken recently to develop contingency plans for the utilization of critical materials that could reduce the adverse effects of supply disruption. This study discusses for cobalt: substitution; conservation through improved processing, design and recycling; stockpiling; resource exploration and development; and diversification of supply.

PREFACE

The topic of critical and strategic materials availability has recently received considerable attention. Past administrations recognized the importance of these materials to the U.S. defense posture and had taken actions to ensure access to needed supplies through, for example, the Strategic War Materials Act of 1939 (P.L. 76-117), the Strategic and Critical Materials Stockpiling Act of 1946 (P.L. 79-520), the Strategic and Critical Stockpiling Revision Act of 1979 (P.L. 96-41), and most recently the National Materials and Minerals Policy, Research and Development Act of 1980 (P.L. 96-479). Current administrative actions are to follow up on the congressionally mandated directives of P.L. 96-479.

The Bureau of Mines collects and interprets minerals information, identifies and analyzes problems and policies relative to the nation's minerals requirements, and conducts research to provide technological advances for the minerals industry in order to assure the nation of continued mineral supplies while maintaining national security, employment, and economic growth; to stimulate the private sector in the production of minerals; and to provide assessments of U.S. minerals supply and demand relative to changing international developments. Accordingly, the Bureau has a continuing interest in critical and strategic minerals and has recently sponsored several studies by the National Academy of Sciences covering columbium (niobium), tantalum, titanium, manganese, platinum-group metals, and chromium (which served as the prototype for this inquiry). The 1978 invasion of Zaire's Shaba Province shook the cobalt-consuming industries and showed impressively the vulnerability of the United States to disruptions in supply. This analysis of alternatives that would reduce U.S. dependence on unstable sources of cobalt supply is a necessary prelude to determining possible future actions.

Options for actions are identified by the committee based on information available from various industrial and governmental agencies through November 1982. When possible, adequate background information is presented so the reader need not consult other references. Two panels, one on processing (J. C. Agarwal and J. J. deBarbadillo, cochairmen) and the other on substitution and design (J. K. Tien and M. Semchyshen, cochairmen), sought technological and possible policy alternatives that might be brought to bear on this critical materials area. The full committee in turn independently assessed the panels' findings and made recommendations for consideration by concerned agencies.

E. L. Pepper
Chairman

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D. L. Klarstrom, Cabot Corporation, Kokomo, Indiana: "Cobalt in Hard Facing Materials"

A. H. Neal, Exxon Research and Development Laboratory, Baton Rouge, Louisiana: "Alternatives to Cobalt-Base Catalysts"

R. J. Parker, Hitachi Magnetics Corporation, Edmore, Michigan: "Magnetic Materials--Cobalt-Bearing Versus Cobalt-Free"

D. L. Paulson, U.S. Bureau of Mines, Rolla Research Center, Rolla, Missouri, and J. T. Dunham, Division of Materials and Recycling Technology, U.S. Bureau of Mines, Washington, D.C.: "Status of Cobalt Lean Ores Resources Processing Technology"

B. J. Reddy, Charles River Associates, Boston, Massachusetts: "Survey of the Cobalt Supply and Demand Picture"

D. H. Rosof, Cabot Corporation, Kokomo, Indiana: "Technology of Recycling and Reclaiming of Cobalt-Containing Materials"

E. N. Smith, Kennametal, Inc., Ligonier, Pennsylvania: "Alternatives to Cobalt for Carbides"

J. R. Stephens, NASA Lewis Research Center, Cleveland, Ohio: "Superalloys--Substitution for Cobalt or Other Alternatives"

J. C. Weaver, Case Western Reserve University, Cleveland, Ohio: "Cobalt in Driers and Other Chemicals"

Special meetings of the processing panel were held in Boston, where representatives of the major continental cobalt producers and the Bureau of Mines graciously supplied data on source of supply and production capacity:

A. F. Barsotti, Division of Minerals Availability, U.S. Bureau of Mines, Washington, D.C.

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J. M. Dahl, AMAX Nickel, Inc., Greenwich, Connecticut

V. N. Mackiw, Sherritt-Gordon Mines, Toronto, Canada

C. E. O'Neill, INCO Metals Company, Toronto, Canada

These data were invaluable to this investigation for assessing the available supply picture and the status of the U.S. processing capability. Charles River Associates is thanked for generously furnishing a conference room for these meetings.

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CONTENTS

Chapter 1

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

Cobalt is an element that is used in a variety of critical applications, such as superalloys, permanent magnets, cemented carbides, alloy and tool steels, and chemicals. In most of these, it is an important and perhaps indispensable component. Production is concentrated in a small number of countries, and the United States currently depends entirely on foreign sources for primary cobalt. The largest suppliers of cobalt minerals by far are the central African countries of Zaire and, to a lesser extent, Zambia. The risks of future disruptions of supply from these sources are very high.

There are many conclusions and recommendations contained in this report; the following are those the committee felt were the most important.

CONCLUSIONS

General

1. The sharply increased price for cobalt in 1978 resulted in a significant reduction in the amount used in this country in applications where more economical alternatives were available. U.S. consumption decreased from 18 million pounds in 1978 to 13.6 million pounds in 1981; it is estimated that half of this reduction was due to economic recession and half to increased prices and concern about availability.

2. In most important uses, such as superalloys and cemented carbides, cobalt will continue to be used in quantity. At the high prices resulting from future supply disruptions, additional cobalt substitution would occur, but not to the extent experienced during the 1978-1981 period. For economic reasons it is not expected that there will be much further substitution for cobalt.

3. Current (1983) estimated essential U.S. cobalt needs amount to 7.7 million pounds per year and will increase to 11.7 million pounds annually in 1992, as shown in Table 1. Potential cobalt savings by 1992, based on current technology, could amount to over 10 million pounds annually - over 4 1/2 million pounds from improved processing and recycling and over 5 1/2 million pounds from substitution and design.

TABLE 1 U.S. Estimated Requirements for Essential Cobalt and Potential Savings Compared with Actual 1980 Consumption (million pounds)[a]

Use	Actual 1980[b]	Estimated Current Essential[c]	Estimated Essential 1992	Estimated Normal 1992[d]	Potential Savings 1992	Remarks
Superalloys	6.3	4.5	8.0	10.0	2.0	Savings from improved processing and recycling Future R&D might make some substitution possible
Magnets	2.3	0.4	0.4	2.0	1.6	Savings from substitution
Cemented carbides	1.3	1.1	1.5	2.5	1.0	Savings from improved recycling
Hard facing	0.6	0.3	0.4	1.0	0.6	Most savings from substitution, some from recycling
Steels	0.4	0.2	0.0	0.5	0.5	Possible savings from substitution
Other metallurgical	0.4	0.2	0.3	0.5	0.2	Most savings from substitution, some from recycling
Catalysts	1.7	0.1	0.1	2.0	1.9	Most savings from recycling, some from substitution
Salts and driers (driers, promoters, etc.)	1.4	0.9	1.0	3.5	2.5	Savings from substitution
Other chemical	0.9					
Total	15.3	7.7	11.7	22.0	10.3	

[a] Committee forecasts as explained in Chapter 2.
[b] Based on Bureau of Mines data.
[c] Using current technology.
[d] Assumes no incentive to conserve cobalt; data based on an average annual consumption growth of 3.0 percent.

Supply

1. Cobalt supply is currently dominated by Zaire and, to a lesser extent, Zambia. These countries will probably continue to dominate supply for the next decade, with the likelihood of some short-term disruptions. However, it is possible that long-term political disruptions, economic mismanagement, and poor maintenance could effectively shut off some of these deposits for long periods of time.

2. There are at present three cobalt refineries on the North American continent: AMAX at Port Nickel, Louisiana; INCO at Port Colborne, Ontario; and Sherritt-Gordon at Fort Saskatchewan, Alberta. If nickel output from Canadian ores is maintained at 400 million pounds annually (during the 1970s, Canadian nickel production averaged 490 million pounds per year), the accompanying by-product cobalt output can amount to 7,500,000 pounds yearly. To secure this on-shore resource, the U.S. government should consider contracting with Canadian refineries for a portion of that supply. To establish a versatile domestic cobalt custom refining capability, the U.S. government should consider contracting with the Louisiana refinery for cobalt output from diverse cobaltiferous materials.

3. Nickel sulfide ores represent a major source of cobalt from which production can be increased in the near future. Further in the future, the large cobalt resources in nickel laterites could become the most important land-based source of cobalt.

4. From a longer range point of view, ocean-based cobaltiferous materials (e.g., deep-sea manganese nodules, and manganese crusts) could provide a major source of cobalt and other strategic metals. However, a great amount of difficult development work is required before these resources can be commercialized. The costs and risks are so large that it is questionable whether private enterprise will be able to afford them. It may be necessary for the U.S. government to participate with industry in developing the necessary ocean mining capability.

5. According to the best available estimates, and assuming existing political conditions, the price of cobalt over the next decade will average within the range of $7 to 12 per pound (1982 dollars) for cathode metal. However, since Zaire and Zambia have completely dominant positions in cobalt supply, significant price volatility could continue in the future, as it has in the recent past. This volatility could threaten the survival of North American and European cobalt refineries.

6. The present quantity of cobalt in the national stockpile--46 million pounds--is sufficient for more than 3 years' requirements in an emergency as identified by the committee.

7. The quality of some of the cobalt in the stockpile (earlier acquisitions) is questionable for certain applications. Proper

identification and complete analyses of present stocks are not available, but a fraction, perhaps a substantial one, is unsuitable for direct use in superalloys.

8. Technology exists to produce cobalt metal from domestic sources, but total production costs would be at least $20 per pound (1982 dollars). The time required to bring domestic sources into production would be at least 5 years.

9. Obsolete, low-grade, and mixed-alloy scrap containing cobalt is not effectively recovered today. Some of the better quality obsolete scrap is recycled for superalloys, but a large quantity is downgraded. Most low-grade scrap is downgraded and much of its cobalt content lost. Treatment of mixed-alloy scrap to recover all elements contained in it is technically feasible but not economically practicable. Segregation of alloy scrap has permitted increased recycling.

Demand

1. By far the largest use of cobalt at present is in superalloys. Current formulations contain cobalt and will continue to do so for the foreseeable future.

2. Readily adaptable superalloy system changes to conserve cobalt were made in 1978-1980. Current research indicates that significant amounts of cobalt in superalloys can be replaced by nonstrategic elements. However, implementation of these results requires costly and time-consuming alloy optimization and engine certification programs, which, unless coupled with engine performance advantages, will begin only when warranted by sufficient economic incentive or sufficiently urgent insecurity of supply.

3. There is opportunity for an additional reduction in the use of cobalt in some magnetic applications. However, there is also some potential for growth in cobalt consumption in magnets, particularly in small motors employing rare earth cobalt magnets.

4. Cobalt in the form of fine powder is a key constituent of cemented carbides, which are critical to high productivity in metal cutting and forming; in mining and oil and gas well drilling; and in other important industrial operations. Improved recycling of spent carbides will limit growth of cobalt in carbides to 3 percent per year.

5. In applications requiring resistance to galling, cavitation, and erosion, cobalt is a desired alloying element. Substitution of alternatives might conserve up to half of the cobalt currently used in wear-resistant alloys.

6. Cobalt is not an essential ingredient in high-speed tool steels, but it is necessary in some grades due to the application involved. Elimination of this portion of the market would save between 600,000 to 800,000 pounds of cobalt annually.

7. Cobalt-free maraging steels would require time-consuming and costly qualification and testing before substitution could be made for critical aerospace applications.

8. The desulfurization and demineralization of petroleum hydrocarbons is the only one of the three major applications of cobalt in catalysts amenable to substitution.

9. Cobalt is the single most effective surface drier additive in paints. Most drier and other chemical applications for cobalt could be eliminated or substantially reduced, but often at significant cost in industrial convenience and product quality.

RECOMMENDATIONS

1. The criticality of U.S. vulnerability to disruption in cobalt supply should be publicized widely in all sectors of the industrial and academic communities, and in the legislative branches of government to alert them on the technical implication involved. Product designers must become more aware of the impact they can have on the conservation of critical materials such as cobalt. Products should be designed to minimize critical materials consumption wherever possible by eliminating unnecessary use, increasing product life, and incorporating recyclability.

2. The vulnerability of supply should be decreased by encouraging worldwide diversification of sources, especially on-shore sources such as Canada, and from the Louisiana cobalt refinery.

3. The recovery of cobalt from spent catalysts and obsolete scrap should be encouraged by continuing to develop the necessary technologies that can be applied when a supply shortage or an abrupt price escalation justifies exploiting this source of cobalt.

4. Sufficient cobalt of a quality and form appropriate for direct use in superalloys required for aircraft engines should be included in the national defense stockpile. A detailed trace element analysis of the stockpiled cobalt must be made to ascertain what amount is applicable to this critical use.

5. Barter, trading, and tolling should be used in North American refineries as more cost-effective ways for upgrading stockpiled materials where necessary. Such action would ensure an on-shore processing capability, by giving these processors a ready supply of raw materials to work on, particularly in times of low industrial demand.

6. The basic mechanism for strategic stockpile release should be reexamined with respect to its effectiveness during crises of various severities.

7. The advantages and incentives for industrial (private) stockpiling should be assessed.

8. More use should be made of near-net-shape processing for a wider variety of shapes and components to significantly reduce scrap generation.

9. Gas turbine alloy scrap should be recycled into aerospace products to prevent losses of cobalt in its most critical application.

10. Consideration should be given by the U.S. government to participating as a partner with industry in the effort of exploiting ocean-based cobaltiferous materials.

11. Research programs for the following should be encouraged:

    a. Development of improved-performance superalloys with directed efforts toward identifying viable and effective alternative alloys that have as a secondary objective the conservation of or the substitution for cobalt and other critical materials.

    b. Improvement of recycling methodologies that can extend limited cobalt supplies in times of need.

    c. Advancement of existing near-net-shape (powder metallurgy) processing techniques that will make possible an extensive and more diverse application of the technology, particularly for components that contain cobalt.

Chapter 2

INTRODUCTION

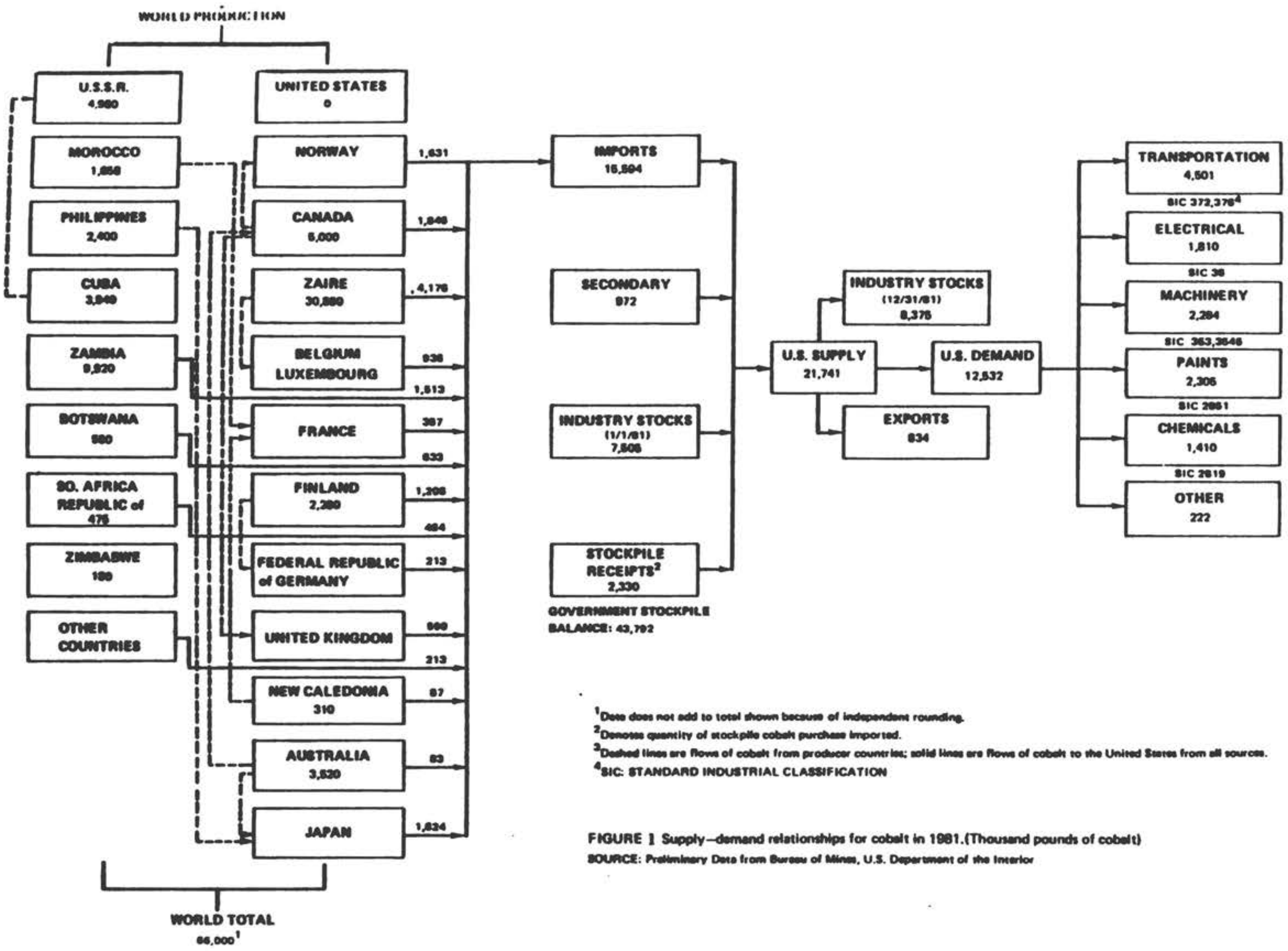
Cobalt is an important and perhaps indispensable metal in high-temperature alloys, abrasion-resistant alloys, alloy and tool steels, cemented carbides, magnets, catalysts, and paint dryers. Some 70 percent of the western world's supply of cobalt comes from central Africa, specifically a by-product of the copper industry from Zaire and Zambia (see Figure 1 for supply-demand relationships for 1981). The United States depends entirely on these and other foreign sources for primary supplies of this critical material, making the nation vulnerable to supply disruptions. The effect of a temporary cobalt supply interruption was well illustrated when in 1978, the invasion of the Shaba Province caused a cobalt scarcity and drove cobalt metal prices up to about 7 times the then-prevailing producer price.

CHARGE AND SCOPE

The Bureau of Mines Division of Minerals Policy and Analysis felt that an in-depth study for cobalt similar to the 1978 National Materials Advisory Board (NMAB) study, "Contingency Plans for Chromium Utilization," would be of value to appropriately direct its policy analysis and research efforts and to help other agencies initiate related programs. NMAB was asked to assemble a committee to focus on various approaches to the conservation of cobalt and recommend appropriate actions to pursue them. Members selected possessed broad technological backgrounds in cobalt metallurgy, tool and die materials, and especially superalloys; electrical applications, particularly magnetics; chemistry, including catalysts and ceramics; and activities. Resumes of the members are given in Appendix A.

The objectives of the study were to analyze options for conserving cobalt and to identify alternatives to conservation that would reduce the U.S. vulnerability to disruption of cobalt supply over the next decade. Technological innovations and alternatives were to be sought in three major areas:

- Design--the use of minimum amounts of cobalt in end products and components



[1] Data does not add to total shown because of independent rounding.
[2] Denotes quantity of stockpile cobalt purchase imported.
[3] Dashed lines are flows of cobalt from producer countries; solid lines are flows of cobalt to the United States from all sources.
[4] SIC: STANDARD INDUSTRIAL CLASSIFICATION

FIGURE 1 Supply—demand relationships for cobalt in 1981.(Thousand pounds of cobalt)

SOURCE: Preliminary Data from Bureau of Mines, U.S. Department of the Interior

- Improved processing practice--melting and refining, casting, mill product fabrication, manufacturing processing, joining, surface coatings, and recycling and reclamation of new and old scrap; use of reclaimed or recycled cobalt as a substitute for primary cobalt; process or cost advantages of foreign processors relative to U.S. processors

- Substitution--the use of alternative materials, including the economic impacts of substitution and consideration of price elasticities of candidate substitute materials

Quantitative estimates were to be derived of the savings in materials and recommendations presented for implementing the identified options.

STUDY APPROACH

To compile much of the data needed to make its overall assessment, the committee organized into three panels to focus on substitution, design, and processing. In their studies, the panels were to consider two types of conservation opportunities: first, those feasible in terms of technical performance and cost using currently available technology; second, those potentially feasible in terms of technical performance and cost with future technology but requiring up to 10 years of research and development.

The committee and panels reviewed the uses of cobalt and categorized them into four types:

- Uses that could be eliminated by using existing substitutes or by other state-of-the-art technological adjustments

- Uses that could be eliminated if a conservation research program were initiated and proved to be successful

- Uses that could not be eliminated by either approach

- New uses for cobalt that could become important in the next few years

The committee also identified alternatives and supplements to conservation, such as:

- Stockpiling--both by government and industry

- Diversification of supply and exploration for domestic and more reliable foreign sources, including deep-sea nodules

- Extraction technology including use of alternate ores, such as laterites, Duluth gabbro, lead ores, high-arsenic sulfides, ocean nodules, and ocean crustal deposits

Three panels were formed at the inception of the study, but it soon became apparent that there was a substantial overlap between substitution and design; therefore, combining those two panels represented the most productive way to proceed with the study. Figure 2 shows the membership of the steering committee and the two panels.

COBALT PRICES AND DEMAND

Consumption by use differs considerably among countries. A large number of cobalt-containing products are needed for different applications.

Cobalt Prices

Cobalt price history for several major cobalt products is summarized in Table 2. All prices are for material produced in Zaire (formerly the Belgian Congo) and sold through the producer's agents. Since early 1978 a vigorous merchant market for cobalt has developed, and many of the producers other than Zaire have sold their material at or near these merchant prices. From 1940 through 1972 the cobalt price was relatively stable, rarely changing more than once a year. In 1973 and 1974, with the general commodity boom and the first major oil price escalation, prices were changed several times. From 1975 through 1977 prices were relatively stable, considering the rates of world inflation in those years.

The situation began to change in 1978. Early in 1978 the price of cobalt cathode was $6.85 per pound, and demand had been relatively weak for several years. Zaire had produced at low levels in 1976 and 1977, partly to prevent inventories from accumulating and partly due to physical and financial problems.

By mid-1978, demand began to increase rapidly. The free-market price (as opposed to the producer price, at which Zairean and some other cobalt is sold) began to creep upward. At the end of April, sales agents for Zaire announced the institution of an allocation program for cobalt, because they did not have enough cobalt to satisfy the surging demand.

Shortly thereafter the market exploded. An invasion of Shaba Province in Zaire and the brief occupation of mining and processing centers by insurgents raised consumers' concerns over the continued availability of cobalt. Although the production facilities in Zaire had suffered minimal damage, these concerns and the growing demand for cobalt kept prices spiraling upward. The free-market price peaked at over $40 per pound in late 1978, after which it began to decline gradually. The producer price was raised, in a series of steps, to $25 per pound in February 1979--four times its level 12 months earlier.

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- Mr. E. J. Dulis, President, Crucible Research Center, Pittsburgh, Penn.
- Dr. R. Gibala, Professor, Dept. of Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio
- Dr. B. H. Kear, Scientific Advisor, Physical Science Laboratory, Exxon Research and Development Co., Linden, NJ
- Dr. P. E. Queneau, Professor, Thayer School of Engineering, Dartmouth College, Hanover, NH
- Dr. M. Semchyshen, V. P., Climax Molybdenum Co. of Michigan, Ann Arbor, MI
- Dr. J. K. Tien, Professor, Metallurgy and Materials Science Dept., Columbia University, New York, NY
- Technical Advisor, Mr. B. J. Reddy, Charles River Associates, Inc., Boston, Mass.
- NMAB Staff and Project Manager, George Economos

PANEL ON PROCESSING PRACTICE

Cochairmen, Dr. J. C. Agarwal, V. P., Technology, Amax Specialty Metals Co., Parsipanny, NJ
- Dr. J. deBarbadillo, Mgr., INCO Alloy Products Co. Research Center, Suffern, NY

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- Dr. P. E. Queneau, Professor, Thayer School of Engineering, Dartmouth College, Hanover, NH
- Mr. S. H. Reichman, Director of Research, Development, and New Products, Special Metals Inc., New Hartford, NY

PANEL ON SUBSTITUTION AND DESIGN

Cochairmen, Dr. J. K. Tien, Professor, Metallurgy and Materials Science Dept., Columbia University, New York, NY
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- Mr. R. J. Dulis, President, Crucible Research Center, Inc. Pittsburgh, Penn.
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- Mr. J. B. Moore, Director, Materials Engineering Technology, P&W Aircraft Group, West Palm Beach, Fla.
- Dr. T. D. Schlabach, Head, Department of Metallurgical Engineering Bell Telephone Laboratories, Murray Hill, NJ
- Mr. R. A. Sprague, Mgr., Materials and Process Laboratories, Aircraft Engines Group, General Electric Company, Cincinnati, Ohio

Figure 2 Chart of the steering committee and its panels.

TABLE 2 U.S. Cobalt Producer Prices, 1940-1982 (dollars per pound)

Year	Month	Day	Granule and and Cathode (250 kg)[a]	Extra-Fine Powder (125 kg)[a]	70 Percent Oxide (100 kg)[a]
1940-46			1.50	-	1.16
1947	July	1	1.65	-	1.28
1949	April	1	1.80	-	1.38
1951	January	1	2.10	-	1.60
	October	1	2.40	-	1.60
	November	15	2.40	-	1.76
1953	November	1	2.60	-	1.96
1956	December	1	2.35	-	1.73
1957	February	1	2.00	-	1.48
1959	February	1	1.75	-	1.29
1960	March	1	1.50	-	1.12
1965	May	1	1.65	-	1.28
1967	January	4	1.85	2.89	1.81
1969	October	20	2.00	3.23	2.01
	November	17	2.20	3.49	2.20
1971	December	27	2.45	3.89	2.27
1973	February	14	3.00	4.65	2.73
	August	13	3.30	5.11	3.00
		28	3.20	4.95	2.91
	November	28	3.10	4.80	2.82
1974	January	7	3.10	5.06	2.90
	April	26	3.30	5.38	3.09
	May	15	3.45	5.63	3.23
	July	8	3.75	6.61	3.63
1975	January	23	4.00	7.05	3.87
1976	April	15	4.40	7.45	4.16
	September	13	4.90	8.29	4.62
	December	24	5.40	9.14	5.09
1977	January	21	5.20	8.80	4.90
	July	13	6.00	9.89	5.57
	December	21	6.40	10.55	5.93
1978	February	24	6.85	11.29	6.35
	May	23	8.50	12.69	7.44
	July	25	12.50	17.42	10.53
	September	14	18.00	23.60	14.76
	October	27	20.00	26.22	16.40
1979	February	1	25.00	31.00	19.91
1980	March	28	25.00	32.25	19.91
1981	March	2	20.00	27.26	16.34
	August	3	17.66	-	-
	September	1	17.26	-	-
1982	February	1	12.50	18.13	9.77
	May	1	12.50	6.36	8.74
	(Producer prices held at this level through February 1983)				

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[a] Standard lots offered for sale are in kilogram units.

Source: Metal Bulletin.

The market began to respond to these price increases. Cobalt generally is recovered as a by-product of nickel or copper operations, so most producers had limited options in the short run. Several new cobalt refineries were rushed into full production; construction, and in some cases minor production, had been started before 1978. Other producers modified their operations to mine ores with higher cobalt content, to improve cobalt recoveries in concentrating and refining, and to eliminate bottlenecks in processing. Cobalt production outside Zaire increased substantially from 1977 to 1979. Construction began on new refineries as well.

Demand, as well as supply, responded to the high prices. Substitution and conservation efforts were made in all of cobalt's uses, some successfully and others less so. Recycling became an important source of cobalt. At the same time, however, the overall demand for cobalt began to fall, due to weak economies in the United States, Europe, and Japan. U.S. cobalt consumption in 1981 was at its lowest level in over 10 years. Demand has fallen similarly in Europe and Japan, partly due to their weak economies and partly due to substitution and conservation measures.

As a result, the cobalt bubble burst in 1981. The producer price was lowered in several steps from \$25 to \$17.26 per pound, with few sales being made at that price. The free-market price plummeted from about \$21 per pound at the beginning of the year to under \$10 by December, after which it rebounded slightly as shown in Table 3. In early 1982 the producer price was cut again to \$12.50 per pound; the free-market price drifted down to under \$10 per pound. Supply is likely to exceed demand for several years, which will continue to apply downward pressure on prices.

Products and Forms

Cobalt is sold in a wide variety of products and forms, the most common being electrolytic cathode. High-purity cathodes have been the product most commonly used in the superalloy industry and other industries with stringent purity specifications. Cobalt is also commonly produced as a hydrogen-reduced powder, with the powder sometimes briquetted or sintered before shipping. Cobalt can be processed into a variety of chemicals for sale to the chemical industries, the most important chemical form being cobalt oxide. Specialty products include extra-fine powder, used in producing cemented carbides.

Table 2 gives the prices of three major cobalt forms. The granule and cathode price refers to high-quality material suitable for use by all cobalt consuming industries. Extra-fine powder and ceramic-grade (70 percent) oxide have generally sold at a premium over the cathode price in terms of contained cobalt. Only in 1982 did the price of ceramic-grade oxide fall as low as the price of cathode. Typical analyses for cobalt from the major producers are summarized in Table 4.

TABLE 3 Metals Week Spot Prices for Cobalt

Year	Month	Date	Price per pound
1981	Aug.	31	$13.25 - 13.75
	Sept.	7	12.50 - 13.00
	Sept.	14	12.00 - 12.75
	Sept.	21	12.00 - 12.50
	Sept.	28	11.25 - 12.00
	Oct.	5	11.00 - 11.75
	Oct.	12	10.60 - 11.00
	Oct.	19	10.00 - 11.00
	Oct.	26	9.75 - 10.25
	Nov.	2	9.50 - 10.25
	Nov.	9	9.50 - 10.25
	Nov.	16	- -
	Nov.	23	9.25 - 9.75
	Nov.	30	9.25 - 9.75
	Dec.	7	9.25 - 9.75
	Dec.	14	9.50 - 10.00
	Dec.	21	10.00 - 11.00
	Dec.	28	- -
1982	Jan.	4	12.00 - 13.00
	Jan.	11	12.50 - 13.25
	Jan.	18	12.25 - 13.00
	Jan.	25	12.50 - 13.25
	Feb.	1	12.00 - 13.00
	Feb.	7	11.25 - 11.75
	Feb.	15	11.00 - 11.50
	Feb.	22	11.00 - 11.50
	Mar.	1	11.50 - 11.75
	Mar.	8	11.50 - 11.75
	Mar.	15	11.30 - 11.75
	Mar.	22	11.30 - 11.75
	Mar.	29	10.75 - 11.25
	Apr.	5	10.30 - 10.75
	Apr.	12	10.30 - 10.75
	Apr.	19	10.10 - 10.60
	Apr.	26	10.00 - 10.50
	May	3	9.75 - 10.25
	May	10	9.50 - 10.25
	May	17	9.50 - 10.00
	May	24	9.30 - 9.90
	May	31	9.30 - 9.75
1982	June	7	$ 9.30 - 9.75
	June	14	9.30 - 9.70
	June	21	9.25 - 9.60
	June	28	9.25 - 9.50
	July	5	9.00 - 9.25
	July	12	8.80 - 9.20
	July	19	8.35 - 8.70
	July	26	8.30 - 8.50
	Aug.	2	8.00 - 8.30
	Aug.	9	8.00 - 8.30
	Aug.	16	7.90 - 8.20
	Aug.	23	7.80 - 8.10
	Aug.	30	7.50 - 7.90
	Sept.	6	7.50 - 7.90
	Sept.	13	6.80 - 7.30
	Sept.	20	6.80 - 7.00
	Sept.	27	6.50 - 6.75
	Oct.	4	5.75 - 6.00
	Oct.	11	5.00 - 5.50
	Oct.	18	4.60 - 5.00
	Oct.	25	4.25 - 4.60
	Nov.	1	4.50 - 4.80
	Nov.	8	- -
	Nov.	15	4.50 - 4.80
	Nov.	22	4.50 - 4.80
	Nov.	29	- -
	Dec.	6	4.60 - 4.85
	Dec.	13	4.60 - 5.00
	Dec.	20	4.70 - 5.10
	Dec.	27	4.50 - 4.75
1983	Jan.	3	4.60 - 4.90
	Jan.	10	4.60 - 4.90
	Jan.	17	4.75 - 5.10
	Jan.	24	4.90 - 5.20
	Jan.	31	5.00 - 5.25

TABLE 4 Typical Analysis of Various Cobalt Producers (percent cobalt; impurities in ppm)

	INCO		Sheritt	Falcon-bridge	AMAX		Outokumpu	Pechiney	Nippon	Sumitomo	ZCCM		Gecamines	SGM
											Kokana	Chambishi		
Element	cathode	72% Oxide	powder	cathode	powder	sinter	powder	cathode	cathode	cathode	cathode	cathode	cathode	X F powder
Cobalt	99.9	72.0	99.85	99.9	99.7	99.9	99.8	99.85	99.98	99.98[a]	99.6	99.4	99.9	99.85
Arsenic	1	-	1	1	8	8	-	-	-	-	-	-	-	-
Antimony	-	-	<1	-	2	2	-	-	-	-	5	7	-	-
Bismuth	1	-	<1	-	2	2	-	-	-	50	-	-	-	-
Cadmium	-	-	800	-	-	-	-	-	-	-	-	15	-	-
Calcium	-	500	7	-	10	10	-	24	-	-	-	4	-	-
Carbon	50	-	500	20	500	30	2330	79	-	10	-	-	50	200
Chromium	-	-	-	-	20	20	-	-	-	-	-	-	-	300
Copper	5	170	40	10	20	20	10	18	10	16	20	15	15	20
Hydrogen	2	-	128	2	-	-	-	-	-	0	-	-	3	-
Iron	25	1400	50	15	100	100	10	33	20	20	56	17	40	200
Lead	3	50	<1	3	20	4	-	-	1	5	5	14	3	10
Magnesium	-	50	-	-	3	3	-	-	-	-	-	4	-	-
Manganese	400	500	3	-	2	2	-	-	-	-	2	5	7	10
Nickel	400	9500	900	700	500	500	900	690	200	1200	3600	4700	400	450
Nitrogen	8	-	150	2	-	-	-	-	-	20	-	-	-	-
Oxygen	80	[b]	2100	30	2000	200	-	-	-	150	-	-	70	-
Phosphorus	-	-	0	-	-	-	-	-	-	10	-	-	-	-
Selenium	1	-	-	-	50	5	-	-	-	5	-	-	-	-
Silicon	tr	1800[b]	77	-	10	10	-	-	-	100	-	-	10	40
Sodium	-	900	-	-	-	-	-	-	-	-	-	-	-	-
Sulfur	15	1000	300	2	300	10	1700	9	-	8	-	-	10	80
Tin	-	-	<1	-	3	3	-	-	-	-	-	-	-	-
Zinc	3	-	5	2	5	5	-	-	1	19	10	15	30	50

Note: - = indicates not available
tr = trace
[a] = includes nickel
[b] = oxygen and silicon are in form of silica

Cobalt Demand

The major uses of cobalt are in superalloys, magnetic alloys, cemented carbides, tool steels, catalysts, chemical salts, and paint driers. Data on cobalt consumption by end use are available only for the United States (Table 5) and Japan (Table 6). Differences in the distribution of cobalt consumption across end uses in the United States and Japan are striking, e.g., ratio between magnet usage and cutting tool usage for the United States is about 1.5 to 1 whereas for Japan it is about 6 to 1. For other market economy countries (Table 7), even total consumption data are not generally available.

U.S. Demand

The data on U.S. consumption of cobalt by use in Table 5 show that during the 1970s superalloys, magnets, and chemical salts and driers provided the three most important uses for cobalt. Cutting and wear-resistant materials (cemented and sintered carbides), welding and hardfacing materials, tool steels, and catalysts required less cobalt.

Superalloys

The major use of superalloys is in gas turbines for either jet engines or industrial applications. Some alloys that are classified as superalloys are used in implanted medical prosthetic devices, such as artificial hip joints.

Concerning cobalt, superalloys can be classified as cobalt-base (40 percent or more cobalt), cobalt-bearing nickel-base (8 to 20 percent cobalt), and cobalt-free nickel-base. Cobalt is used in superalloys because it enhances high-temperature mechanical properties and processability. In addition, cobalt-base alloys can be air-melted, and those with low carbon content are easily weldable. Nickel-base alloys, whether or not they contain cobalt, are usually vacuum melted (several are air melted in an electric arc furnace and used in wrought products) and generally are not readily weldable. They are usually stronger than cobalt-base alloys, and if coated appropriately they often can provide acceptable resistance to corrosion.

Oxide dispersion-strengthened (ODS) alloys derive their strength less from composition than from stabilization of structure by the dispersion of fine oxides throughout the alloy. They need not contain cobalt. Costs for ODS alloys currently are quite high, compared with those of superalloys, so they have found only limited applications to date.

TABLE 5 Cobalt Consumption by Use, United States (million pounds)

Year	Super-alloys	Magnets	Cutting & Wear-Resistant	Welding & Hard-facing	Tool Steels	Other Metal-lurgical	Catalysts	Salts & Driers	Other Chemi-cal	Total	Metric tons[a] (1000)
1970	2.32	2.37	1.40	0.18	0.53	1.78	0.40	2.62	0.36	13.37	6.06
1971	1.98	2.28	1.23	0.25	0.32	1.25	0.47	2.74	0.44	12.50	5.67
1972	3.01	3.44	1.27	0.20	0.36	1.59	0.70	2.69	0.54	14.13	6.41
1973	3.28	4.30	2.51	0.39	0.52	1.85	1.15	3.57	0.64	18.74	8.50
1974	4.09	3.46	2.58	0.42	0.69	1.72	1.38	3.64	0.53	18.86	8.55
1975	2.26	2.03	1.40	0.48	0.29	1.31	1.11	2.87	0.47	12.79	5.80
1976	2.78	3.53	1.59	0.52	0.22	1.74	1.45	3.99	0.33	16.48	7.48
1977	3.71	3.48	1.43	0.42	0.31	1.36	1.29	3.78	0.30	16.58	7.52
1978	4.30	3.77	1.84	0.73	0.38	1.36	1.62	5.40	0.32	19.99	9.06
1979	5.28	3.27	2.12	0.44	0.41	1.03	1.88	1.79*	1.18*	17.40*	7.89
1980	6.29	2.27	1.34	0.62	0.32	0.52	1.66	1.41*	0.90*	15.32*	6.95
1981	4.20	1.69	1.08	0.49	0.17	0.43	1.28	1.44*	0.90*	11.68*	5.30

* The definitions of the reporting practices for the chemical categories changed in 1979. As a result, the chemical end-use and total consumption data are not comparable with those for earlier years.

Source: U.S. Bureau of Mines, Minerals Yearbook (annual) and Mineral Industry Surveys, Washington, D.C. (annual).

TABLE 6 Cobalt Consumption by Use, Japan (metric tons)

Year	Magnets	Special Alloys & Steels	High-Speed Steels	Heat-Resistant Alloys	Cemented Carbides	Other	Total
1970	2395	NA	265	251	127	410	3448
1971	1315	NA	180	231	91	382	2199
1972	1545	NA	186	363	108	357	2558
1973	2125	NA	525	527	171	575	3924
1974	1244	NA	351	627	154	431	2806
1975	836	NA	171	455	85	432	1979
1976	1550	NA	201	490	128	627	2996
1977	1117	NA	252	461	112	517	2459
1978	1116	NA	232	218	112	740	2388
1979	872	420*	NA*	NA*	144	788*	2227
1980	667	385*	NA*	NA*	165	695*	1912
1981	457	265*	NA*	NA*	153	636*	1511

* The definitions of categories in available data sources changed after 1978.

NA = Data not available

Source: Ministry of International Trade and Industry, Yearbook of Nonferrous Metals, Demand and Supply Statistics (annual).

TABLE 7 Cobalt Consumption in Other Countries (metric tons)

Year	United Kingdom	France	West Germany	Other Europe	Market Economy Countries	Total
1970	3224	1525	2600	2369	985	10703
1971	3028	1242	1739	2154	863	9026
1972	1833	1039	1805	2106	1005	7788
1973	2387	1314	2328	2453	1411	9893
1974	3677	1693	2510	2887	1371	12138
1975	2772	1495	1798	2168	1198	9431
1976	1503	1168	2261	2494	1357	8783

Source: Berlin: Deutsches Institut für Wirtschaftsforschung; and Hanover: Bundesandtalt für Geowissenschaften und Rohstoffe, 1978, Kobalt.

Magnets

Permanent magnets made with cobalt are generally superior to other magnets because cobalt is the strongest magnetic element. Cobalt increases the saturization magnetization of iron and has the highest Curie temperature known. The most commonly used magnetic materials are aluminum-nickel-cobalt alloys, collectively known as Alnicos. The most important of these is Alnico V, containing 24 percent cobalt. Other magnetic materials containing cobalt include Remalloy, rare earth-cobalt (RE-Co)* (usually cobalt-samarium), chromium-iron-cobalt alloys (chromindur), and soft magnetic alloys such as Permendur and Vicalloy. In any given application, the first two types of alloys use less cobalt per unit of magnetic strength than Alnicos.

A number of trade-offs must be made when magnetic materials are specified for any given application--magnetic strength, size of magnet, operating conditions, and cost. Ceramic magnets are significantly lower in cost than Alnicos, but they must be substantially larger to provide the same magnetic strength, and their performance varies markedly with temperature changes. They have virtually replaced Alnicos in all but the largest loudspeakers and other demanding applications. Chromindur is replacing Alnicos, Remalloy, and other cobalt-bearing magnetic materials in certain telecommunications and electrical applications. The demand for cobalt-rare earth alloys is on the rise, although it is relatively small at present. At higher cobalt prices, manganese-aluminum-carbon alloys may be used more widely.

Cutting and Wear-Resistant Materials

Cobalt is used in cutting and wear-resistant materials as a binder for tungsten carbides and mixed carbides. Tungsten carbide powder, and lesser amounts of tantalum, titanium, and other carbide powders, are mixed with powders in the iron group (cobalt, iron, and nickel) and sintered to form cutting tools, drill bits, and the like. The iron-group metals form a matrix to bind the carbides; of these, cobalt is by far the best binding agent known.

Welding and Hardfacing Materials

Hardfacing materials are welded onto base materials to provide a layer resistant to abrasion and corrosion, particularly where lubrication is not possible. Engine valves provide a major use for hardfacing alloys, but a number of other applications are important as well. Over 15 hardfacing

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* Re is often used in describing rare-earth elements, but RE is used in this text because Re is the official designation for the element <u>rhenium</u> in the periodic table of elements.

alloys are commonly used to provide selected combinations of shock resistance, corrosion resistance, hardness, and abrasion resistance in special applications. Hardfacing alloys most commonly are applied in the form of welding rods, but plasma and other spraying techniques are used as well. The most important cobalt-bearing alloys used in hardfacing have cobalt contents ranging from 45 to 65 percent.

Tool Steels

Tool steels constitute a relatively minor use for cobalt in the United States. High-speed tool steels are the most important as far as cobalt is concerned. Cobalt is added to high-speed steels to increase attainable hardness and improve hot hardness and hardness retention. In general, high-speed steels retain cutting ability even at elevated temperatures (at dull red heat). Carbides formed with elements such as tungsten, molybdenum, and vanadium give high-speed steels this property.

Catalysts

Cobalt catalysts are used in the production of isooctyl alcohols (for manufacturing polyvinyl chloride) and unsaturated polyesters. Cobalt-molybdenum catalysts on an alumina carrier are used widely to desulfurize petroleum fractions. Molybdenum is the active catalyst in the reaction, and cobalt acts as a promoter. The demand for cobalt catalysts could expand several-fold in the next 20 years if coal liquefaction and gasification plants become common and if the processes in these plants use cobalt catalysts.

Salts, Driers, and Other Chemicals

Oxides, inorganic salts, and organic salts of cobalt are used widely. Organic cobalt salts, such as cobalt naphthenate and oleate, are used as driers in inks, varnishes, and oil-base paints because of this catalytic action. Cobalt is primarily a surface drier, so it is normally used with other driers, such as manganese, to promote fast, even drying of paint films. The same types of compounds are often used to catalytically speed the curing time for certain plastics. Inorganic salts and oxides find wider applications, such as pigments, animal feed additives, electroplating, and ground-coat frit.

Foreign Consumption

Data on foreign consumption of cobalt by use are available only for Japan (Table 6), where magnets are the most important application. Estimates of total cobalt consumption are available for some other market economy countries (Table 7). The substitution and conservation possibilities by use generally are the same as in the United States. Because the consumption patterns differ, however, the overall substitution and conservation possibilities differ in each country.

PHYSICAL FLOW OF COBALT IN DOMESTIC MATERIALS CYCLE: A MATERIALS BALANCE

This section summarizes the physical flow of cobalt in the domestic economy. It provides a perspective for judging potential impacts of technological alternatives on various parts of the cycle. In attempting to make materials balances, the committee reconciled data and estimates from several sources as described below. Additional analyses are given in Appendix B.

Initial Reconciliation of Data on Cobalt Consumption

The Bureau of Mines (Kummer 1980) presents data on cobalt consumption under two headings; "reported consumption" and "apparent consumption." Table 8 gives the "reported consumption" of cobalt in the United States in 1980 as 15.32 million pounds. "Apparent consumption" is calculated from imports, less exports, plus or minus changes in industrial and government stocks, plus purchased scrap. Table 9 shows that the total "apparent consumption" of cobalt in the United States in 1980 was 16.96 million pounds.

Neither "reported" nor "apparent" consumption necessarily represents actual consumption of cobalt in 1980. "Actual consumption" is in excess of "reported consumption" because some companies, by policy, do not report such data to the Bureau of Mines. "Actual consumption" of cobalt may be greater or less than "apparent consumption" because there appear to be stock increases and decreases that are not reported to the Bureau of Mines, perhaps by traders or speculators. Mineral Facts and Problems (Sibley 1980) presents time series data on "reported consumption" and "apparent consumption." In recent years, on a 3-year running average, "apparent consumption" is about 7 percent in excess of "reported consumption."

On the assumption that the "reported consumption" of cobalt in 1980 represented only 93 percent of "actual consumption," the "estimated consumption" of cobalt by major product in 1980 was calculated (Table 10). Instead of prorating the additional 7 percent to all major uses, it was allocated in this table to "other metals" and "other chemicals" in proportion to the amounts reported.

Estimated Flow of Cobalt, 1980

Figure 3 shows estimates of the flow of cobalt in the U.S. economy in 1980; detailed data are given in Appendix B. About 9.7 million pounds of contained cobalt was imported directly from countries in central Africa and indirectly through Belgium. Imports from Canada and all other countries amount to about 6.6 million pounds. During the course of these analyses, attempts were made to reconcile conflicting data. As will be shown later, a number of assumptions were made to bring about a reconciliation. A final materials balance was achieved by assuming that the Bureau of Mines reduction of industry stocks figure of 0.9 million pounds (Kummer 1980) was in error and that actually these stocks increased by 0.4 million pounds. This change is not unreasonable. During the shortage of cobalt, traders bought and sold cobalt in substantial quantities and could have been missed by the Bureau's survey. Further, 1980 consumption was about 2 million pounds less than that in 1979. Cobalt in the supply "pipeline" may well have gone into industry stocks.

TABLE 8 Reported Consumption of Cobalt in the United States, 1980 (millions of pounds of contained cobalt)

Superalloys	6.29
Magnets	2.27
Cemented carbides	1.37
Hardfacing alloys	0.62
Steels	0.50
Other metals	0.45
Catalysts	1.66
Other chemicals	2.21
Total	15.32

Source: Kummer 1980.

TABLE 9 Apparent Consumption of Cobalt in the United States, 1980 (millions of pounds of contained cobalt)

Imports	16.30
Exports	-1.37
Industrial stock release	0.85
Scrap recycled	1.18
Total	16.96

Source: Sibley 1980.

Flows of cobalt through processing and manufacturing stages are summations of the cobalt flows related to production of each of the following: catalysts, other chemicals, superalloys (cast and wrought), magnets (cast and wrought), cemented carbides, hardfacing alloys, steels, and other metallic uses.

TABLE 10 Estimated Consumption of Cobalt by Major Product Class, 1980 (millions of pounds of contained cobalt)[a]

Superalloys	6.3
Magnets	2.3
Cemented carbides	1.3
Hardfacing alloys	0.6
Steels	0.5
Other metals	0.6
Catalysts	1.7
Other chemicals	3.2
Total	16.5

[a] Kummer 1980.

In 1980 about 4.9 million pounds of cobalt was used in the production of catalysts and other chemicals. Of that amount, an estimated 4.5 million pounds was embodied in catalysts and other chemical-based products. The 0.2 million pounds lost in processing and the similar amount lost in manufacturing (shown in triangles) represent unrecovered cobalt processing and handling wastes.

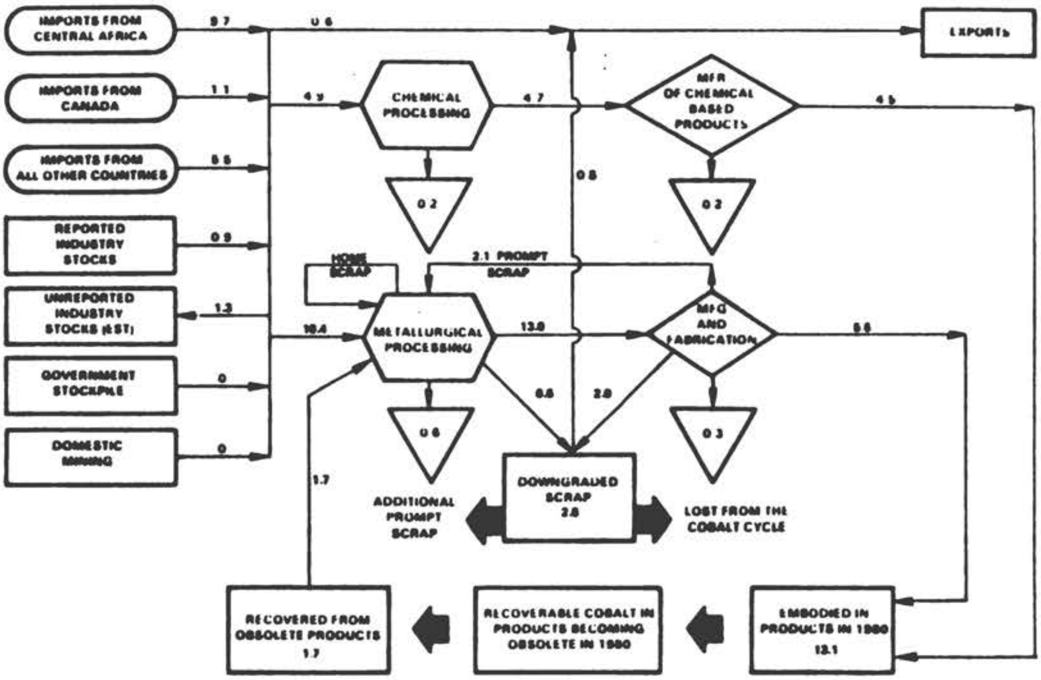

Figure 3 Estimated cobalt cycle flows and losses in U.S. economy, 1980 (millions of pounds of contained cobalt).

About 10.4 million pounds of new cobalt was used in metallurgical processing. In addition, 2.1 million pounds of cobalt in prompt scrap (Curwick et al. 1980) and 1.7 million pounds of cobalt in obsolete scrap was used. The output of manufacturing and fabrication operations amounted to about 8.6 million pounds of contained cobalt. A substantial amount of downgraded scrap is produced (Curwick et al. 1980). Some fraction of this may be used for its cobalt content and should be considered as an additional amount of prompt scrap. Most of this downgraded scrap, however, is lost from the cobalt cycle when it is used for its content of other alloying elements, such as nickel. To the extent that this downgraded scrap is used as prompt scrap, the estimated value of cobalt embodied in metal products, 8.6 million pounds, will have to be modified.

Estimates of the life of cobalt-containing products that might be recovered and recycled for their cobalt content (Table 11) show that about 6.3 million pounds of recoverable cobalt is from products that became obsolete in 1980, as calculated from historical patterns (Sibley 1980) and estimated life cycles. About half of the cobalt that became obsolete in 1980 in the form of superalloys was recycled in 1980. Overall it appears that a little over 25 percent of the cobalt that became obsolete in 1980 was recycled.

TABLE 11 Estimated Obsolescence and Scrap Recovery (in millions of pounds of contained cobalt, except where noted)

Product	Estimated consumption in 1980	Life cycle (years)	Amount in obsolete products in 1980	Estimated recovery
Superalloys	6.3	5	2.4	1.2
Magnets	2.3	10	*	-
Cemented carbides	1.3[a]	2	1.8	0.5
Hardfacing	0.6	5	*	-
Steels	0.5	5	0.6	Nom.
Other metal	0.6[b]	5	*	-
Catalysts	1.7	2	1.5	Nom.
Other chemicals	3.2	5	*	-
Total	16.5[b]		6.3	1.7

* Uses are either dissipative in nature or the cobalt in products sufficiently difficult to separate and recover so as to be considered unrecoverable.

[a] Probably does not include estimated 0.5 million pounds of cobalt contained in obsolete scrap, that trade sources indicate was used (Sibley 1980).

[b] Reported consumption of cobalt adjusted to reflect estimated amount of cobalt consumption not reported to the Bureau of Mines. The total adjustment of 1.2 million pounds was allocated to the "other metal" and "other chemical" categories of use.

Curwick and coworkers (1980) presented data on input materials, yields, and scrap generation for nickel- and cobalt-based alloys. Their data shows that about 2.1 million pounds of prompt scrap (scrap generated by in-house normal metals-processing operations) was generated and used in 1980. Also 1.2 million pounds of purchased scrap was reported (Sibley 1980). Most prompt scrap represented either intraplant and interplant transfer and not purchases, or it was missed by the Bureau of Mines survey. There is no way to determine what fraction of the reported purchased scrap is obsolete scrap (scrap contained in spent, rejected, or discarded components or materials). It was, therefore, necessary to arrive at an estimate of obsolete scrap use in some other way.

General knowledge of the industry suggests that virtually no cobalt in 1980 was recycled from the following types of obsolete products: catalysts, chemicals, magnets, hardfacing alloys, steels, and other metallic uses. It would appear then that the total of 1.2 million pounds of purchased scrap might have been in the form of obsolete and prompt superalloys, obsolete cemented carbides, and prompt hardfacing alloys.

It is likely that the cobalt in obsolete cemented carbides has not been counted in the Bureau of Mines survey. According to committee member William Reich, nearly 0.5 million pounds of cobalt is currently being recovered from obsolete cemented carbides. By adding this amount to the raw material reportedly used in the production of cemented carbides, a total production of carbides is calculated that is in line with industry estimates. If the cobalt in obsolete cemented carbides is not accounted for in the Bureau of Mines survey, then the entire amount of purchased scrap reported by the Bureau must consist only of prompt and obsolete superalloy scrap plus a small amount of hardfacing alloy prompt scrap. It was assumed that 1.1 million pounds of superalloy scrap and 0.1 million pounds of hardfacing alloy scrap were accounted for in the Bureau's survey.

Referring again to Figure 3, scrap recovery from obsolete products was estimated to be 1.7 million pounds consisting of 0.5 million pounds in obsolete cemented carbides and 1.2 million pounds of obsolete superalloy scrap. In addition, 2.1 million pounds of prompt scrap was recycled in 1980. Thus 2.6 million pounds of recycled cobalt was not accounted for in the Bureau of Mines figures.

Summary of Materials Balance

Numerous estimates and assumptions were made to prepare the materials balance given in Figure 3, and further effort would be required to confirm or reject the assumptions applied for this compilation. For the purposes at hand, the flows shown are believed to be reasonable approximations of reality. A systematic review of the data presented in this analysis shows the following:

- It is important to increase imports from Canada and from other producing countries to reduce dependence of the United States on central African countries.
- The opportunity for increasing cobalt recovery from various classes of obsolete products needs emphasizing.
- Actions should be taken to improve segregation and control of prompt scrap in superalloy production and fabrication to reduce the proportion that is downgraded.
- A substantial amount of cobalt conservation is achievable through recovery of cobalt from spent catalysts.
- The quantity of cobalt in the metal system in the form of prompt scrap and downgraded scrap is large in relation to the amount embodied in various products.
- The 1980 stockpile goal of 85 million pounds is significant in relation to the critical industrial and military uses.
- The data and estimates on use in superalloys are open to some question, mainly because of inadequate data on scrap use and new cobalt requirements.

EXTENT OF CURRENT U.S. VULNERABILITY

To determine the extent of U.S. vulnerability to cobalt supply disruptions, the committee studied in detail each end use. This led to determinations of how much cobalt used today was essential and how much could be replaced through substitution, design, and improved processing using state-of-the-art technological adjustments and through conservation research programs if these were initiated and proved successful. (These analyses are discussed further in Chapters 4 and 5.)

The results of these analyses were given in Table 1, which showed that the estimated current (1983) annual essential U.S. requirement for cobalt is about 7.7 million pounds. By 1992, annual requirements are estimated to have increased to 11.7 million pounds. The only significant demand increases appear to be in superalloys which are expected to increase at an average rate of 6 percent per year, and in cemented carbides, which are expected to increase at an average rate of 3 percent per year. In all other applications, little if any additional cobalt will be required by 1992 than is essential today. It is unlikely that any conservation research programs either under way or that could be initiated would have any real impact on reducing the amount of essential cobalt needed within the next 10 years.

Past experience has shown that sharp increases in the price of cobalt, both in the open market (spot price) or by the producer countries, causes consumers to rapidly turn away from its use wherever possible. These actions and reactions alter the proportion of the limited supply available for more critical uses, such as superalloys and cemented carbides, where strategic issues are dominant. Similar responses can be expected whenever abrupt market deviations occur and, in turn, the direction of the entire user market will be altered from the methodical and systematic behavior patterns discussed in this report.

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Chapter 3

WORLD COBALT RESOURCES

In addition to its analyses of technological options for reducing primary cobalt consumption (Chapters 4 and 5) the committee also assessed the potential for countering possible supply disruptions through methods other than conservation, i.e., resource exploration and development, diversification of supply and stockpiling.

Cobalt is almost universally recovered as a by-product of other mining and refining operations, so even at historic price levels the potential for increasing cobalt output around the world except in Zaire is quite limited. The high prices of 1978 encouraged increases in by-product recovery worldwide, especially from nickel resources. Reliable historical data for the cobalt market are difficult to obtain, so no attempt is made to assess post production and use trends. This chapter discusses cobalt production, reserves, and resources, and alternative stockpiling actions.

This chapter contains a description of current world cobalt resources (Young 1960; Sibley and Kirk 1981; Peterson et al. 1981). The best available information on the location, tonnage, and analysis of cobalt-containing ore deposits is summarized in Table 12. It should be noted that the U.S. is relatively poor in cobalt mineral resources. Details on the concentration and extractive metallurgy of cobalt-containing ores are given in two papers (De Cuyper 1981; Lenoir et al. 1981) in Appendix C.

Zaire is the most important source of cobalt in the world (Tables 13 and 14). The state mining company, Gecamines, recovers cobalt in the course of its copper mining and processing operations. Zambia is the second largest source of cobalt, where it is also a by-product of copper operations. Cobalt-rich intermediates are recovered from nickel operations in Canada, Australia, and the Philippines, then processed further in Canada, Japan, and the United States for cobalt output. Intermediate cobalt-containing nickel products from Canada, Indonesia, Botswana, Guatemala, and New Caledonia are processed for cobalt in Norway, Japan, the United States, Britain, and France. Finland recovers cobalt from its copper and nickel ores, as well as from East German copper residues. South Africa recovers by-product cobalt from its platinum operations, almost all of which is refined in that country. A small amount of cobalt is recovered as a by-product of nickel mining in Zimbabwe. Morocco has the only ore exploited primarily for its cobalt content; refining is done in France, although these operations are both suspended currently.

TABLE 12 World Cobalt Resources

			Demonstrated Resources[a]				Inferred Resources[a]				
Country	Deposit	Deposit Type	Ore (million tons)	Co	Ni	Cu	Ore (million tons)	Co	Ni	Cu	Status[b]
				percent				percent			
Africa											
Botswana	All	Sulfide	32	0.08	1.2	1.3	14	0.06	1.0	1.1	E+P
Morocco	Bou Azzer	Arsenide	0.25	1.2	0.15	-	1.0	1.2	0.15	-	E+P
Uganda	Kilembe	Sulfide	5.0	0.17	2.1	10.0	0.2	-	-	-	E+P
South Africa	All	Sulfide	950	0.006	0.19	-	-	-	-	-	E+P
Zaire	All	Sulfide	370	0.42	-	5.5	500	0.3	-	4.0	E+P
Zambia	All	Sulfide	480	0.14	-	2.5	370	0.13	-	2.5	E+P
Zimbabwe	All	Sulfide	100	0.02	0.75	-	-	-	-	-	E+P
South America											
Brazil	All	Laterite	250	0.13	1.5	-	300	0.13	1.5	-	E+P
Columbia	Cerro Matoso	Laterite	25	0.10	2.7	-	70	0.10	2.7	-	E+P
Cuba	All	Laterite	50	0.1	1.3	-	1600	0.07	0.8	-	E+P
Dominican Republic	Falconbridge	Laterite	70	0.05	1.64	-	-	-	-	-	E+P
Guatemala	All	Laterite	50	0.05	1.8	-	450	0.07	1.5	-	E+P
Peru	All	Sulfide[c]	250	0.03	-	-	-	-	-	-	E
Puerto Rico	All	Laterite	90	0.09	0.9	-	-	-	-	-	E
Venezuela	All	Laterite	40	0.03	1.7	-	-	-	-	-	E
North America											
Canada	All	Sulfide	600	0.05	1.5	0.6	400	0.04	1.0	0.5	E+P
U.S.A.	All	Laterite	55	0.08	1.0	-	140	0.08	0.8	-	E+P
	All	Sulfide	650	0.015	0.16	0.5	3500	0.015	0.16	0.5	E
	All	Arsenide	6	0.55	1.3	-	-	-	-	-	E+P
	All	Sulfide[d]	200	0.03	-	-	-	-	-	-	E+P
	Cornwall	Sulfide[c]	50	0.05	-	-	-	-	-	-	E+P

TABLE 12 (continued)

			Demonstrated Resources[a]				Inferred Resources[a]				
Country	Deposit	Deposit Type	Ore (million tons)	Co percent	Ni percent	Cu percent	Ore (million tons)	Co percent	Ni percent	Cu percent	Status[b]
South Pacific											
Australia	All	laterite	155	0.1	1.3						E+P
	All	sulfide	740	0.015	0.8						E+P
Papua NG	All	laterite					100	0.12	1.2		E
New Caledonia[f]	All	laterite (high Ni grade)					300	0.09	2.6		E+P
	All	laterite (low Ni grade)					2500	0.12	1.4		E
Indonesia	All	laterite	800	0.10	1.5		1200	0.10	1.5		E+P
Philippines	All	laterite	200	0.1	1.3		500	0.10	1.3		E+P
Solomon Is.	All	laterite	25	0.1	1.3						E
Europe											
Greece	All	laterite	70	0.07	1.7		150	0.07	1.5		E+P
Finland	All	sulfide	13	0.23	0.1	3.8					E+P
Yugoslavia	All	laterite	100	0.05	1.3						E+P
Asia											
India	All	laterite	70	0.06	0.8		75	0.04	0.7		E
Others											
USSR	(Inferred to have 500,000 tons of cobalt in a variety of nickel ores.)										E+P
Deep Sea[e]	All	nodules	2100	0.22	1.3	1.0	50,000	0.2	1.0	1.0	E
Shallow Marine	Mn crusts	(recently recognized resource contains potentially large amounts of 1% Co)									

Note: [a] Demonstrated resources plus inferred resources equals total resources.

[b] E denotes some exploration carried out. P denotes production of deposit's principal commodity

[c] Cobaltiferous pyrite in magnetite mined for iron.

[d] Siegenite in galena mined for lead.

[e] Mineral content presented is for example only; reports range is discussed in the text.

[f] Figures include both demonstrated and inferred resources.

TABLE 13 Cobalt Refineries (market economy countries, December 1982)

Country	Company	Capacity (mt Co/year)	Products
Canada	INCO	900	Cobalt cathodes
	INCO	1200	Cobalt oxide
	Sherritt Gordon	1000	Cobalt briquettes and powder
Belgium	SGM	2000	Cobalt powder; cobalt salts and oxide
Finland	Outokumpu	1400	Cobalt briquettes and powder; cobalt sulfate
France	Metaux Speciaux	1000	Cobalt cathodes; cobalt chloride and oxide
	SLN	300	Cobalt chloride
Japan	Nippon Mining	1700	Cobalt cathodes
	Sumitomo Metal Mining	1300	Cobalt cathodes
Norway	Falconbridge Nikkelverk	1800	Cobalt cathodes
South Africa	Impala Platinum	200	Cobalt cathodes
	Matthey Rustenburg	200	Cobalt sulfate
USA	AMAX	450	Cobalt briquettes and powder
Zaire	Gecamines	15000	Cobalt cathodes and granules
Zambia	ZCCM	6300	Cobalt cathodes

This review excludes in-depth discussion of the cobalt supply in central economy countries. However, these countries are net importers of cobalt, typically consuming about 10 percent of market economy countries' production. The USSR produces an important quantity of refined cobalt extracted from its domestic nickel ores. Cuba also recovers an important amount of cobalt from its domestic nickel ores; it is refined in the communist bloc.

Copper mines in central Africa are by far the most important source of cobalt at present. Most of the rest of the world's cobalt is a by-product of nickel mines in the form of both sulfide and laterite--primarily the former at present (Boldt and Queneau 1967; Queneau 1971). The future production of cobalt from specific ores will depend on the economics of producing the metals of primary importance. The world's greatest terrestrial cobalt resources are in the nickel laterites--mainly in the limonites of New Caledonia, Indonesia, Cuba, and the Philippines. Potentially significant production of cobalt from New Caledonia ores will depend on whether the nickel can be extracted economically by processes that permit by-product output of cobalt. This is not now the case because the main New Caledonia product is ferronickel, in which the cobalt is

TABLE 14 Mine Production of Cobalt in the Market Economy Countries (metric tons)

Year	Australia	Botswana	Canada	Finland	Morocco	New Caledonia	Philippines	Zaire	Zambia	Zimbabwe	Total
1975	NA*	81	1354	1402	1961	NA*	117	13,638	1843	--	20,396
1976	544	132	1356	1278	934	82	492	10,686	2175	--	17,679
1977	1000	163	1485	1227	1015	109	1084	10,215	1704	--	18,002
1978	1350	261	1234	1212	1134	150	1191	13,299	3741	18	23,590
1979	1500	294	1640	1065	961	210	1370	14,996	4280	210	26,526
1980	1600	226	1603	1035	838	180	1331	15,500	4400	120	26,833
1981	1600	250	2270	1035	752	140	1090	15,500	4500	80	27,217

* Data reported for Australia and New Caledonia in 1975 are inconsistent with data for later years, so are not presented here (NA); data for South Africa are not available.

Source: U.S. Bureau of Mines, Minerals Yearbook (Annual) and Minerals Industry Surveys (Annual), U.S. Government Printing Office, Washington, D.C.

lost, locked to the nickel it contaminates. Sometime in the future, the vast cobalt resources in ocean-based manganese nodules and manganese crusts will become available.

ZAIRE, ZAMBIA, SOUTH AFRICA, BOTSWANA

Zaire's leading position in cobalt production is the result of ores that are the richest in the world--about 0.3 to 0.5 percent cobalt and ten times as much copper, in the deposits now being exploited. Most of Zaire's cobalt comes from open-pit mines, although two underground mines are important. The ore treated for cobalt recovery is milled to produce bulk concentrates rather than separate copper and cobalt concentrates. The concentrates are fed to one of two large plants and subjected to roast-leach, electrowinning processes for production of cobalt cathodes and large amounts of copper. The Luilu refinery produces higher quality cathodes than the old Shituru refinery. Their combined capacity is about 15,000 metric tons of cathode yearly. Small quantities of cobalt are sometimes produced in the form of "white alloy," a copper-cobalt matte that is refined in Belgium. Zaire has the potential for greatly increased cobalt output. The P2 expansion project of Gecamines, deferred indefinitely at present, would add 6,000 metric tons to the current capacity. The Tenke-Fungurume project could eventually add another 4,500 metric tons to Zaire's capacity. However, due to shortages of operating and maintenance supplies, Zaire is experiencing difficulties in maintaining its present copper-cobalt output.

Zambia is the second most important source of cobalt in the market economy countries; here also the cobalt comes from copper mining and processing operations. Two companies have produced cobalt in Zambia--Nchanga Consolidated Copper Mines (NCCM) and Roan Consolidated Mines (RCM). These companies merged in 1982 to form Zambia Consolidated Copper Mines (ZCCM). The ore has cobalt contents ranging from 0.1 to 0.2 percent, together with copper contents of 1.5 to 3.0 percent. It is subjected to differential flotation to produce separate copper and cobalt concentrates. Cobalt recovery from the ore into the cobalt concentrate has increased markedly in recent years, from about 50 to 70 percent. The cobalt concentrates are processed in cobalt plants that resemble scaled-down versions of those in Zaire. NCCM's cobalt refinery at Kitwe has an effective capacity of 1,300 metric tons. NCCM now also has a new 2,600 metric ton cobalt refinery and plans to increase the capacity of its original refinery. RCM has a new cobalt refinery at Chambishi with a rated capacity of 2,400 metric tons annually. Zambia could produce considerable quantities of cobalt by cleaning old copper smelter slags. These slags, accumulated over many decades, have a cobalt content averaging about 0.6 percent.

Three South African platinum producers recover a modest amount of by-product cobalt. Because of new refinery installation most of the cobalt is refined locally, the output reporting in metal and cobalt sulfate. Old gold tailings in South Africa are currently leached and processed to recover gold and uranium, in the course of which significant quantities of cobalt are lost. The Selebi-Pikwe copper-nickel operation in Botswana produces a cobalt-bearing matte that is refined at Port Nickel, Louisiana, and the cobalt recovered.

AUSTRALIA, INDONESIA, NEW CALEDONIA, PHILIPPINES, JAPAN

Western Mining Corporation mines, concentrates, and smelts nickel sulfide ores in Australia. It refines most of its nickel matte in Australia, but mixed nickel-cobalt sulfides from the refinery are shipped to Sherritt-Gordon in Canada for cobalt recovery. Some nickel matte is exported to Sumitomo in Japan, which recovers the modest amount of cobalt it contains. The Agnew operation in Australia consists of a nickel sulfide mine and concentrator. Nickel concentrates are smelted to matte by Western Mining, and the matte, containing a modest amount of cobalt, is refined in the United States by Amax. Metals Exploration and Freeport-McMoran operate a lateritic nickel mine (Greenvale) and extraction plant (Townsville) in Australia, recovering a cobalt intermediate that is refined in Japan.

Marinduque operates a lateritic nickel mine and extraction plant in the Philippines, recovering a cobalt intermediate that is refined in Japan. INCO operates a lateritic nickel mine and smelter in Indonesia (Soroako, Sulawesi), which produces a cobalt-containing matte that is refined in Japan (Sumitomo) and Britain (INCO) and the cobalt is recovered. The several large deposits of cobalt-rich nickelferous limonites in Indonesia make it a potential major producer of cobalt. SLN operates lateritic nickel mines and a smelter (Doniambo) in New Caledonia, producing cobalt-losing ferronickel and a modest amount of cobalt-containing matte that is refined in France. The immense cobalt-rich nickelferous limonites of this island make it a potentially leading producer of cobalt.

Two Japanese companies, Nippon Mining and Sumitomo Metal Mining, refine cobalt, largely from imports of mixed nickel-cobalt sulfides. Nippon Mining processes mixed nickel-cobalt sulfides from the Greenvale mine in Australia, and Sumitomo processes similar sulfides from the Marinduque mine in the Philippines. Their electrolytic refineries have yearly capacities of 1,700 metric tons and 1,300 metric tons of cathode respectively.

CANADA, BRITAIN, NORWAY, GREECE

INCO smelts and refines nickel sulfide ores in Canada and is the world's largest nickel producer. It is completing construction of a new 900 metric ton per year cobalt electrowinning refinery at Port Colborne, Ontario. Cobalt that in the past has been made into salts in Wales will now report as cathode metal. INCO also has the refinery capacity to produce 1200 metric tons per year of cobalt as oxide. Improvements in cobalt recovery in its Canadian smelting operations, presently low, would permit INCO to greatly increase its production. Cobalt-containing nickel matte from INCO's nickel laterite operations in Indonesia and Guatemala (now mothballed) is processed in Britain (INCO, Wales), with a cobalt intermediate being recovered and returned to Canada (INCO, Ontario) for refining.

Sherritt-Gordon Mines (SGM) operates a cobalt custom refinery in Canada that has a capacity of 1,000 metric tons annually. The company no longer operates a nickel mine, so feed for its hydrometallurgical nickel and cobalt refineries includes cobalt-containing materials from around the world. Because some of its suppliers have installed new cobalt refining facilities, Sherritt-Gordon may have difficulty obtaining sufficient feed to operate its cobalt refinery at capacity.

Falconbridge mines and smelts nickel ores in Canada, then ships its cobalt-containing nickel-copper matte to Kristiansand, Norway, for refining. The refinery also processes matte, cobalt intermediates, and superalloy scrap from other suppliers on a custom basis. Although the capacity of Falconbridge's electrolytic cobalt refinery is 1,800 metric tons annually, Falconbridge currently has only enough refinery feed to produce at a rate of 1,200 metric tons of cathode.

The Larymna lateritic nickel operation in Greece produces ferronickel in which the cobalt is lost.

COLOMBIA, DOMINICAN REPUBLIC, GUATEMALA

Both the Cerro Matoso lateritic nickel operation in Colombia and the Bonao lateritic nickel operation in the Dominican Republic produce ferronickel in which the cobalt is lost. The Izabal lateritic nickel operation of INCO in Guatemala produces cobalt-containing matte that is refined in Wales and the cobalt is recovered.

FINLAND, BELGIUM, MOROCCO, FRANCE

The Finnish state mining company, Outokumpu Oy, operates a cobalt refinery with a capacity of about 1,400 metric tons annually. Low-grade cobalt concentrates from local copper mining are produced and processed, as well as some cobalt intermediates from Outokumpu's nickel refinery. Some 400 metric tons are recovered from old copper furnace residues imported from the German Democratic Republic, and the refined cobalt is returned there.

SGM has a cobalt refinery at Hoboken, Belgium, with a capacity of about 2,000 metric tons per year.

Only one company presently operates a mine primarily for its cobalt content: Compagnie de Tifnout Tiranimine in Morocco. The cobalt arsenide ores near Bou Azzer in Morocco, which average about 1.2 percent cobalt, are concentrated in Morocco and shipped to France for processing. In recent years production has been about 750 to 1,000 metric tons of cobalt annually, but known ore reserves are nearing exhaustion and operations were suspended recently. An exploration program has been initiated to locate additional deposits.

France has two cobalt refineries. Metaux Speciaux, a subsidiary of Pechiney Ugine Kuhlmann, processes cobalt arsenide concentrates imported from Morocco. Mainly cathode is produced, along with some cobalt chloride and oxide, and with gold and arsenic as by-products. The nominal capacity of this plant is about 1,000 metric tons annually, but production in recent years has suffered because of decreased levels of concentrate production in Morocco. SLN operates a cobalt recovery circuit in its new electrolytic nickel refinery at Sandouville near Le Havre, producing some 300 metric tons of cobalt annually in the form of cobalt chloride. This plant treats the small amount of nickel matte produced in SLN's New Caledonia lateritic nickel operations.

UNITED STATES

The United States is poor in cobalt-containing ore deposits, although there is adequate tonnage to supply a substantial fraction of requirements for more than a decade (Peterson et al. 1981). It is estimated that total production cost of any output of domestic origin would be at least $20 per pound of cathode (1982 dollars). There are currently no operating cobalt mines. One cobalt refinery is operated by AMAX in Louisiana. This refinery treats cobalt-containing nickel matte from a number of foreign sources, currently Botswana and Australia, and has a capacity of 450 metric tons of cobalt annually.

Noranda Mines has considered developing the old Blackbird Mine in Idaho, which has important cobalt resources. The ore averages about 0.55 percent cobalt in arsenide, which can be concentrated and could yield about 2,000 metric tons of cobalt annually. Auschutz Mining has considered developing the old Madison Mine in Missouri. The ore averages about 0.25 percent cobalt in sulfide, which can be concentrated and could yield about 1,000 tons of cobalt annually. Neither of these developments will proceed without major government financial support.

California Nickel has considered developing a small, very low-grade nickel laterite deposit near Gasquet Mountain, California, averaging perhaps 0.08 percent cobalt. It has not been demonstrated that this project can materialize without extraordinary government financial support.

Other domestic cobalt-producing operations will be considered in the United States sometime in the future. During the treatment of lead ores mined in Missouri, about 500 tons of cobalt is now lost annually. The huge copper-nickel sulfide deposits of Minnesota's Duluth Gabbro contain significant amount of cobalt (Lawver 1975). There are scattered small nickel laterite deposits in Oregon and Washington, such as the Riddle mine in Oregon, which Hanna Mining has operated for ferronickel output.

There are considerable differences of opinion regarding the amount of cobalt that can be recovered from domestic sources at a given price (Peterson et al. 1981). Some of this speculation is based on the possibility of employing the findings from exploratory extraction process work done by the U.S. Bureau of Mines (Siemens and Corrick 1977, Brooks 1981, Paulson et al. 1980). Other important studies have been performed, but most of these efforts are proprietary to the institution or company responsible for them. At least two major obstacles seem to make domestic cobalt recovery impractical. On the one hand, the nature of the mineral occurrence discourages profitable extraction, while on the other, the quantity of cobalt contained does not allow for long-term recovery on a scale sufficiently large to be economically acceptable. Nevertheless, the Federal Emergency Management Agency (FEMA) has proposed to congress the use of the provisions of the Defense Production Act (operating on a temporary extension) to encourage domestic production by setting a floor price for domestically produced cobalt (Nulty 1983, Hamilton 1983).

DEEP-SEA MANGANESE NODULES AND SHALLOW MARINE MANGANESE CRUSTS

Deep-sea manganese nodules represent one of the world's largest untapped deposits of nonferrous metals (Agarwal 1979). Nickel, copper, cobalt, and manganese are present in enormous quantities, enough to supply hundreds of years of demand at current consumption levels. The nodules typically contain about 1-1.5 percent nickel, 1-1.5 percent copper, 0.1-0.5 percent cobalt, and 25-35 percent manganese on a dry basis. However, they cannot displace current resources of these metals until economically competitive methods for mining the nodules are developed. The technology required for mining nodules on the ocean bottom at great depths, and transporting them to dry land, is complex and expensive. Insofar as processing is concerned, the nodule matrix is a mixture of iron and manganese oxyhydroxides, which cannot be easily physically beneficiated, in contrast to sulfide minerals. The nickel, cobalt, and copper are not present as separate minerals but are distributed throughout the porous matrix. A number of processes have been investigated for nodule treatment, and extractive processes based on hydro-metallurgy are considered technically feasible. The nodules are a large and rich resource, containing metals of great importance to the Unitd States and the world at large. However, prevailing unfavorable market conditions and uncertainty of ownership rights present major deterrents to the current feasibility of deep-sea mining.

Recent discoveries of sizable marine manganese crusts containing perhaps 1 percent cobalt at relatively shallow depths (less than 2,500 meters) provide an additional important future source of cobalt. Deposits of this type have been located in the Pacific Ocean south of Hawaii and in the Atlantic Ocean off the southeastern shoreline of the United States. Data on the potential for industrial exploration of these new deposits has not been developed, but some assessments are in progress.

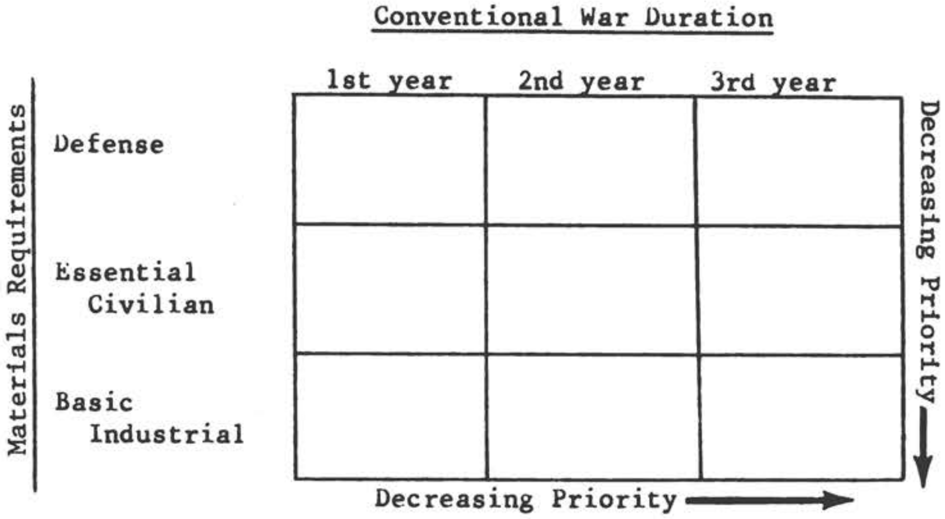
STOCKPILING

The National Defense Stockpile

One way of increasing the availability of cobalt in times of supply disruption is to accumulate stockpiles and hold them for release in times of short supply. In fact, about 46 million pounds of cobalt are held in the National Defense Stockpile; this includes the 1981-1982 acquisitions. The purpose of this stockpile is to serve the national interest only during a defense emergency, and it is not to be used for economic or budgetary purposes. However, there are serious questions as to the actual availability of materials such as cobalt from the stockpile even in times when they may be badly needed exclusive of a military situation. The Strategic and Critical Materials Stockpiling Act (P.L. 96-41) of 1979 authorizes the President to release materials from the stockpile at any time he "determines the release of such materials is required for purposes of national defense." While the act does not limit the President's disposal authority simply to military requirements, it does not permit release of strategic stockpiles for economic reasons.

Current policy makes release of materials from the stockpile difficult, if not impossible, even in very tight market conditions. Industry is reluctant to request release(s) of materials from the stockpile, or even to activate the system of priority preferences for purchases of free-market material, as either of these actions could result in forced curtailment of use in civilian markets. Since 1939, there have been 28 releases from the stockpile - six during World War II, twelve during the Korean conflict, six during the Vietnam conflict, and only four peacetime releases, one each in 1956, 1959, 1973, and 1979. The committee did not ascertain the basis for these releases; issues such as by whose authority, which industrial sector made the request, and the types and amounts of materials involved.

In order to determine whether or not there is sufficient directly usable cobalt in the stockpile to meet immediate U.S. defense needs, data on quantities, lot analyses, and storage locations of the cobalt in the stockpile must be available. While the quantities and storage locations are published, the chemical analyses of each lot are not always available or are incomplete in terms of today's needs in strategic applications such as superalloys. The committee is aware that the FEMA stockpile goals encompass a 3-tier, 3-year conventional war matrix (shown below) and that the material in the stockpile has application in a wide variety of important applications within this matrix. The recent GSA acquisitions in 1980-1981 of 5.2 million pounds of cobalt are reported to be consistent with current superalloys specifications which require an analysis for 21 trace elements.



Questions by the industrial sector on the immediate usefulness of the stockpile materials for various industrial needs have prompted government actions in this area. Studies to examine the quality of all stockpiled materials, including cobalt are in progress; ASM is assessing the cobalt inventory and NMAB is compiling a priority list of other stockpile materials needing examination. At present, the quality of the existing cobalt stockpile (excluding the 1981-1982 acquisitions) apparently is not known adequately enough to determine whether it can meet the requirements of a 3-year supply for all essential uses. This committee feels that the studies now under way are necessary to ascertain the quality (and quantity) of the cobalt in the stockpile and to make recommendations as to the proper remedial actions that should be taken if this is judged necessary. The ASM panel study now examining the cobalt inventory at the request of FEMA, will help clarify the cobalt situation.

It is known that some-but not how much-of the material in the stockpile cannot be used directly for certain end use applications, particularly superalloys, which accounted for 45 percent of 1980 U.S. demand. Present U.S. capacity to reprocess cobalt is very limited. If large quantities needed reprocessing to meet high-performance specifications, this could not be done rapidly in existing U.S. facilities without affecting normal industrial output. Delays also would occur if the upgrading requires changes in existing processing technology and equipment. In Canada, INCO and Sherritt-Gordon have excess capacity that could be used to upgrade lower-quality cobalt.

Barter, trading, and tolling are cost-effective ways that should be considered for upgrading stockpiled materials. Of these, trading electrolytic cobalt that belongs to industrial companies for lesser-quality cobalt in the stockpile is perhaps the least expensive way to upgrade enough stockpiled material to meet FEMA goals for 3 years' essential needs. GSA has examined available alternatives but in most cases has been unable to act, primarily because of stockpile transaction policy, authorization bottlenecks (from Congress), political pressures, and prevailing market conditions.

Industrial Stockpiles

There is a need to make the stockpile dynamic and ongoing so that the quality, quantity, and form of materials in the stockpile meet current industrial specifications that enable them to be utilized directly, on a timely basis, when and as needed. Industrial stockpiling as a means for doing this is worthy of consideration (Manly 1981). At a time of federal budget cutbacks, private industrial stockpiling could provide a low-cost, reliable supplement to the National Defense Stockpile. A typical issue raised is what happens when a company having such a stockpile must liquidate to go out of business. This and similar business decisions, not national defense decisions, must be considered before justifying industrial stockpiling. Nevertheless private industrial stockpiles are used by a number of countries, although the amounts of material in these private stockpiles are relatively small (GAO 1982).

Through the use of limited government support, possibly requiring only tax subsidies, industry could be encouraged to hold minimum stocks of critical materials dedicated to government use during an emergency. Complications have been cited in the ultimate use of this "dedicated" material because the government does not have title to it. The government may have to sieze or expropriate it in an emergency and equitable payment in a shortage market could lead to bad industrial relations. Private industrial stockpiling has 3 advantages: (1) it can be less expensive than government stockpiles because of reduced acquisition and carrying costs; (2) consuming companies are intimately acquainted with the materials used in their own manufacturing processes and so will keep only the proper materials on hand (for its own specific use but not necessarily usable by others); and (3) materials and forms can be kept current by using a FIFO rotation system. Thus, there is a high probability that the quantity, quality, and forms of privately stockpiled materials will be optimum for their use at any given time because inventories will be rotated and accurate records of stockpiled materials will be effectively maintained.

CONCLUSIONS

1. Zaire and Zambia will continue to be the two most important suppliers of cobalt to the market economy countries, at least through this decade, barring political upheavals.

2. According to the best committee estimates based on committee discussions with the major U.S. and Canadian producers and processors, assuming existing political conditions, the price of

cobalt over the next decade will average within the range from $7 to $12 per pound of cathode metal (1982 dollars). However, since Zaire and Zambia have a completely dominating position in cobalt supply, significant price volatility could continue in the future as it has in the recent past. This type of instability could threaten the survival of North American and European cobalt refineries.

3. Increased supplies of cobalt are now coming on stream as a by-product from nickel operations in Canada. Future nickel capacity expansions are likely to be accompanied by increased cobalt output, but little new nickel capacity is likely in the next decade.

4. There are presently three cobalt refineries on the North American continent: AMAX at Port Nickel, Louisiana; INCO at Port Colborne, Ontario; and Sherritt-Gordon at Fort Saskatchewan, Alberta (American Metal Market 1982). Based on a nickel output of 400,000,000 pounds yearly from Canadian ores, accompanying by-product cobalt output can amount to at least 7,500,000 pounds yearly. To secure this on-shore source, the U.S. government might give consideration to contracting with Canadian refineries for a portion of the output.

5. Assurance of the supply of cobalt from the stockpile is questionable for some highly critical applications until proper identification and complete analysis of present stocks is known. The purchase requirements for the older lots were considerably looser than todays, so to designate a portion of this stock for critical applications requires that the new specification be met.

6. Three North American refiners have some limited excess capacity to upgrade the cobalt stockpile to a grade needed for superalloy use.

7. Mining of deep-sea ocean nodules and sea-bed crusts for cobalt and other metals is still in the economic-evaluation and process-assessment stage. Prevailing market conditions appear at present to be a major deterrent to obtaining the necessary industrial funding commitment to move ahead. The costs and risks are so large that only the U.S. government as a participant is capable of helping develop the necessary capability of exploiting this potentially major source of cobalt and other strategic metals.

8. Increasing the sources of cobalt supply requires both cobalt refineries and refinery feed. Existing refineries in North America can be expanded within 1 or 2 years, but sources of refinery feed material may be more difficult to develop within the same time frame.

9. To establish a versatile domestic cobalt custom refining capability, the U.S. government has an option of contracting with the Louisiana refinery for cobalt production from an input of diverse cobaltiferous raw materials. It is expected that the cost of such contracting would be within the range of predicted free-market cobalt prices.

10. Technology exists to produce cobalt metal from domestic resources but the economics to do so are unattractive at present. Total production costs would be at least $20 (1982 dollars) per pound. The time required to bring domestic sources into production would be at least 5 years.

11. Nickel sulfide ores represent a major source of cobalt from which production can be increased in the near future. Further in the future, the large cobalt resources in nickel laterites could become the most important land-based source of cobalt.

12. Of all the potential North American cobalt resources, Canadian nickel deposits have the greatest potential of being competitive alternatives to existing cobalt supply sources.

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Chapter 4

TECHNOLOGICAL ALTERNATIVES: PROCESSING

This chapter addresses the opportunities for reducing requirements for cobalt through improved processing methods. These opportunities include refinements for conventional processing techniques, development of new technologies, and increased efficiency of recycling. Superalloys and tool steels, where the greatest potential for improved processing efficiencies lie, are covered in detail. Processing and recycling of hardfacing and coating alloys, magnets, and cemented carbides as well as the potential of rapid solidification technology are treated in less detail. Recycling of cobalt from catalyst uses, currently an active subject of development, is discussed in Chapter 5.

SUPERALLOYS

Superalloys as a class are one of the most highly engineered alloy families in the field of metallurgy. Their raw materials, composition, primary production, and fabrication processes are dictated more by the need to meet stringent property and reliability specifications than by economic considerations such as cost or efficiency of production. While the latter are certainly important, their secondary role is evident in many ways: superalloys are the subject of intense research and development activities; they have spawned many special-purpose alloys and processing techniques, with technology being led by the aircraft gas turbine industry; the production heat sizes are small compared to those in the steel, copper, or aluminum industries; the emphasis is on high purity and strict control of certain impurities (sometimes at levels of less than 1 part per million); and the production yields may be extremely low and consequently large quantities of scrap are generated. Although costly raw materials, including a number of strategic elements, are consumed by the industry, the raw materials costs are not high in relationship to the final product cost; this is due to the many difficult and costly processing steps, special care in qualifying parts for service, and the multiplying factor of low product yield and the high cost of qualifying new alloys. Accordingly, despite expressed interest and actions taken by the industry in conservation, what little new alloy development is in progress and the new processing technologies under study for superalloys is in the direction of meeting more severe service conditions involving temperature, strength, and environment.

Melting, Casting, and Primary Processing

The family of superalloys is normally divided into two broad categories, investment cast and wrought. Each in turn is further subdivided into nickel-base, cobalt-base, and iron-base to designate the principal element. Alloys within each group can be further categorized by general production methods, such as into air-melting or vacuum-melting grades. Although there are some exceptions, most of the cobalt-bearing alloys fall into four categories: wrought nickel-base, primarily vacuum melted; wrought cobalt-base, air or vacuum melted; cast nickel-base, always vacuum melted; and cast cobalt-base, air or vacuum melted. The approximate production of alloys in these categories and quantity of cobalt contained are shown in Table 15. The quantities in the table are based on the Bureau of Mines estimates of the consumption of cobalt for superalloys in 1980 (Kummer 1980). The breakdown by category is derived from alloy production data developed by the Bureau of Mines (Curwick et al. 1980a). The table indicates that, despite the high cobalt content of cobalt-base alloys, the actual total cobalt consumption is about equal for nickel-base and cobalt-base alloys.

Since the materials specifications for superalloys are influenced so greatly by rapidly advancing gas turbine engine technology, it is hardly surprising that the field has spawned many innovations in melting, casting, and fabrication. This has proceeded to the point where nearly every producer has unique methods of production; hence, it is difficult to describe production methods in general terms. Following is a brief overview of the principal production techniques used in each of the four superalloy categories that contain cobalt. For further details the reader is referred to some standard references on superalloys (Sims and Hagel 1972, Betteridge and Heslop 1974, Bunshah 1958) or to the proceedings of major conferences dealing with the production of these alloys (e.g., Proceedings of the Annual Vacuum Metallurgy and Electric Furnace Conferences, Biennial International Conference on Electroslag Remelting, Quadrennial International Superalloy Symposium.)

Wrought Nickel-Base Alloys

The cobalt-bearing alloys are almost exclusively produced by "vacuum melting." Most material is currently vacuum cast into ingots for subsequent forging or hot rolling. Powder metallurgy techniques, however, now in widespread commercial use, are increasing in importance for fabricating these alloys. Powder metallurgy is discussed in a subsequent section. Vacuum melting has two principal purposes--to remove certain impurity elements by volatilization and to prevent oxidation of reactive alloying elements. Because of this, vacuum-melted alloys cannot use large quantities of light or highly contaminated scrap or other inexpensive primary raw materials often used for alloys that are processed in air by the electric furnace argon-oxygen decarburization (EF-AOD) process.

TABLE 15 Use of Cobalt in Superalloys and Tool Steels (short tons)

Category	Superalloys				Tool Steels
	Nickel-Base		Cobalt-Base		
	Wrought	Cast	Wrought	Cast	
Apparent primary cobalt consumption in 1980[a]		(total)	3,142.5		160.5
Estimated cobalt consumption by subclass[b]	1,450	200	650	850	160.5
Average cobalt content (percent) in Alloy subclass[c]	10	10	45	60	7.5
Primary production of alloys containing cobalt[d]	18,000	3,625	1,800	2,500	2,650
Cobalt contained in raw materials (scrap + primary)[e]	3,625	450	1,650	1,900	401
Cobalt contained in primary product[e]	1,800	350	800	1,500	200.5

[a] U.S. Bureau of Mines Mineral Statistics (1980).
[b] Estimated from alloy production figures (Curwick et al. 1980a).
[c] Of those alloys containing cobalt.
[d] Estimated from entries above.
[e] Estimates based on figures for charge make-up and melting yields reported (Curwick et al. 1980a).

Although originally melted in a single step in one furnace, vacuum melting is now frequently performed in a succession of furnaces to develop the desired purity and ingot structure. Frequently the charge is first melted and the composition adjusted in the vacuum induction melting (VIM) furnace and an ingot in the shape of a remelt electrode is cast in vacuum. These ingots are then remelted one or more times in a consumable electrode process such as electroslag remelting (ESR) or vacuum arc remelting (VAR).

After the final melting step, ingots are hot rolled or press forged into billets for final processing. Continuous casting is not used in the production of superalloys because of the relatively small heat sizes, the number of different alloys cast, and some technical difficulties in the casting process itself. Generally, primary hot-working and forging practices employed in the steel industry are used for superalloys.

Wrought Cobalt-Base Alloys

Cobalt-base alloys are produced generally in the same facilities as those used for nickel-base alloys. Cobalt alloys do not contain large quantities of reactive elements and, hence, in the past, were often produced by the air-melting procedures used for cobalt-free, nickel-base alloys. These include electric arc furnace melting, followed by refining in the argon-oxygen decarburization (AOD) vessel. In current practice these alloys are usually further refined by VAR or ESR processes; some of these alloys also are produced by VIM. Subsequent casting and working operations are similar to those of nickel-base alloys.

Cast Nickel-Base Alloys

Conventional wrought alloys do not have adequate strength to be used in very hot components of advanced gas turbine engines. A specialized industry has developed to produce components such as blades and vanes using investment casting processes. Many of the casting alloys cannot be hot-worked because of their high hardener content and, as the industry matured, highly sophisticated procedures for producing unique directional grain structure were developed.

Processes in commercial use produce directionally aligned grains or oriented single crystal parts, and extensive work has been done on directionally aligned eutectic alloys. Generally, these expensive processes are justified by the demanding and critical nature of the application. Because they are cast a few at a time, the final melting step involves the use of comparatively small vacuum induction furnaces that are essentially just remelting operations. All of the alloying and compositional control is done in a preceding process that may itself involve more than one refining operation. The material used for melt stock by the investment casting foundry is called the master alloy and the producers have come to be known as "master melt producers." Production of master melt is in many respects similar to that of wrought nickel alloy production with the difference being in the end product--remelt ingot versus rolling or forging ingot.

Cast Cobalt-Base Alloys

The cast cobalt-base alloys, although somewhat more tolerant of certain impurities than are the nickel-base alloys, today generally are produced with the same methods by the same companies that produce cast nickel-base alloys.

Hot Working and Fabrication

Wrought Nickel- and Cobalt-Base Alloys

Conventional processing of wrought alloys involves steps common to many metal-producing operations. These include initial breakdown of ingots in a blooming mill or press forge followed by secondary hot working to intermediate product size. This may involve hot rolling, extrusion, or forging. The products also may be forging billet, bar, plate, or tube.

Superalloys are extremely hard at hot working temperatures and are sensitive to cracking because of trace impurities and complex solidification structures. Consequently, greater care, smaller reductions, and more frequent reheats are usually required. Scaling is minimal, but product losses from crops and grinding significantly reduce the product yield.

Fabrication of finished products involves virtually all of the operations used in metal fabrication (such as precision forging, tube drawing, wire drawing, sheet rolling, stamping, bending, spinning, machining, and grinding). Intermediate steps may include operations such as shot blasting, pickling, stress relieving, and annealing. Each of these operations results in a loss of material in the form of scrap and waste. The magnitude and character of these losses are discussed in a following section.

Cast Nickel- and Cobalt-Base Alloys

As described earlier, most cast alloys are produced by the precision molding or investment casting process. After casting, the gates and risers are cut from the castings; subsequent operations may include grinding or machining of bearing surfaces, drilling of holes and cooling channels, preparation of surfaces for coating or joining, and usually multistep heat treatment.

Scrap Generated During Conventional Production of Superalloys

Many different types of scrap are generated in the course of the primary production of superalloys and in the fabrication of finished parts. The amount of scrap, and its composition and character, varies from process to process. In general, however, the production of wrought superalloys involves lower product yields and larger amounts of scrap than is typical of most alloys. Production of cast alloys is more efficient, but the quantity of scrap generated is still significant. In recent years, most companies have placed a great deal of emphasis on reducing the quantity of scrap generated, since this represents a major operating inefficiency as well as a potential loss of costly and strategic materials and sometimes is a source of hazardous waste. The actual quantity of scrap in inventory within a metal-producing facility varies with time and from shop to shop but may range up to 50 percent or more of annual alloy production. At current interest rates, the hidden financial penalty for carrying such large metal inventories can be enormous. This provides additional incentive for recycling.

A wide spectrum of scrap and waste materials is generated in the production of superalloys. Recently the U.S. Bureau of Mines published a comprehensive report that discusses both the character and quantity of scrap and waste generated by this industry (Curwick et al. 1980a). Information derived from this report is adapted for the narrower class of cobalt-containing superalloys. Table 16 characterizes the major types of scrap and waste generated by the industry. The quantities differ widely from process to process; however, for present purposes, an industry-wide average figure for the principal forms of scrap and waste is given. Figures derived from the Bureau of Mines data in Table 15 were used to estimate the quantities of scrap for the four classes of cobalt-bearing superalloys (Table 17).

The principal characteristics that describe scrap materials and ultimately influence their suitability and method of recycling are the following:

1. Physical size and weight of pieces; this may range from a several-ton ingot down to 1 micron-diameter powders.

2. State of oxidation; this may range from fully metallic to fully oxidized.

3. Dilution, i.e., content of other materials such as slags, water, and oil.

4. Contamination with elements that significantly degrade the properties of nickel- or cobalt-base alloys, such as lead, silver, bismuth, and sulfur.

5. Alloy grade; this may range from pedigree (single alloy) to fully mixed alloy.

6. Collection and handling factors such as quantity available, ease of collection, prevention from further dilution, degree of hazard in handling and storage, transportation costs, and grade and quality verification costs.

Listed in Table 16 is an additional form of scrap known variously as obsolete, old, or post-consumer scrap. This type of scrap, which results from the removal of parts from service, is usually in the form of solid metallic pieces; it may, however, be oxidized or otherwise contaminated by undesirable elements from the service environment. Its quantity is extremely difficult to assess, since no mechanism exists for monitoring the trade of superalloy scrap. An estimate, based on Bureau of Mines data, is included in Table 17.

TABLE 16 Types of Superalloy Scrap

Origin	Type of Scrap	Classification[a]	Character	Typical Contaminants (Percent)	Disposition[b]
Home	Solids	P, MA	Solid, many shapes	1 oxide	Recycled (SA)
	Turnings	P, MA	Chips	5 oil	Recycled (SA)
	Grindings	P, MA	Dust	20 grinding wheel debris	Recycled (SA or S)
			Swarf	30 oil, 10 grinding wheel debris, may contain P,S	
	Slag cleanings	MA	Grit	20 slag	Recycled (SA or S) or discarded
	Furnace dust	MA	Dry dust	Fully oxidized; 40 recoverable metal, may contain Pb, Zn, Na, Cl, S, etc.	Recycled (S) or discarded
	Mill scale	MA	Flaky grit	Fully oxidized, 5 oil or water	Recycled (S) or discarded
Prompt Industrial	Solids	P	Punchings, parts	1 oxide	Recycled (SA, S)
	Turnings	P, MA	Chips	5 oil	Recycled (SA, S)
	Grindings	P, MA	Sludge	Wet or oily, grinding wheel debris	Recycled (SA, S)
	ECM and pickle sludge	MA	Wet sludges	80 water, sodium salts, or lime	Recycled (SA, S) or discarded
	EDM sludge	MA	Oily sludges	50 oil	Discarded
Obsolete	Solids	P, MA	Many shapes	Maybe oxidized, coated or contaminated with Pb, Bi, S, etc.	Recycled (SA, S)

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[a] (Classification) P = pedigree; MA = mixed alloy (does not conform to a standard alloy specification).
[b] (Disposition) SA = remelted for use in superalloys; S = remelted for use in steel.

TABLE 17 Scrap Generated in the Production of Superalloys and Tool Steels (short tons)[a]

Type	Superalloys				Tool Steels
	Nickel-Base		Cobalt-Base		
	Wrought	Cast	Wrought	Cast	
Finished Product	9,700	1,450	950	1,000	1,325
In-House Scrap					
Solids	15,800	400	1,500	300	1,800
Turnings	1,100	-	100	-	150
Grindings	500	100	50	50	100
Mixed[b]	200	150	50	100	300
Wastes[c]	800	250	50	150	300
Total	18,400	900	1,800	600	2,650
Prompt Industrial Scrap					
Solids	2,500	1,750	250	1,150	400
Turnings	3,800	100	400	100	300
Grindings	1,450	250	150	200	550
Wastes	550	50	50	50	50
Total	8,300	2,150	850	1,500	1,300
Current Obsolete Scrap					
Solids recycled	4,400	650	425	450	250
Solids downgraded	3,050	450	250	300	600
All lost scrap	1,300	200	175	150	350
Total	8,750	1,300	850	900	1,200

[a] Cobalt-containing alloys only.
[b] Oxidized materials primarily recovered by downgrading.
[c] Including lost materials of recyclable quality.

Opportunities for Reduction in the Quantity of Scrap Generated in Conventional Processing

As noted previously, the superalloy industry generates a higher proportion of scrap and waste than do other related metal-producing industries such as alloy and stainless steel production. Some of this is probably inherent to superalloys because of the large number of different and complex alloys produced by most companies. However, considerable effort in research and manufacturing has been directed over the past 10 years to reducing the amount of scrap. This has taken the form of a continuing trend to production of "near-net-shape" components--i.e., substitution of investment castings for forgings and recent development of powder processing. While these processes do not eliminate scrap, they do significantly reduce the quantity.

Several other trends have worked to reduce the amount of scrap. Modern melting and analytical methods have significantly reduced if not eliminated the generation of "off-spec" heats. Vacuum or controlled atmosphere teeming greatly reduces ingot defects that require major surface conditioning or produce cracking during hot-working. Care is now taken to minimize the quantity of material removed with end crops, edge trimming, and finish conditioning. For the most part these are evolutionary changes already well under way that may reduce the actual quantity of in-house scrap produced by perhaps 25 percent. These actions have the additional important benefit of making the individual producers more conscious of the need to control the generation of scrap so that it is more suitable for recycling.

The best opportunity for significant further reduction in scrap is the adoption of near-net-shape processing for a wider variety of shapes and components. Many superalloy producers have considered continuous or semicontinuous casting, which has provided significant yield improvements for the production of steels. Horizontal casting machines are already being used to a limited extent for the production of master melt ingot for the investment casting industry. Such methods might also be used by wrought alloy producers to cast billet directly for extrusion or forging or slab for rolling. Many wrought alloy producers have considered or actually tried the conventional continuous casting processes but have not implemented the technology because the equipment size was not compatible with their scale of operation or because of operational difficulties associated with production of superalloys. However, a new generation of horizontal continuous casting systems is appearing. While not applicable to all alloys or product forms, this process will see limited application for wrought alloy production within the next five years, even possibly for some superalloy forms.

As noted previously, powder metallurgy processes have significant potential for the reduction of the amount of cobalt used in superalloys because of an overall improvement in product yield that results from a reduction of in-process raw material. The powders for superalloys are typically formed by melting under vacuum or inert atmosphere followed by argon gas atomization. The powder yield is a relatively large fraction of the melt weight. The powders are separated into various particle size ranges by screening or by gas classification, and the oversized or undersized powders are recycled through remelting in subsequent heats. The desired particle sizes are then consolidated either into a billet or into a near-net-shape. Consolidation can be by hot isostatic pressing, by extrusion, or by sintering. In some cases, parts have been used directly as consolidated, i.e., hot isostatic pressed (HIPed) near-net-shape components. Other product forms, such as extruded, HIPed, or sintered billet, must be further thermomechanically processed. Thermomechanical processing is performed by techniques similar to those used for the static cast and wrought versions of the alloys. However, the yields of the HIPed near-net-shaped products tend to be higher, since the powder metallurgy product is finer in structure and does not have as large a material loss as in the thermomechanical processing steps.

Although the volume of superalloys produced by powder processes is still small relative to total superalloy production, virtually all wrought alloy producers are actively implementing this technology, and its share of production is certain to grow significantly over the next 10 years. In recent years, additional technological developments in the powder metallurgical field have produced new families of alloys that are just entering the marketplace. These new alloys may have a major impact on future requirements for cobalt in superalloys. Mechanical alloying is a method of producing oxide dispersion-strengthened alloys by high-energy milling of prealloyed or elemental powders. Unique alloy compositions with outstanding elevated-temperature properties can be produced by this process (Benjamin 1970).

A second process that has received considerable attention is rapid solidification technology (RST). This technology involves the production of powders by extremely rapid solidification from the molten state (Cox et al. 1976). Unique structures and properties are produced that are unattainable in conventional cast and wrought alloys (NMAB 1980). Although the cost of these powder alloys is currently very high, it is justified for use in many critical aerospace applications. Further development of the technologies will certainly produce significant cost reductions. It is not possible at this time to predict the ultimate effect of these technologies on cobalt requirements, although the initial trend of development suggests that cobalt consumption could ultimately be lower. Additional general information on RST processing is contained in a separate section of this chapter.

Another process receiving consideration is the oxide dispersed system (ODS) alloys. These have not as yet resulted in significant commercial use but their potential is being examined carefully. The three current ODS superalloys (Inconel MA956, MA754, and MA6000) are slated for use in burner cans and MA6000 for vanes or blades. Massive items are not expected to be replaced by this technology.

Current Scrap Recycling Practice

Scrap recycling has become a popular topic in recent years as the ecology movement brought the practice into the home in the form of recycling of consumer products. However, scrap recycling was already an established practice in the superalloy industry. Figure 4 is a generalized materials flow circuit showing the generation and recycling of

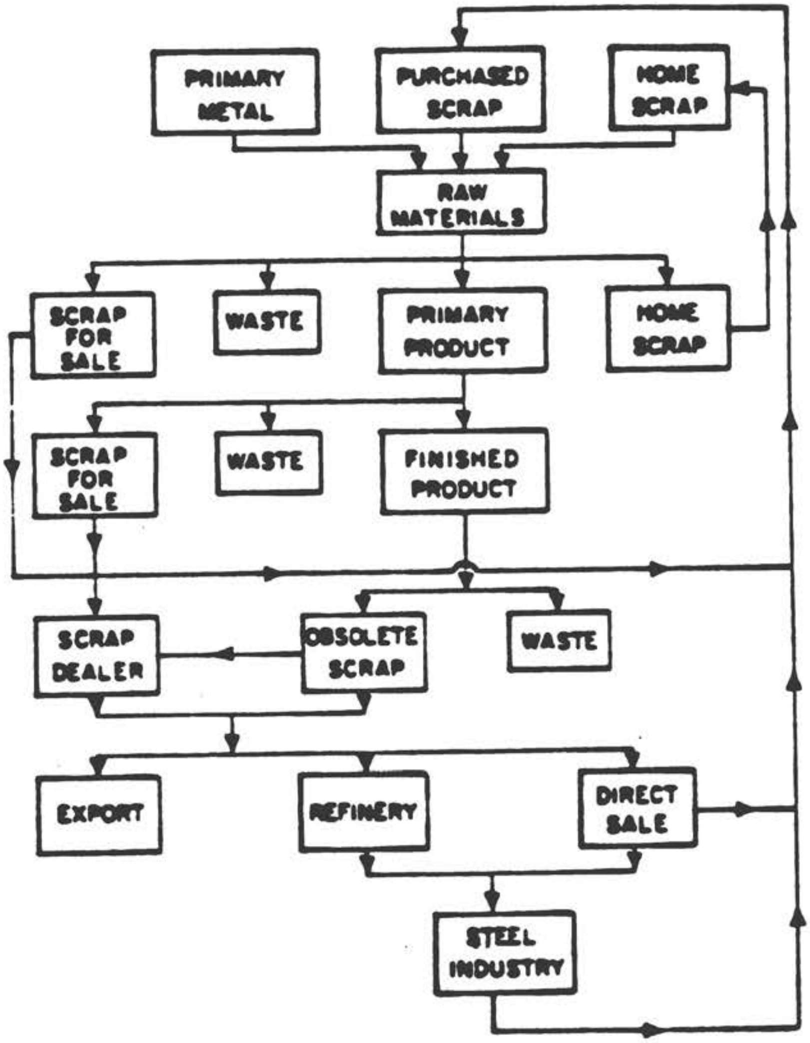

Figure 4 Materials flow circuit used for production model.
Source: Curwick et al. 1980b.

scrap in the superalloy industry. Most alloy producers use a substantial quantity of scrap in their melting charge. The amount used in any given heat or alloy may range from zero to 100 percent, but industry-wide averages of 55 percent for cast alloys and 60 percent for wrought alloys are reported (Curwick et al. 1980a). Most of this material is solid metallic scrap from primary production sources. Obsolete scrap and the poorer grades of producer scrap are not as efficiently recycled. Much of this material is currently reprocessed by secondary alloy producers, with the product ultimately downgraded for use in the steel industry. Valuable elements, including cobalt, are usually lost during the process, since nickel is often the only element effectively recovered. Extensive discussions of scrap recycling in the superalloy industry have appeared recently (Curwick et al. 1980b, deBarbadillo 1981, deBarbadillo 1982, Cremisio and Wasserman 1977). Consequently, only those aspects relating to improved recovery of cobalt are discussed here.

The approximate disposition of the various types of scrap derived from the Curwick report (1980a) is shown in Table 16. In general, cobalt is fully recovered from scrap that is directly remelted by the alloy producer, although recoveries of some other valuable elements, such as columbium and tantalum, are much lower. An unknown but significant amount of cobalt is lost whenever cobalt-bearing alloy scrap is deliberately or inadvertently used in the melting of cobalt-free alloy. Alloy producers carefully segregate melting scrap according to cobalt content, but for a variety of reasons this segregation is never perfect. The ability to reuse scrap actually places a limit on the degree to which alloy substitution strategies for cobalt conservation can be effective, since producers may find that availability of low-cost cobalt from scrap justifies continued production of cobalt-bearing alloys.

Opportunities for Increased Cobalt Recovery Through Improved Efficiency of Recycling

Approximately 40 percent of the wrought superalloy scrap and 50 percent of the cast superalloy scrap is not directly recycled domestically for production of these alloys. The remainder of this material is either downgraded, lost, or exported (Curwick et al. 1980a). The materials now recycled are the predominantly clean, well-identified solids and processed turnings. These have the advantage of being relatively easy to collect, handle, and melt and their composition can be readily verified. Recovery of the principal elements is very high, and thus a minimum of uncertainty is placed on the alloy melting operation.

Obsolete scrap solids are not efficiently recycled for several reasons. Gas turbine engine components may become contaminated in service with elements such as lead and sulfur. These are highly detrimental to superalloy properties if they are picked up during melting. Frequently, superalloy products are fabricated into more complex assemblies by welding, brazing, or coating. Separation of these components during equipment salvage is sometimes very difficult and costly. Finally, the collection of obsolete scrap is necessarily on a small scale, which presents a number of difficult logistical problems. Consequently, producers of some superalloys used for the gas turbine industry have used little or none of this material.

At one time most obsolete scrap solids were downgraded. In recent years important advances have been made in the processing of this type of scrap (Cremisio and Wasserman 1977). Small portable instruments that provide instantaneous identification of alloys have become available, and techniques for cutting, cleaning, and packaging scrap for remelting have been devised.

Probably the most important factor is the growing awareness of superalloy users who ultimately initiate the scrap recycling process, of the potential value of their materials. This is countered, however, by the continuing trend to greater complexity of alloys and the use of composite structures, both of which make recycling more difficult. Consequently, although it is likely that a greater proportion of obsolete scrap solids will be directly recycled in the future, a significant amount will continue to be downgraded unless a process is developed that can separate scrap into its elemental components. This possibility is discussed later in this section.

Recycling of the forms of scrap other than solids and coarse turnings presents a variety of problems that limit the degree to which they can be directly recycled or, in the case of sludges, recycled at all. Dusts, grindings, furnace scale, and pickle sludges are often mixtures of every alloy produced in the plant and hence have inherently limited use in recycling. These materials are of low grade and are finely divided and thus present major difficulties in handling and melting. The cost of drying sludges may exceed the value of the contained elements. On the other hand, treatment for metal recovery has become more attractive in recent years as the cost of disposing of hazardous waste sludges has escalated (Rosof 1981).

Superalloy turnings and grindings are generally recycled directly by the alloy producers if they possess argon-oxygen decarburization (AOD) refining capabilities, by master melt producers, or by secondary alloy producers (Cremisio and Wasserman 1977, Woulds 1980). The master melt producer may blend a number of types of scrap to produce a certified remelt ingot that may or may not correspond to a specific alloy grade. Usually an effort is made to maximize recovery of valuable elements, and this material is usually recycled to the superalloy industry. On the other hand, secondary alloy producers aim to recover only nickel, cobalt, and sometimes molybdenum; the product of this industry is nearly always downgraded.

In the past, very low-grade materials such as dusts, furnace scale, and pickle sludges were generally dumped. One large producer with AOD refining capabilities has implemented a program to recycle some of these materials (Mankins and Shields 1980). Producers of vacuum-melted alloys cannot use these low-grade materials. Some stainless steel producers also produce superalloys, and the two types of wastes are collected together. Flue dusts, mill scale, and grinding wastes from the specialty steel mills are currently recycled by a pyrometallurgical process to produce an ingot for remelting by the stainless steel industry (Pargeter and Weil 1980).

Nickel, chromium, cobalt, iron, and molybdenum are recovered in this process, but the cobalt essentially has no value for stainless steel. Technologies for recovering cobalt from such dual source wastes can be developed rapidly, but this effort requires an economic motivation which is not present at this time. Additional quantities of low-grade materials are recycled by primary nickel producers and specialty secondary alloy producers. In some cases the cobalt is recovered. A significant increase in the amount of recycling of low-grade materials has taken place over the past 5 years, and it is reasonable to project that nearly all this material will eventually be treated in some way for recycling. However, the prospects for a significant increase in the amount of cobalt obtained from this source for use in superalloys are remote.

The possibility of treating complex superalloy scrap by separating it into its individual elemental constituents has stimulated research interest for many years. A number of processes have been proposed and studied on a laboratory scale. Most of them are hydrometallurgical, but some have preliminary pyrometallurgical steps. The U.S. Bureau of Mines has been especially active in development of this technology. Publications based on two studies recently sponsored by the Bureau contain reviews of the literature of recycling by element separation (deBarbadillo et al. 1981, Kusik et al. 1981). Although many of these processes demonstrate the ability to recover some or all of the valuable elements in the scrap in a form and purity suitable for use in superalloys, all of them are by nature very complex. Economic studies have repeatedly shown that commercial-scale recycling plants would be costly and marginally profitable, although a disruption in the supply of cobalt could provide the incentive to develop separation technology. From 2 to 5 years of research and development would be needed before a commercial-scale process could be placed in operation.

It should be emphasized that the foregoing comments do not generally apply to chemical treatment of wastes to selectively recover nickel and cobalt (Pearson 1981). Indeed, chemical processing of some wastes has been done successfully on a commercial scale in the United States and may be the best technique for treating sludges.

Summary of Prospects for Superalloys

It appears that the best prospect for improving cobalt recovery for use in superalloys is in improving the efficiency of recovering obsolete solid scrap. Ongoing trends in the recycling of low-grade materials will ultimately result in metallurgical or chemical treatment of nearly all of this material. However, most of the product will be downgraded for use in steel, and only a small fraction of the cobalt will be effectively used.

Powder metallurgy (P/M) processing, especially the near-net-shape consolidation processes, has shown promise of resulting in the more efficient processing of superalloys. Near-net-shape P/M processing can certainly reduce scrap by factors of as much as five to nine, thereby requiring initially less cobalt to produce hardware (Tien et al. 1980). P/M superalloys are currently being used commercially for hot isostatic pressed (HIP) parts and also in some instances, for less materials-efficient consolidated P/M billets which are further isothermally forged to net shapes.

Scrap recovery and near-net-shape processing programs are still in progress at various government and industrial laboratories. In the next 5 years these efforts can be expected to further reduce superalloy cobalt requirements by as much as 0.5 million pounds per year.

TOOL STEELS

Although tool steels constitute a distinctly different metallurgical group of alloys, tool steel production methods and equipment resemble in many ways those used for superalloys (Roberts and Cary 1980). Use of cobalt is restricted almost exclusively to high-speed tool steels. These steels are metallurgically complex, with six or more major alloying elements and a large number of commercially recognized compositions. A careful balance of alloying elements is necessary to produce the desired cutting properties, and the level of residual elements can seriously affect this balance. Accordingly, careful control of the raw material charge composition is essential. Furthermore, because these alloys require special control in processing, raw material costs are only a fraction of the overall product cost. In addition, since tool bits are used in critical applications, improved performance often justifies the continued use of critical materials despite their cost and scarcity.

Melting, Casting, and Primary Processing

At one time, tool steels were produced exclusively by electric arc furnace melting. However, over the past 15 years many of the processes developed for superalloy production have been adapted for high-speed tool steels as well. These materials may now be melted in electric arc or high-frequency induction furnaces and refined by the argon-oxygen decarburization, electroslag remelting, or vacuum arc remelting process.

The raw materials normally used for high-speed tool steels include in-house scrap, primary metals, and small quantities of purchased scrap. The primary metals are generally of steelmaking grade and include ferroalloys, refractory metal oxides, and, in the case of cobalt, pure metal cathode, briquette, or shot. The electric furnace or induction furnace melting steps are mainly designed to quickly melt and homogenize the charge. Limited refining can be achieved through slag control; however, removal or control of impurities is primarily done in the AOD or ESR operations. Impurities of significance include phosphorus, sulfur, nitrogen, hydrogen, and aluminum. Nickel and copper residuals make it difficult to achieve maximum hardness in tool steels, and because they are not removed in refining their presence must be limited in the charge materials. This is a significant point that limits the recycling of scrap, because many companies produce both superalloys and tool steels. Tool steels are normally static cast into 5- to 10-ton ingots.

Hot-Working and Fabrication

Tool steel ingots are normally broken down by rolling or press forging and subsequently rolled to a bar. Hot-working of high-speed tool steels is especially difficult because they have relatively low melting points and hence are subject to liquation and hot-tearing. At the same time, they may form primary alloy carbides during solidification, which can initiate cracking during hot-working. Consequently, their hot-working range is narrow and the maximum reduction per pass is small. In addition, these alloys have a low chromium content and scale significantly when hot. As a general rule, processing difficulty increases as the ingot size increases, which ultimately limits the size of a part that can be produced by conventional ingot metallurgy. Some consideration has been given to the use of continuous casting for production of these alloys; however, many of the problems associated with use of this technology for superalloys also apply for tool steels.

Powder Metallurgy

In recent years, the use of powder metallurgy for the production of tool steels has increased substantially because it provides three significant processing advantages: refinement of the as-cast microstructures, reduced scrap losses, and opportunity to produce alloys with improved properties not possible by conventional ingot metallurgy. Powder metallurgy has been commercially implemented more quickly for tool steels than it has for superalloys because performance specifications, while critical, are not as severe as those for rotating parts in gas turbine engines. Also, high-speed tool steels have a two-phase alloy carbide-matrix structure that is readily refined through powder metallurgy techniques. Accordingly, it is quite likely that the powder metallurgy approach will continue to increase its share of the tool steel market.

Powder metallurgy, as it is applied to tool steels, may utilize any or all of the preliminary melting and refining processes, followed by atomization, usually by an inert gas such as argon or nitrogen. The powder is collected, screened, and compacted to a billet, which is subsequently consolidated to bar stock by conventional methods.

Scrap Generated During Tool Steel Production and Opportunities for Conservation

Tool steel scrap is similar in nature to that produced in the manufacture of wrought superalloys. The various types of scrap are described in Table 16. The quantities of various types of scrap are estimated in Table 17. Although tool steel scrap physically resembles superalloy scrap, there are some important differences, and the proportions of the various forms are different. Because they constitute a small fraction of the total quantity of steel produced at a given mill, the particulate forms of scrap tend to be of mixed alloy grade and nearly always are leaner than the high-speed alloy composition. There also is a higher proportion of mill scale because tool steels, with their rather low chromium content, scale readily at hot-working temperatures. One of the major forms of prompt industrial scrap is grindings; these are generally a mixed-alloy material saturated with lubricating oil.

The opportunities for an actual reduction in scrap generated during conventional processing are somewhat limited. As noted earlier, the introduction of new processing methods such as ESR have provided improved microstructure and surface quality. This translates directly to better product yield and hence less scrap. A 10 percent improvement in product yield is a reasonable expectation for broad implementation of this technology. Further improvement in yield can be expected from the adoption either of semicontinuous casting of intermediate-size billets or powder metallurgy. However, neither process comes close to entirely eliminating scrap.

Recycling of Tool Steel Scrap: Current Practice

Although a substantial portion of tool steel scrap is recycled, the efficiency of recovery of the alloying elements is significantly poorer than that achieved in the superalloy industry. This is the result of a number of factors, including the lower intrinsic metal value of tool steels, the difficulty in maintaining grade separation during collection of scrap (especially particulate scrap), and fewer options for metallurgical recycling.

Almost all solid in-house scrap is separated by grade and recycled in the electric furnace melt charge. Cobalt recovery from this material is nearly 100 percent. Prompt industrial scrap solids are similarly identified and remelted. Some obsolete scrap is also recycled; this is primarily large monolithic industrial cutting tools. Small tools, such as drill bits and single-point cutting tools, are sometimes discarded, and those used by small consumers are almost never recycled. Particulate scrap, such as furnace dust and mill scale, is generally collected with other tool steel and alloy steel wastes produced by the mill. Some shops remelt this material, some send it out for reclaiming, and some discard it. The cobalt in this material is essentially lost to the industry, since it is in dilute form.

One major class of tool steel scrap that is currently not recycled is the oily grindings produced by tool fabricators. These grindings have a high metal content but are usually of mixed alloy. Although these materials could be recovered by melting in an arc furnace to produce a mixed grade ingot, the residual phosphorus content is so high that it is generally unacceptable to tool steel manufacturers. Accordingly, much of this material is either lost entirely or used for very low-value purposes.

Opportunities for Increased Cobalt Recovery Through Improved Efficiency of Recycling

Theoretically, all tool steel scrap could be carefully identified during collection and recycled directly or after further processing. However, the fact that it is so often mixed with much lower grade scrap makes more efficient collection of materials such as furnace dust and mill scale impractical. No change in this practice is foreseen for many years.

However, improved sorting and identification techniques have made it possible to recover virtually all solid scrap for recycling directly within the mill. Programs for collection of obsolete scrap solids from the user could significantly increase recovery of this material. Research aimed at devising methods of treating tool steel grindings to make them suitable for recycling are currently under way. It seems only a matter of time until a satisfactory method is developed. Procedures for recovering mixed alloy sludges generated by the electrical discharge machining (EDM) process are also likely to be developed in the next few years. Treatment methods for these materials are likely to involve deoiling, chemical cleaning, and briquetting for direct remelting (Ellis and Vellella 1980, MacLellan 1981). Some work has also been done on chemical separation of elements in tool steel scrap (Menashi 1981). A review of some of these processes was presented in a U.S. Bureau of Mines report (deBarbadillo et al. 1981). Chemical separation, while effective in producing high-quality products with maximum flexibility of use, may be too costly to apply to tool steels, except in times of severe shortage. The lead time for implementation of a process would be at least 3 years.

HARDFACING AND COATING ALLOYS

Hardfacing and coating alloys, which are typically cobalt-base, are utilized in either rod or powder form. They are generally too highly alloyed to be processed conventionally--that is, by thermomechanically processing into final form after being melted and cast. The processing and use of these alloys offer some opportunity for conservation of cobalt. These are to be examined in this section and an assessment is made of where conservation and recycling actions could be taken.

It is known that impurity levels need to be controlled in wear-resistant alloys to ensure trouble-free hardfacing layers. However, in light of current melting technology, the initial cobalt purity need not be very high. Specifically, with respect to the government stockpile, it is believed that a significant portion of the cobalt held there could be melt-refined and used in wear-resistant alloys as well as in other high-performance materials requiring cobalt.

Powder Metallurgy

Hardfacing and coating alloys are often utilized as powder metallurgy products, being typically air-induction melted and atomized with either gas or water. The production yield of powder is rather low, since the allowable range of particle sizes must be narrow in order for the powder to flow into a torch or a plasma gun for deposition. Oversized and undersized powders are recycled into subsequent heats. The materials making up the charge can be either virgin raw materials or various types of scrap, and since the composition of the alloys is not generally critical, the specifications have a fairly wide range of permissible purity. It is important, however, that the gas content (interstitial elements) of the powder be controlled since this affects the deposition characteristics of the powders and the integrity of the coating.

For some applications wear-resistant parts are made directly from powders. In these cases the powders are atomized, pressed, and sintered to shape. This market is somewhat limited and is considerably smaller than the spray-process area. The overall yield of material from the direct processing of powders is rather high, with actual material losses somewhat under 2 to 3 percent.

In the end use of either the plasma- or flame-sprayed powders, the system typically does not recycle the overspray, the scrap, or the recovery of hardfacing or coating material from obsolete parts. Therefore, the material that is shipped to the user of the hardfacing or coating alloy powder is lost permanently from the system. This represents a fairly significant loss of cobalt, since none of it goes back into cobalt-bearing materials.

Continuous Casting

Continuous casting is used predominantly to make hardfacing rod. These are typically high-cobalt alloys that are produced in rod form under 1/4 in. in diameter either by continuous casting, by investment casting, or by aspiration casting into glass tubes. The yield of these processes is relatively high, with little material lost from the system. The rods are abrasively cleaned, with losses of 1 to 2 percent of the cobalt. Once the rods are in service however, the cobalt, like the powder metallurgy material, is essentially lost from the system. The typical market for these materials is as valve seats and components for diesel engines. These materials are not recycled once the seats are taken out of service. One of the reasons for the lack of recycling of these alloys is the intolerance for the high iron contamination. Typically, the cobalt alloy is hardfaced or sprayed onto an iron substrate. Removal of the hardfaced deposit would involve significant contamination by iron, which would affect the recycled product. One producer estimates that less than half of the material is returned to the system, either as swarf or as overspray material. The hardfacing area, as previously noted, is one that does not effectively utilize the raw materials it consumes.

Opportunities for Improved Recycling of Hardfacing and Coating Alloys

A number of different aspects need to be addressed in the area of recycling. Hard scrap generated in manufacturing operations can certainly be recycled. How this can be performed depends to a certain extent on the particular product mix of a given manufacturer; that is, certain alloys may use the scrap from a variety of different alloys from a chemistry viewpoint, while others may not. Scrap segregation at the source greatly facilitates recycling, since compositional identifications can be preserved. Problems can be encountered with scrap mixes or with purchased scrap, since "real-time" chemical analyses are not generally used because of the small heat sizes involved. However, heat reclaiming procedures could be used to overcome these problems as part of an overall approach to scrap recycling. Another source of scrap comes from the wear alloy user in the form of grindings generated during dimensional finishing operations. Since a major portion of hardfacings is on steel substrates, iron contamination would be expected to occur. Such contamination might make the grindings unsuitable for recycling back into the original hardfacing alloy. However, these grindings might be satisfactory for use in tool steels.

A final aspect involves used parts. For non-bonded materials, such as powder metallurgy parts, bushings or half-sleeves, and castings, no peculiar recycling problems are foreseen. However, the quantity of such material is small in comparison to the bonded hardfacings. For bonded hardfacings, it seems likely that only relatively thick layers would be suitable for recycling back to the original alloys. Thin deposits, on the other hand, might be considered for recycling in tool steels.

RECYCLING OF COBALT FROM OTHER MAJOR USES

The primary production and component manufacturing techniques employed for the other major uses of cobalt are discussed in the appropriate sections of Chapter 5 on magnetic devices, cemented carbides, catalysts, driers, and chemicals. Brief discussions of recycling opportunities for these classes of materials are presented here.

Magnetic Devices

The magnet industry makes effective use of home or runaround scrap generated during magnet manufacture, but there is little recycling of post-consumer (obsolete) magnet scrap. The exceptions are large magnets found in scrapped equipment known to specialty scrap dealers and the magnets in devices that are leased by suppliers to users. The Bell System, for example, recovers and reuses telephone receiver and ringer magnets from obsolete telephone handsets, and public utilities could do the same for damping magnets in watt-hour meters. With cobalt at its present price, little will be done in this area, but at a sustained price of 3 times its present level much more recycling could and would be done.

Specific recycling techniques depend on the type of magnetic material involved. Chemical contamination generally is not a major deterrent to recycling magnet material. The primary barriers are identification and collection of obsolete scrap from widely dispersed locations and the cost of removing small components from scrapped units.

Cemented Carbides

Recycling of cemented carbide scrap is well established in the United States. Because of the inherent value of both cobalt and tungsten, virtually all cemented carbide manufacturing scrap is recycled. However, obsolete scrap recycling is much less extensive and presents a number of practical problems for implementation because of the wide dispersion of carbide users. Traditionally some carbide scrap was crushed for use in other industries, such as hardfacing and bonded abrasives, where less pure raw material is acceptable. However, with the high cost and occasional scarcity of these metals, direct recycling of obsolete scrap cemented carbide has become established.

Several process routes for recycling carbide scrap are available. A good description of the technology is available in the literature (Kieffer and Baroch 1980). A flow chart of the most important recycling methods is shown in Figure 5. The specific choice of recycling method depends on the degree of contamination of the scrap.

The capacity for recycling of cemented carbide scrap has been estimated to be more than 25 percent of the production capacity of new carbide material (Kieffer and Baroch 1980). Clark (1982) has estimated that recycling could be increased significantly given the economic incentive of high metal prices. Those estimates of the theoretical and probable limits for carbide recycling are given in Table 18.

Recycling of cemented carbides is increasing and is judged to approach 30 percent of the total weight of the cemented carbides currently shipped by the U.S. industry. A recent survey yielded the estimates shown in Table 18 (Clark 1981).

Catalysts

The production of cobalt catalysts is an aqueous chemical process described in Chapter 5. In the past, recycling of spent catalyst was performed on a sporadic basis, with incomplete recovery of the contained metals. However, considerable advancements have occurred in the technology for recycling these materials, and it is believed that nearly all cobalt will be recovered from spent catalyst in the near future.

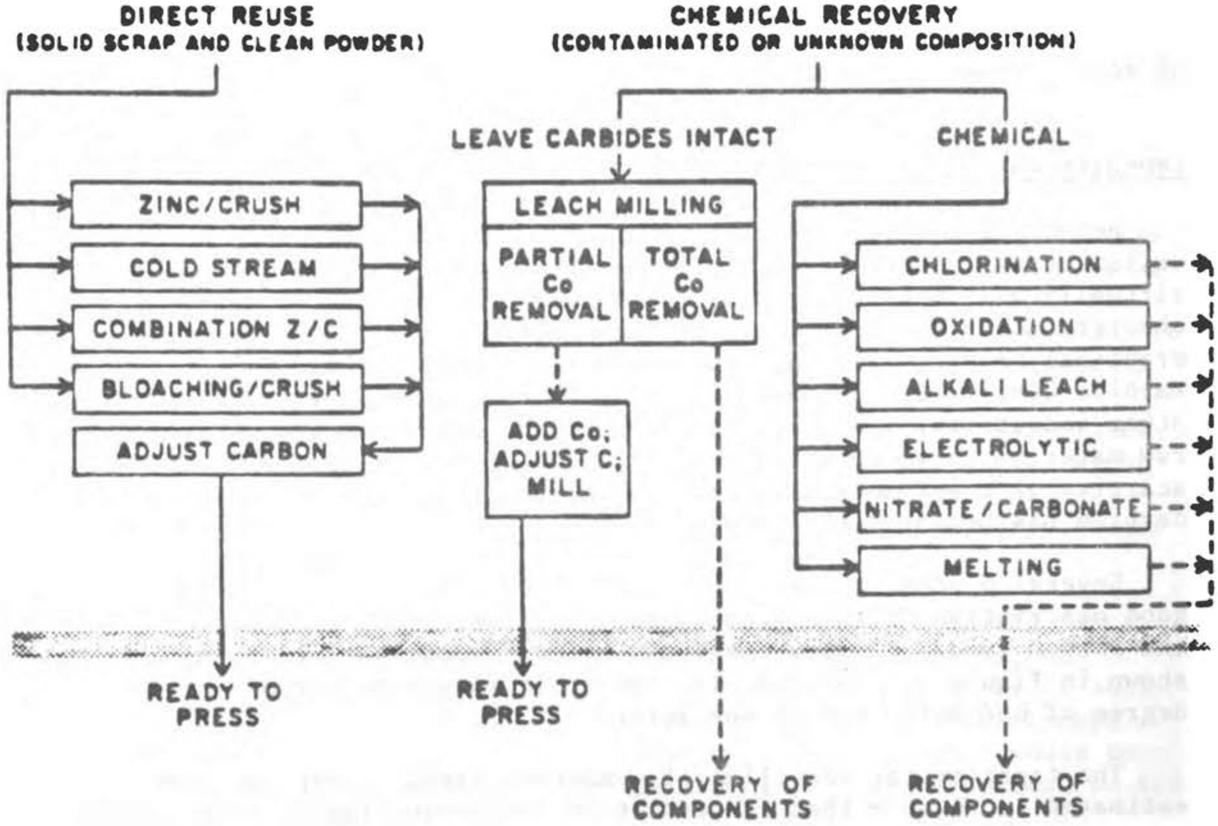

Figure 5 Cemented carbide scrap recycling methods.
Source: Kieffer and Baroch 1980.

TABLE 18 Estimated Percentage of Cemented Carbide Scrap That is Recycled

Application	Theoretical Maximum	Probable Practical Limit	Current Practical Limit
Cutting tool inserts	95	60	40
Brazed tools	75	40	15
Oil drilling	90	85	80
Coal mining	65	50	15
Mining	85	85	65
Wear parts	90	85	80

Source: Clark 1982.

Other Cobalt Uses

A large quantity of cobalt is used for a variety of applications where recycling is impractical. These include such important uses as pigments, porcelain enamels, glass decolorizers, agricultural chemicals, paint driers and plastic accelerators and stabilizers. No technological developments are foreseen that could improve the feasibility of recovering cobalt from these uses.

Some cobalt is used in power cells and nickel-cadmium batteries. Almost none of this is recovered today but up to 40 percent could be recovered if necessary.

Rapid Solidification Technology

Rapid solidification processing--processing to cause freezing of liquid metals at extremely high rates--is being evaluated by scientists and engineers from almost all sectors of the materials community as a means of altering and improving upon the alloying features of a metal for subsequent better properties in a service environment (NMAB 1980, Kear et al. 1982). Depending on the alloy system and the specific method of quenching from the liquid, metals of complex alloying can be produced as crystalline materials with near-perfect chemical homogeneity, as metastable extended solid solutions, or as amorphous (glassy) solids. Typically, the regime for rapid solidification involving crystalline material has been described as those rates causing quenching to occur at 10^3 to 10^6 degrees per second and for glassy alloys, greater than 10^6 degrees per second.

The field of rapid solidification processing has already shown large potential benefits for numerous classes of metals (Waniek 1976). The following are some examples: aluminum can be effectively alloyed with elements such as lithium to produce high specific moduli (airframe structures) (NMAB 1981a). Steels can be altered to generate submicron-size phase dispersions (higher-speed bearings, improved fracture toughness). Eutectic iron alloys can be made glassy for unique magnetic properties (electrical applications). Nickel alloys can be produced with abnormally high refractory metal concentrations for better creep resistance (gas turbines).

The process routes for rapid solidification are varied and many, but with a singular principal aim: production of a droplet, flake, or ribbon in an environment of high heat extraction and in sizes or thickness whereby thermal conductivity within the metal does not impede the overall heat-release profile. Depending on the actual mechanisms for this purpose, droplet sizes can vary from about 100 microns and finer, and flake and ribbon thickness from about 50 microns and finer. The following briefly describes several of the better known procedures for rapidly solidified powder processing.

Gas atomization involves the disintegration of a liquid metal stream through a symmetrical arrangement of arrayed high-velocity gas jets. The working fluids in gas atomization are argon, hydrogen, and nitrogen. These methods of atomization are in production for numerous alloy systems and applications and can achieve solidification rates 4 to 6 orders of magnitude faster than those derived from conventional ingot casting. The rotating electrode process is used to produce spherical powder for specific commercial application and is under evaluation for superalloy powder production. Other powder-making processes under study include centrifugal atomization, various melt extraction techniques, and other advanced concepts.

Consolidation of these as-produced rapidly solidified materials into useful engineering forms has been based with good success primarily on powder metallurgy procedures. Examples of such processing include hot isostatic pressing and extrusion followed by superplastic deformation.

Specifically, in addressing the need to reduce the use of cobalt in jet engine superalloys, research and development work has been done and is continuing in using rapid solidification techniques and materials for this purpose (NMAB 1981b). The particular components that are being examined include disc and turbine airfoils. The work in this field has been directed both at the development of superalloys with low strategic element content and near-net-shape processing.

Work is continuing in the field of rapid solidification and its applicability to the reduction of strategic elements. Work to date indicates that this method of processing holds much promise for attaining at least a degree of independence from such elements as cobalt and chromium in various systems of alloys. However, it must again be emphasized that, for critical alloy applications, the principal motivation in alloy and process development is the achievement of improved mechanical, physical, or chemical properties. Whether the successful application of RST will be accompanied by a reduction of the use of strategic elements cannot be foreseen at this time.

CONCLUSIONS

1. The most important factor influencing alloy production and fabrication technology in the superalloy and tool steel industries is the achievement of better properties through increased purity and microstructural refinement. Cobalt conservation has little effect on this trend.

2. Another significant trend is the increasing emphasis on improved yield of usable product from the raw material purchased. Near-net-shape technologies such as isostatically pressed powders and investment casting are specific examples. The reduction of raw materials purchases, costs of maintaining an

inventory of metals, and inherent losses of accumulated processing give impetus to this trend. Simultaneous conservation of many strategic metals in addition to cobalt is involved.

3. The development of new recycling technologies is important, and all producers seek to efficiently recycle as much scrap as possible. Today, most in-house and prompt industrial scrap is recycled. Cobalt is generally recovered, but some other important elements are lost.

4. Superalloys are particularly sensitive to the presence of trace element impurities that may be present in scrap. Advances in rapid and precise chemical analysis and in the sorting and processing of scrap, have improved the viability of recycling. Accurate sampling of mixed scrap remains a problem.

5. Obsolete scrap is not efficiently recovered today. Some of the better quality scrap is recycled for superalloys, but a large quantity is downgraded. This area presents the best opportunity for increased cobalt recovery.

6. Low-grade scrap (e.g., dusts, mill scale, and grindings) is largely downgraded and much of the cobalt is lost. Some material such as sludges is now discarded. More of this material would be recovered if cobalt prices were significantly higher. Some of these materials are considered hazardous, and the associated high disposal costs may stimulate treatment for recovery of metal values.

7. Treatment of mixed-alloy scrap to recover all contained individual elements in pure form is technically feasible but does not appear economically viable at current prices. Recovery processes could be installed after 2 to 5 years of research, but these could be accomplished only through government incentives.

8. Improved processing and recycling could save over 4 1/2 million pounds of cobalt annually within a few years using currently available technology. Spent superalloys, cemented carbides, and catalysts are especially amenable to cobalt recovery.

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Chapter 5

TECHNOLOGICAL ALTERNATIVES: SUBSTITUTION AND DESIGN

This chapter addresses the substitutability of cobalt in the major end-use categories. These categories are superalloys, magnetic materials, wear-resistant materials, tool and other steels, catalysts, driers, and other chemicals. Sufficient technical discussions on the role of cobalt in these uses are included to substantiate the conclusions reached with respect to near-term and long-term substitutability of cobalt with nonstrategic or less strategic elements. Whenever possible, substitutability is quantified with respect to cobalt cost sensitivity. The scenario of a complete disruption of cobalt supply is also discussed in this chapter.

SUPERALLOYS

The demand for cobalt in superalloys in the United States has shown an interesting pattern since 1978 (see Table 19). From 1978 to 1980, there was a dramatic increase in consumption, averaging about 21 percent per year from 2.78 to 6.29 million pounds. In 1981, however, cobalt consumption declined by one third from the 1980 level due not to substitution but to the general recession in the aircraft sector of the economy. Future needs for superalloys are expected to grow at about 6 percent per year.

The initial rapid rates of growth in consumption of superalloys that followed the price increases of 1978 were due almost entirely to the high rates of aircraft engine production and the prosperous period experienced by energy-producing industries from 1978 to 1980. The potential for using substitutes for cobalt in superalloys is limited in the short run, especially for aircraft applications, because of the stringent standards and the associated high costs and long lead times required to certify substitute alloys (Tien et al. 1980). A new alloy usually requires about 5 years for certification at a cost of about $1 million per year. Accelerated certification can be accomplished in about 2 years with attendant higher total cost.

In 1980 it was estimated that shipments of superalloys to the aircraft industry accounted for about 75 percent of total superalloy consumption. Almost none of this demand was substitutable in the short run. At the same time, superalloy demand by the stationary gas turbine industry and the "other" sector was also strong.

TABLE 19 U.S. Reported Cobalt Consumption by Use (million pounds)

Use	1978	1979	1980	1981
Tool steel	0.38	0.41	0.32	0.17
Other steel	0.40	0.38[a]	0.16[a]	0.18
Superalloys	4.30	5.28	6.29	4.20
Carbides	1.84	2.12	1.34	1.08
Hardfacing	0.73	0.44	0.62	0.49
Magnets	3.77	3.27	2.27	1.69
Other alloys	0.97	0.67	0.36	0.25
Catalysts	1.62	1.88	1.66	1.28
Driers and other chemicals	5.72	2.59	2.21	2.19
Miscellaneous	0.28	0.38	0.10	0.16
Total (BOM data)	19.99	17.40	15.32	11.69

[a] Does not include high-strength, low-alloy steels (about 0.01 to 0.02 million pounds)

Sources: U.S. Bureau of Mines 1981 edition, Minerals Yearbook and Charles River Associates estimates.

Price Sensitivity

At a current price of about $10 per pound (1982 dollars), there will be no active industrial programs on substituting low-cobalt or no-cobalt superalloys for the currently used higher cobalt-containing superalloys (about 10 to 20 percent cobalt). It must be emphasized that only about 200 to 900 pounds (Stephens 1982) of cobalt are required to manufacture a jet engine; at $10 per pound this gives a cost for the cobalt between $2,000 and $9,000. At $50 per pound, the cost is $10,000 to $45,000, a substantially increased outlay for the engine manufacturer. Even the higher dollar amounts are of less concern than availability, given the multimillion-dollar cost of the finished jet engine. The problem, even during the 1978 period, was and is one not only of cost but also of availability and security of supply.

In 1978 major efforts were made by Pratt & Whitney and General Electric to displace existing high-cobalt alloys with cobalt-free alloys (Tien et al. 1980). Some savings in cobalt use did occur with cobalt-free alloy substitutions. These programs were driven both by the high cost of cobalt at that time (about $25 to $30 producer price and up to $50 dealer price) and the fear of supply disruption and shortages caused by panic buying. The consensus is that much of the alloy cobalt substitution that could readily take place has now been accomplished as a result of the 1978-1980 programs. Additional, but more difficult to realize, cobalt savings can be expected from substitution alternatives if cobalt prices again rise disproportionately to those of other metals. Further large savings would require longer term, high-cost development and certification programs; this is discussed in the following sections.

Research Programs and Their Long-Term Impacts

Federal agencies, such as NASA's Lewis Research Center through its recently launched but modestly funded Conservation of Strategic Aerospace Materials (COSAM) program (Stephens 1982), are not insensitive to the fact that U.S. dependence on imported cobalt must be alleviated through research. Limited laboratory microstructural and mechanical testing results (Tien and Jarrett 1982) have shown that current U.S. superalloys may contain about 50 percent more cobalt than is necessary for most turbine applications.

These research projects are expected to be ready for engine-scale confirmation in about 3 years. Accordingly, the fruits of these studies may not be realized as engine-qualified alloys before the late 1980s. Of course, such realization is possible only if the government and industry increase funding levels substantially.

Coatings

Many of the high-temperature superalloys in service today are used with protective coatings, some of which are rich in cobalt--e.g., certain advanced MCrAlY-type coatings, where M is cobalt and nickel. This raises a question as to the extent that cobalt may be reduced or even replaced in such coatings without impairing coating performance. A review of the current situation makes it clear that the possibility of using other metals in place of cobalt in MCrAlY coatings will depend on the particular application for which these coatings are intended. The following are some examples:

- In the case of high-temperature oxidation (e.g., about 1050°C and above) in environments where the reactant is essentially oxygen, cobalt can probably be replaced by nickel with no loss in the usable life. Replacement of cobalt with iron should also be possible, but increased interdiffusion of the coating with the alloy may occur and cause a reduction of coating life.

- In the case of high-temperature exposures, where hot corrosion conditions and gases containing substantial amounts of sulfur are present (e.g., above 900°C with deposits such as Na_2SO_4 and in low-BTU gases), cobalt plays a very significant role in determining coating life. Replacement of cobalt by another metal can be expected to decrease service life.

- At low temperatures, coating degradation by hot corrosion is important. Cobalt-base coatings are currently used to provide protection, and most new advanced coatings also contain cobalt. More research is required to determine if other metals can be used to replace cobalt in these coatings. At present, it appears reasonable that replacement is possible.

Further development of thermal barrier (ceramic) coatings may permit cobalt to be replaced in coatings, but again it is necessary to consider the environments that cause the attack. As mentioned above, cobalt is effective in inhibiting oxidation and hot-corrosion or mixed-gas attack at high temperatures. Therefore, it may be possible to move out of such a temperature regime by using a thermal barrier coating to decrease the temperature. Care would have to be exercised to ensure that the lower temperature would not cause low-temperature hot corrosion to take place. Thermal barriers may also inhibit hot-corrosion attack in general by preventing salt deposits from covering the coating surface.

Another consideration is the possible effect on coatability of decreased cobalt in the substrate alloy. This is being investigated at the NASA Lewis Research Center, but sufficient data are not yet available to permit definitive conclusions. The coatings to be examined in that study are plasma-sprayed MCrAlY and aluminide coatings. The evaluation will include cyclic-oxidation and hot-corrosion tests in a burner rig.

Many methods of processing MCrAlY overlay coatings have been tested, including diffusion bonding, powder sintering, plasma spraying, vacuum evaporation-sputtering, and ion plating. Of these, electron beam evaporation has emerged as the preferred method of coating high-temperature alloy components. However, this technique is now being replaced by vacuum plasma spraying. It does not appear that the presence or absence of cobalt in the alloy substrate or in the overlay coating will have much bearing on the processability of coatings using these advanced techniques.

Design Aspects for Cobalt Use in Gas Turbine Engines

Apart from the foremost consideration of flight safety, there are many factors that relate to the design selection of components for gas turbine engines. Obviously, these considerations vary with the criticality of the component. The acceptability of a materials design change is, therefore, strongly dependent on component loading, environment, and criticality. Acceptability is also governed in part by the extent of the change; for example, a change from a cast to a wrought alloy, while probably more costly, may be readily acceptable because of the higher reliability of wrought material in certain applications. However, a change from a wrought alloy to a cast alloy implies lower design capability and therefore may be more difficult to justify and verify.

In general, the desirability of change is governed by the payoff. The payoff must be an initial benefit to the system at an acceptable cost, a change that results in a mission life benefit directly applicable to reducing system ownership cost or a sought-after systems performance improvement. In any case, the state of technology is such that reasonably accurate cost estimates of the benefits changes that affect initial costs, ownership cost, or performance payoffs are determinable to both manufacturers and users of gas turbine engines. Beyond the cost benefit, one must also consider the chances of developmental program success. In general, it is true that a high cost benefit is obtained only through taking commensurate risks. It would be desirable if one could, with a small risk in terms of success probability, realize a large benefit. However, the near full-maturity state-of-the-art gas turbine engine technology makes this type of opportunity rare indeed. As opposed to cost benefit, developmental chance of success is a more difficult criterion to assess properly. It must be remembered that technology advocates may not always fully understand the total criteria for application success associated with their advocacy. Therefore, it is mandatory that design engineers, as well as all materials and program managers, partake in the cost-benefit analysis. Overall developmental success means that reliable weight- and fuel-efficient and recyclable parts of the longest possible design life are developed.

Because of their flight safety criticality and, to a lesser degree, the extensive secondary damage to the turbines caused by failure, much time and effort have been devoted to improving the understanding of turbine disk design criteria. Turbine disks are subjected to a wide spectrum of mechanically and thermally induced stress during any given mission. The cumulative effect of these missions is to produce component degradation by several possible mechanisms--e.g., dimensional aspects of yield strength growth, creep growth, low-cycle fatigue capability, and environmental degradation. Further, the manufacturing process itself can have a major effect on part life. Thus, to determine disk life, or more importantly, minimum disk life to a degraded but unfailed state, a complex set of interacting variables including design configuration, mission profiles, and manufacturing sequence as well as alloy properties must be properly assessed. Improper analysis can result in a flight safety problem (unlikely) or a conservative design that results in decreased engine performance relative to actual system capability.

An understanding of these criteria suggests the obvious: When an alloy and manufacturing process has been selected, only a major systems benefit can provide sufficient incentive for change.

The disk alloy and process development cycle is shown in Figure 6. Three important things can be noted: the process takes several years, it is costly, and the alloy development costs are a small fraction of these total costs. Figure 7 shows turbine disk raw materials cost relative to total cost. The point here is that raw material cost per se is a small fraction of the component cost. It should also be noted that most disk alloys contain less that 20 percent cobalt.

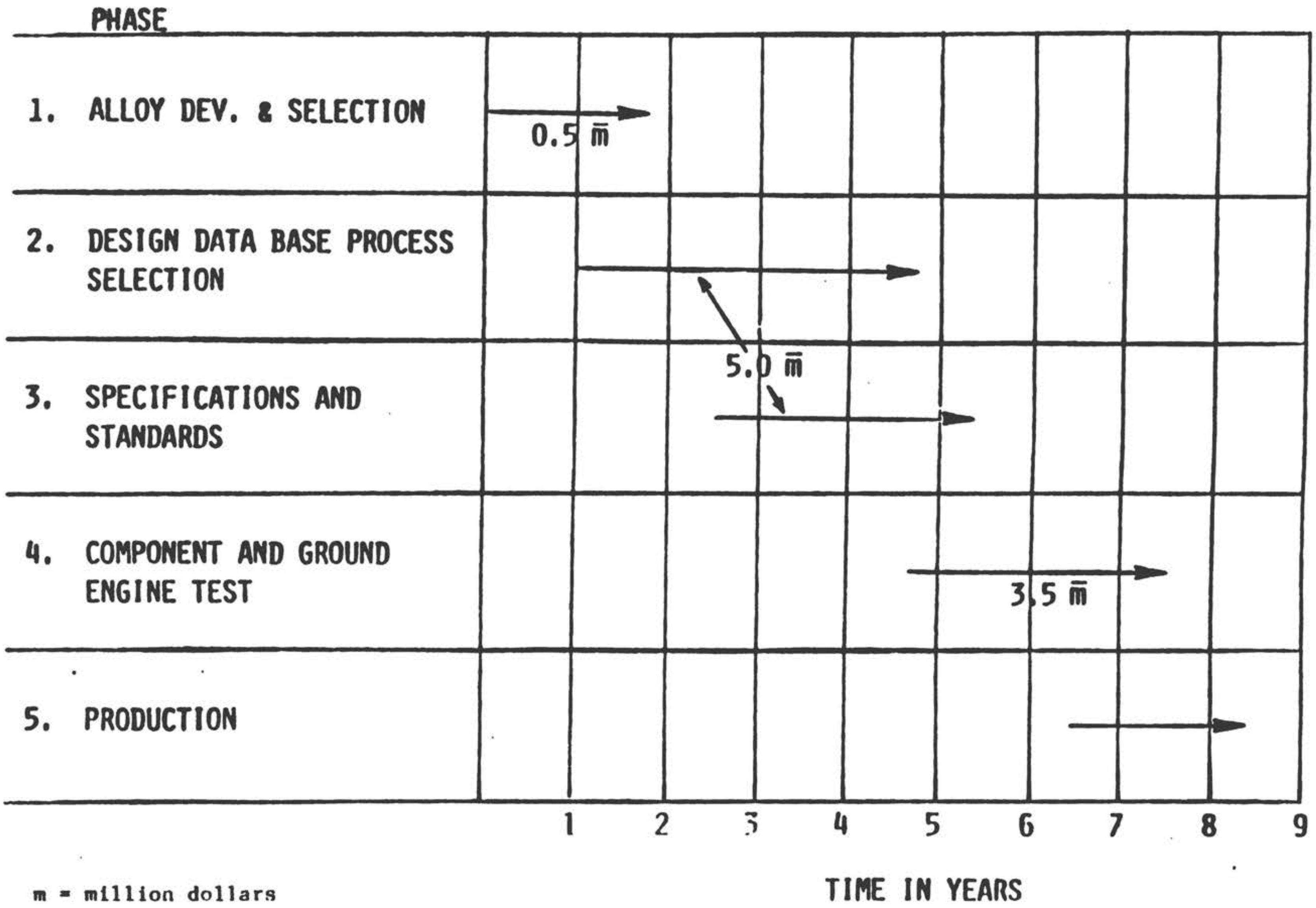


Figure 6 Typical turbine disk development cycle and cost.

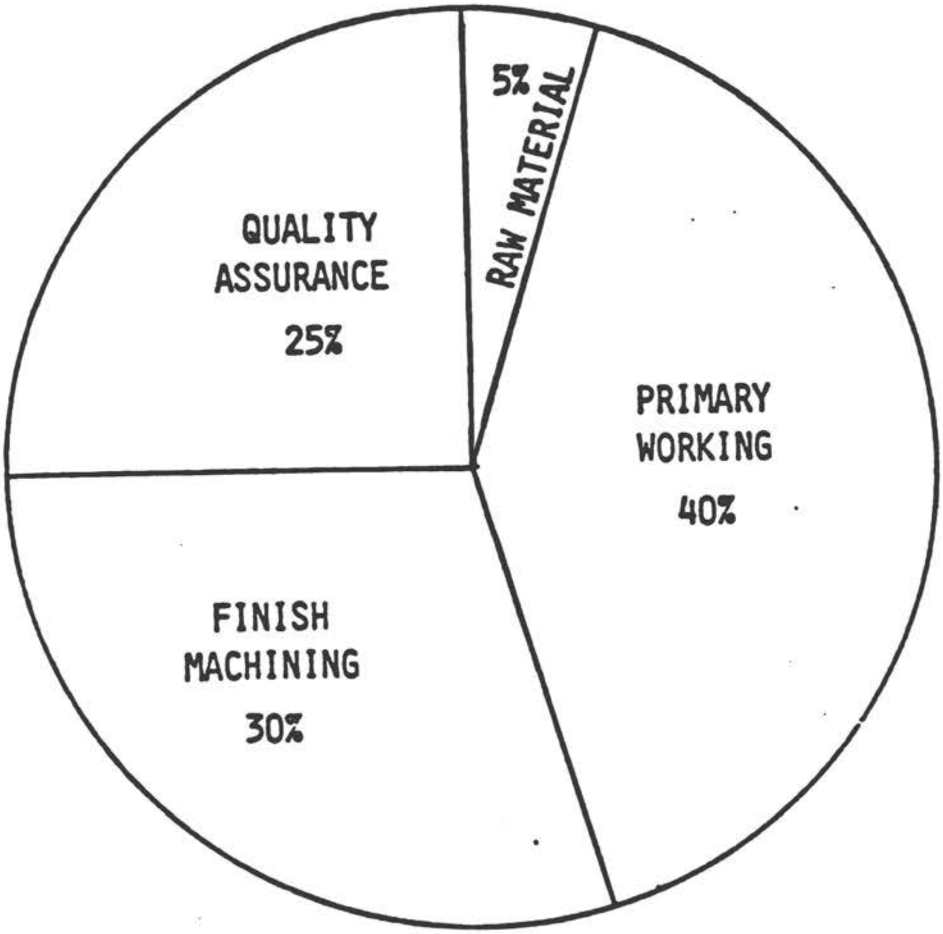


Figure 7 Typical superalloy turbine disk cost drivers.

The overall conclusion is also obvious: A major change in elemental material cost will not drive the designer toward an alternate material selection unless he has previously established a parallel alloy and process that he can readily put to use--generally an unlikely event. As already mentioned, the cobalt cost escalation of 1978 did produce this exact reaction; many readily adaptable alloy changes that could be made were made by the engine producers in the 1978-1980 period.

The next question is: What forces the designers to risk a new alloy system? The need for new disk alloys is established by mission requirements of performance or weight that are not achievable with any available material. To develop needed properties, metallurgists will first consider process alteration or current alloys. If this is found by an early judgment or limited evaluation to be impractical, the metallurgist will then turn to alloy development. The development process would be directed toward achieving the goals on a schedule consistent with the product implementation needs and the lowest possible impact on component cost.

Although not as critical as disks from a flight safety viewpoint, the reliability of turbine airfoils is strongly related to operational cost because turbine airfoil failure can result in rather extensive secondary damage, with attendant high engine removal and overhaul cost. The design criteria for turbine airfoils necessitate a balanced set of environmental, physical, and mechanical properties. While the effects of cobalt on airfoil properties are not yet completely understood, the deletion of cobalt would probably also require other alloy compositional modifications, extensive laboratory evaluation (which is ongoing), and engine verification; all of which are costly and usually require years of concentrated effort.

As with turbine disks, the designer is not sufficiently motivated to consider the elimination of cobalt without an offsetting technology benefit.

Figure 8 shows a typical turbine airfoil development plan and the cost involved. Reducing cobalt from 10 percent to zero in a 1 pound airfoil by substituting nickel would save a 0.1 pound of cobalt. At a cost differential of $20 per pound, a cost savings of about $2 per airfoil would then be realized. This is little incentive for a large-scale development effort in the face of component unknowns such as coating compatibility and thermal fatigue life. Therefore, as in the disk case, the designer would be motivated for change only when a significant and marketable (needed) mission benefit can be achieved. This trend is evident when one realizes that the most recent changes in turbine airfoil technology are driven by alloy and process innovations such as directional solidification of tailored alloys, in which case a significant and desired technological benefit is gained.

Conclusions Petaining to Superalloys

1. Many current superalloys contain cobalt for improved high-temperature properties and processability and will continue to do so in the foreseeable future.

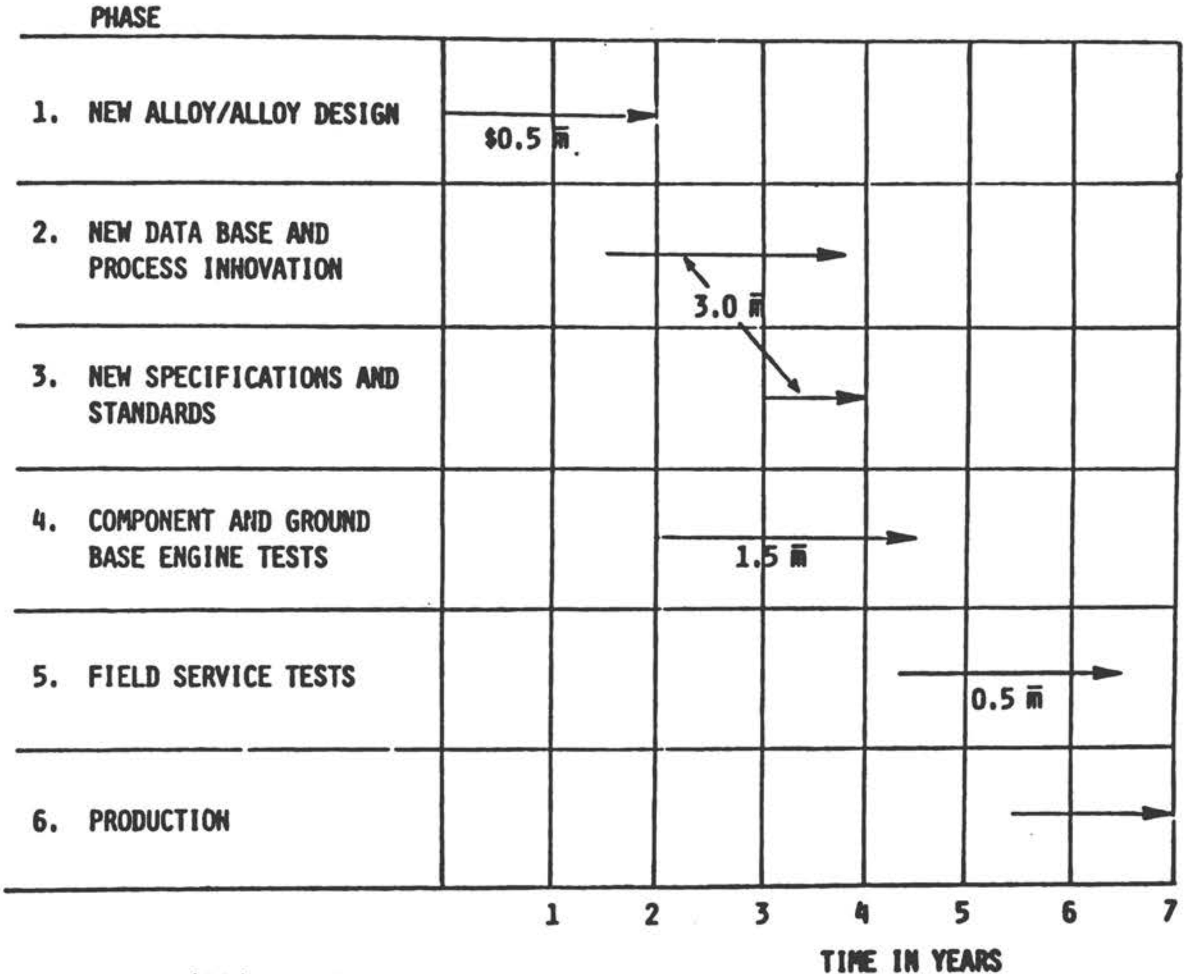
2. Several adaptable superalloy system changes to conserve cobalt have already been adopted; others are possible but are not economically warranted now.

3. Results from current research in progress indicate that significant amounts of the cobalt in superalloys can be replaced by nonstrategic elements.

4. Exploitation of these results requires costly and time-consuming alloy development and subsequent optimization and engine certification programs that must be funded by both government and industry.

5. These programs, unless coupled with engine performance advantages, will begin only when they are warranted by sufficient economic incentive or by a sufficiently urgent insecurity of supply.

6. Improvements in coating technology offer possible strategic metals conservation by reducing surface temperature and by tailoring the base metal and coating composition to minimize the use of the strategic metal.



m = million dollars

Figure 8 Typical turbine airfoil development cycle.

MAGNETIC DEVICES

At present, by far the largest use of cobalt in magnetic devices is in Alnico permanent magnets. Together with Fe-Cr-Co deformable magnets, about 90 percent of the use of cobalt in magnetic materials is in this type of permanent magnets. The use in rare earth-cobalt magnets is still small (about 10 percent) but rapidly increasing. The amorphous cobalt-base alloys obtained by rapid quenching from the melt are only beginning to enter the market, primarily in audio devices made in Japan, and their share is still negligibly small.

Use of Cobalt in Magnetic Materials

The Alnico magnets are used in a wide variety of instruments and devices, but demand is quite price-sensitive. Because of this, a significant amount of replacement or substitution by other materials has been taking place for some time, and at a more accelerated rate since the cobalt price increase in 1978. For instance, it is estimated that 100 percent of the magneto applications and 70 percent of the loudspeaker applications that formerly used Alnico now use ceramic hard ferrites (Chin 1979). These substitutions alone represent 30 percent of the Alnico production in 1977 and have been primarily responsible for the decrease in cobalt consumption in the magnetics area. In 1977, magnetic materials consumed 3.48 million pounds of cobalt, accounting for 21 percent of all cobalt consumed in the United States. By 1981, these figures had fallen to 1.69 million pounds and 14.4 percent, respectively (Sibley 1980). At present prices and with cobalt readily available, consumption in magnets will remain relatively constant.

The rare earth-cobalt (RE-Co) magnets, on the other hand, represent a growing demand for cobalt. Because of its very high magnetic-energy density, the rare-earth (RE) containing magnet makes more effective use of cobalt. Even though the cobalt content of the RE-Co magnet is twice that of Alnico, the magnetic energy density is 3 to 4 times greater; therefore, it retains 1.5 to 2 times more energy for a given amount of cobalt. Furthermore, this excellent volumetric advantage means that small, high-torque, fast-response electric motors can be built with the RE-Co magnets. Since these devices are high-performance, high-price items, the demand is relatively little influenced by high cobalt prices, and their use is expected to grow even in the face of a higher price of cobalt--even up to 5 times the current price. It is also possible that large RE-Co motors will be used in power devices, such as electric power generators and motors for ships. However, a substantial growth in this field is unlikely because of the cost factor. It is more likely that the use will be initiated in strategic applications, such as in the Navy fleet.

The future of cobalt-base amorphous alloys in device applications is quite bright--for instance, in read-out/write-in heads for audio and video tape-recorders and digital memory devices. Cobalt is used in these applications because some cobalt-base alloys with small amounts of iron show zero magnetostriction and very high permeability. However, since only a small amount of material will be used for each device, its impact on cobalt consumption will remain minimal.

Trends in Technology and Demand

Alnico and Iron-Chromium-Cobalt Magnetic Materials

The Alnicos are a family of alloys that contain substantial amounts of iron, nickel, and cobalt, together with smaller amounts of aluminum, copper, and sometimes, other elements, as seen in Table 20. The isotropic alloys exhibit moderate remanent induction, B_r, coercivity, H_c, and energy product, $(BH)_{max}$, while the more popular anisotropic grades exhibit high remanent induction and energy product with moderate coercivity. The anisotropic grades are obtained principally by means of heat treatment in a magnetic field below the alloy's Curie temperature.

Alnico 5 is the most widely used grade, and its energy product of 5 megagauss-oersteds (MGOe) is a useful benchmark against which to judge substitute materials. Because of its high remanent induction, Alnico 5 magnets are used most effectively in rod form. Only magnetic materials with a demagnetization curve similar to that shown in Figure 9 for Alnico 5 can serve as a substitute without redesign of the component.

The iron-chromium-cobalt alloys are an important recent addition to permanent magnets; they offer magnetic properties similar to those of the Alnicos but at much lower cobalt content (Chin 1981). The anisotropic grades are obtained by heat treatment in a magnetic field or by deformation aging. These alloys are readily processed and exhibit good cold formability.

Since these alloys provide energy products comparable to Alnicos at lower cobalt content, they use cobalt more efficiently than Alnicos in producing such energy products. This comparison is made in the last column of Table 20, which lists the maximum energy product per unit of cobalt relative to Alnico 5. The Fe-Cr-Co alloys perform very well here and, in fact, can exceed the cobalt efficiency values for the RE-Co magnets listed. The nearly identical magnetic characteristics of the Fe-Cr-Co alloys to those of the Alnicos facilitates substitution, which is happening in a number of applications (Chin 1979). These alloys are also ideal substitutes for Cunife, Vicalloy, and Remalloy and have been so used.

Rare Earth-Cobalt Magnets

The maximum energy product of present commercially available RE-Co magnets ranges from 10 to 25 MGOe, while the laboratory values approach 30 MGOe (Zijlstra 1978). This represents a two-fold or greater improvement over the Alnico magnets. It makes the permanent magnet competitive with

TABLE 20 Cobalt-Containing Permanent Magnet Materials

Type	Composition (Wt. pct. remainder Fe)	B_r (KG)	H_c (Oe)	$(BH)_{max}$ (MGOe)	$(BH)_m$ per unit Co	$(BH)_m$/Unit Co relative to Alnico 5
Alnico						
1	12Al,21Ni,5Co,3Cu	7.2	470	1.1	28	1.2
2	10Al,19Ni,13Co,3Cu	7.5	560	1.7	13	0.6
4	12Al,27Ni,5Co	5.6	720	1.4	28	1.2
5(A)	8Al,14Ni,24Co,3Cu	12.5	640	5.5	23	1.0
5(A)(B)	8Al,14Ni,24Co,3Cu	13.3	670	6.5	27	1.2
5(A)(C)	8Al,14Ni,24Co,3Cu	13.5	745	7.6	32	1.4
8(A)	7Al,15Ni,35Co,4Cu,5Ti	8.2	1650	5.3	15	0.7
9(A)	7Al,15Ni,35Co,4Cu,5Ti	10.5	1500	9.0	26	1.1
-(A)(C)(D)	7Al,14Ni,40Co,3Cu,8Ti	9.7	1890	11.5	29	1.3
FeCrCo						
-	28Cr,10.5Co	9.8	400	1.7	16	0.7
(A)(E)	33Cr,7Co	11.9	485	3.3	47	2.0
(A)(E)	33Cr,7Co,2Cu	11.8	525	4.2	60	2.6
(A)	28Cr,7Co	12.5	510	5.2	74	3.2
(A)(E)	33Cr,23Co,2Cu	13.0	1080	9.8	43	1.9
(A)(C)	24Cr,15Co,3Mo	15.4	840	9.5	63	2.7
RE-Co						
$SmCo_5$(A)	35Sm,65Co	9.0	8500	20	31	1.3
$Sm(Co,Cu,Fe)_{7.5}$(A)	25.5Sm,50Co,8Cu,1.5Zr	11.0	6400	30	60	2.6
Miscellaneous						
Vicalloy	10V,52Co	8.8	300	1.0	2	0.1
Remalloy	17Mo,12Co	10.5	250	1.1	9	0.4
E.S.D.32(A)	71Pb,11Co	7.3	940	3.5	32	1.4
PtCo	77Pt,23Co	6.5	4300	9.5	41	1.8

(A) Anisotropic, magnetic field treatment
(B) Directional grain
(C) Columnar
(D) High coercivity
(E) Deformation aging

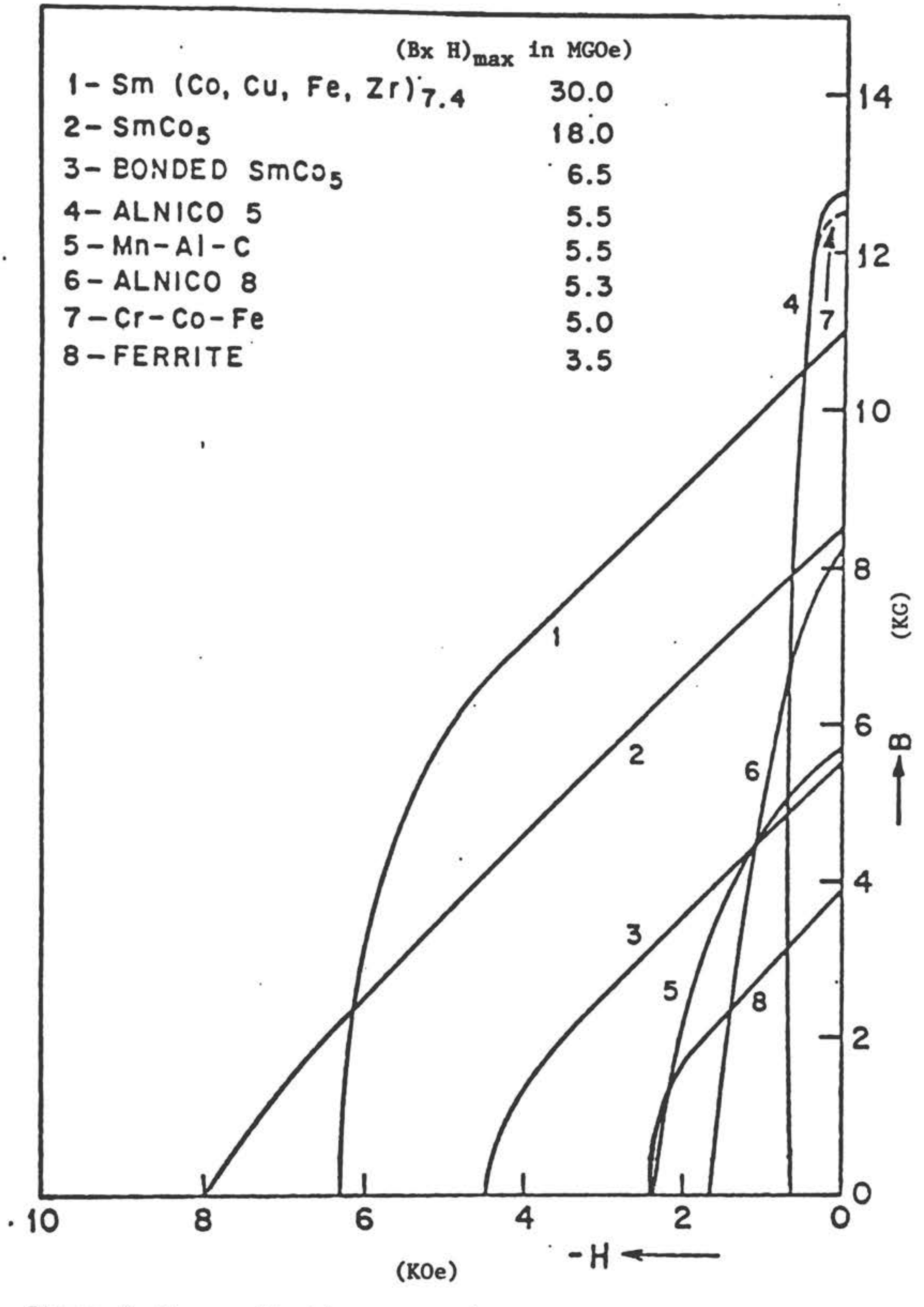


Figure 9 Demagnetization curves for permanent magnet materials.

the electromagnet in many applications, particularly since the permanent magnet saves energy and is inherently more reliable. The RE-Co magnets can also be gainfully used in motors to convert induction motors to synchronous motors. The higher energy density of the RE-Co magnets makes it possible to build smaller and stronger motors. This is important not only in terms of the miniaturization of the devices, but also because reduced inertia means faster response. Such fast-response motors are increasing in demand for motion-control devices such as servo motors and linear actuators of magnetic recording devices. The RE-Co magnet has very high coercivity, quite often exceeding its own saturation flux density. This permits the use of magnets in most unfavorable demagnetizing conditions and, along with the linearity of the B-H curve, removes constraints on design in many devices such as wave amplifiers or certain synchronous motors.

Soft Magnetic Materials and Applications

Commercially important alloys are 2V Permendur and Supermendur, which both contain 49 percent iron, 49 percent cobalt, and 2 percent vanadium. These soft magnetic materials find use in aircraft generator laminations and cores and in telephone receiver diaphragms. An Fe-27Co alloy is commercially available and acceptable for some applications, as is an Fe-6Co-8Ni for receiver diaphragms. These substitutions decrease significantly the need for cobalt in this minor use.

In 1974 it was found that Fe-Ni-base or Co-base amorphous alloys exhibit permeabilities as high as those of Permalloys. While Fe-base alloys are being considered for use in power transformers, the cobalt-base alloys are beginning to be used for high-permeability applications, since by addition of small amounts of iron or other transition metals it is possible to make the magnetostriction virtually zero (Graham and Egami 1978; Boll and Warlimont 1981). An example is $Fe_{4.7}Co_{70.3}Si_{15}B_{10}$. A tape recorder head made of such an alloy is very sensitive to high frequencies and yet free of stress-induced noise. Such a device is beginning to be marketed in Japan and has a high commercial potential. However, since the amount of cobalt used is small (about 10 g per device), the total consumption of cobalt will not be significant.

Semi-Hard Magnetic Materials and Applications

Semi-hard magnetic materials have coercivities intermediate between those of soft (less than 5 Oe) and hard (greater than 150 Oe) magnetic materials and find use in reed switches, memory applications, and hysteresis motors. Overall, they represent an important but minor use of magnetic materials and of cobalt. Some of the traditional alloys have high cobalt contents, however, and substitutes for these have been sought and found. One example has been the Fe-Mo-Ni alloys that can substitute for Type 27 Remendur (49Co-48Fe-3V) or Nibcolloy (85Co-12Fe-3B) in reed switches (Jin and Tiefel 1981). The Fe-Cr-Mo alloys can also substitute in this application, and iron-manganese alloys are also a possibility here. All of these cobalt-free substitutes are ductile, easily processed, and capable of exhibiting high magnetic hysteresis loop squareness--an important characteristic in many semi-hard magnetic applications.

Conservation of Cobalt by Substitution and Design

Replacement of Alnicos by Ceramic and Other Cobalt-Free Magnetic Materials

Hard ferrites, sometimes referred to as ceramic magnets, are a very important and inexpensive class of permanent magnet materials. They have the general formula $MO.6Fe_2O_3$. The anisotropic magnets, listed in Table 21, are prepared by wet-pressing particles in a magnetic field to align them, followed by sintering. The starting materials required, namely Fe_2O_3 and $BaCO_3$ or $SrCO_3$, are cheap, reasonably pure, and readily available.

The low remanent induction and high coercivity of hard ferrites (ceramic) as listed in Table 21 and shown in Figure 9 require that the magnet be in disk form with a thickness-to-diameter ratio of about 1 to 2 in order to work at the point of maximum BH. Hard ferrites and RE-Co magnets resist demagnetization fields much better than Alnicos or Fe-Cr-Co magnets. Thus, depending on the application, the remanent induction, coercivity, and energy product or some combination of these will determine the optimum magnetic material to be used and the possibility of viable substitutes.

Although hard ferrites have been the principal cobalt-free substitute material for Alnicos, other possibilities are shown in Table 21. The Alnico and Cunife materials are readily available commercially, while the rest have seen only limited commercial use. The Mn-Al-Cu type has excellent magnetic properties, but it is both difficult and expensive to process and its Curie temperature is low. The Fe-Mo-Ni and Fe-Mn alloys are readily processed. The elongated single-domain iron-particle magnet also appears to be commercially feasible. This last material is closely related to the elongated single-domain (ESD) lead-cobalt particle magnet listed in Table 20 and commercially available now.

Use of Cobalt in Rare-Earth Magnets

At present, most of the RE-Co magnets in the market are made of sintered fine particles of single-phase $SmCo_5$. However, various multiphase RE-Co magnets that are based on domain wall pinning by defects and precipitates are also known. Well-known examples are $(Sm,Ce)(Co,Fe,Cu)_7$, and $Sm_2(Co,Fe,Mn,Cr)_{17}$, with cobalt content of 70 percent (Zijlstra 1978). The latter is considered to be the second generation RE-Co magnets that may replace the $SmCo_5$ type of magnets. In either case, the use of cobalt is reduced slightly. In the single-phase form, $Sm_2(Fe,Co)_{17}$

shows a rather low coercive force, although its magnetization is higher than $SmCo_5$. Only recently, special heat treatments were developed to produce very small-scale microstructure to pin the domain walls. This type of magnet has a higher saturation flux density and appreciably higher energy product than the $SmCo_5$ type of magnet--up to 30 MGOe compared to about 25 MGOe for $SmCo_5$ (Ojima 1977). Commercial magnets of this type are just becoming available. It is therefore entirely likely that the research effort in this field will produce good permanent magnets with higher iron concentration. The use of special techniques, such as the rapid solidification process, to produce metastable phases and unusual microstructures may well prove quite beneficial.

TABLE 21 Cobalt-Free Permanent Magnet Materials

Type	Composition Wt. percent	B_r (KG)	Hc (Oe)	$(BH)_{max}$ (MGOe)
Metallic				
Fe-Mo-Ni (A)	20Mo,5Ni,Bal. Fe	10.5	210	1.1
Fe-Mn	12Mn,Bal. Fe	15.0	85	1.1
Fe-Mn	16Mn,Bal. Fe	10.0	240	1.7
Alni	13Al,29Ni,Bal. Fe	6.6	600	1.4
Cunife (A)	60Cu,20Ni,Bal. Fe	5.5	530	1.4
ESD Fe (A)	72Pb,Bal. Fe	9.0	700	3.5
Mn-Al-Cu (A)	70Mn,29.5Al,0.5Cu	5.5	3000	7.5
Ferrite				
Ceramic 1	Mo.6Fe_2O_3	2.3	1860	1.1
Ceramic 2 (A)	(for all where	2.9	2400	1.8
Ceramic 3 (A)	M equals one	3.3	2200	2.6
Ceramic 4 (A)	or more of	2.5	2300	1.5
Ceramic 5 (A)	Ba, Sr, Pb)	3.8	2400	3.4
Ceramic 6 (A)		3.2	2820	2.5
Ceramic 7 (A)		3.4	3250	2.8
Ceramic 8 (A)		3.9	2950	3.5
Ceramic (A)		4.2	2900	4.2

(A) Anisotropic.

For permanent magnet use, it is not necessary that cobalt raw material have high purity. A small amount of impurities can be tolerated with minimum degradation of the properties. For instance, 4 percent nickel substitution in Sm_2Co_{17} will reduce the saturation induction by only 3 percent and leave the anisotropy field unchanged (Merches et al. 1978).

The reduced magnetization can be compensated for by the addition of iron. Furthermore, addition of a small amount of copper and manganese is known to improve the coercivity (Walkiewicz and Wong 1979). Such a replacement of cobalt by other transition metals is unimportant from the conservtion point of view since the amount saved is small. However, it is quite important in that it may mean that low-grade cobalt can be used.

In most of the small, high-performance magnetically oriented devices, the cost of the raw materials occupies a relatively small portion of the total price, so a high cost of cobalt--for instance, above 3 times its present price--can be tolerated. In an emergency condition in which the price of cobalt exceeds 10 times its present price, however, appreciable substitution in electromagnet-type motors would take place. Small RE-Co motors that are used in electronic devices, including audio and digital devices and medical equipment and devices, will see a steadily increasing demand. Perhaps the rate will double in 10 years in the steady supply environment.

As the size of the device or machine becomes larger, the material costs become more important. Therefore, it is not cost-effective to use the RE-Co magnet in a medium-size motor with power ranging from 10^2 to 10^4 watts. However, for larger systems, it is possible that the high-energy-density permanent magnet motors will become more competitive once again with electromagnet motors for volumetric and economic reasons (Parker 1981). The large RE-Co magnet motor is smaller, lighter, and consumes much less energy than the electromagnet motor of equivalent power. In this case, the cost and supply of cobalt is clearly a major factor in predicting the probability of such applications to occur. For limited strategic use, such as in the propulsion system of the Navy fleet, this application appears feasible. Such a market, however, is relatively small, perhaps below 100 tons per year. Whether a sizable consumer-oriented market for large permanent magnets would open up is a more difficult question to answer. At the present price range for RE-Co magnets ($75-100 per pound), the likelihood appears to be rather small. It would be necessary that the price decrease to the range of $20 to $30 per pound, before a significant conversion of large electromagnet motors into permanent magnet motors takes place.

Another current large-machine application is for telecommunications or radar systems as a part of the microwave generator or amplifier. In this case, in addition to high energy density, a very high coercivity exceeding the saturation flux density is required because of the geometry of the magnetic circuit; the RE-Co magnet is the only system that satisfies the requirement.

Projected Use and Substitutions in Magnetic Applications as a Function of Cobalt Price

It has been estimated (Sibley 1982) that the cobalt permanent magnet market breaks down into the following major use categories: loudspeakers, 25 percent; rotating machinery, 25 percent; indicating meters, 25 percent; telecommunications, 20 percent; and other, 5 percent. The nearly complete substitution of Alnicos by hard ferrites in all the large speakers was noted earlier, and this trend is not likely to be reversed even at present, or base, cobalt price. For smaller speakers the more cobalt-efficient Fe-Cr-Co magnets appear feasible, and for the smallest speakers the RE-Co magnets have merit. Thus, further cobalt savings in this area through substitution are unlikely at the present price of cobalt, and only modest further savings would be expected at 3 times the present price. Even at 10 times its present price, there would still remain some small (about 10 to 20 percent) segment of the loudspeaker market that could justify the use of cobalt for size, weight, and temperature reasons.

Rotating machinery utilize primarily permanent magnet generators, motors, and magnetos. Here, according to Parker (1981), hard ferrites are used widely in the power range up to 10 kW because of their cost-effectiveness; beyond this, high-energy-density magnets, particularly RE-Co, are indicated. At the present price of cobalt magnetos and other devices that have been switched to hard ferrites will probably remain with ferrites. In both larger and smaller motors, however, very high growth rates (some 10 to 20 percent per year) are predicted for cobalt at its present price. Even with cobalt at 3 times the present price, this would still be viewed as an important growth area for high-energy-density magnets with cobalt. A growth rate of some 8 percent per year is possible, well above the 2.6 percent per year growth rate forecast by the U.S. Bureau of Mines (Sibley 1982). With cobalt at 10 times the present price, strenuous efforts would be made to use cobalt-free materials or very cobalt-efficient materials, or to revert to electromagnetic designs. Nonetheless, as with loudspeakers, there would be some small segment of the market (about 10 to 20 percent) that could justify cobalt use even at this price level because of the size, weight, or energy-efficiency of the device.

Instruments and indicating devices are a segment in which only modest cobalt conservation is likely to occur, even at up to 3 times present cobalt price levels. This stems mainly from the nature of the designs, which are tied closely to specific materials. The watt-hour meter, for example, uses an Alnico damping magnet that must provide reliable and accurate operation up to 40 years and over a wide range of operating temperatures. Substitution in this most important application is difficult. Cobalt at 10 times the present price would naturally spur the use of more cobalt-efficient materials having similar magnetic properties but, perhaps more importantly, would also spur the development of indicating meters operating on wholly different principles.

In the area of telecommunications, it is expected that only a tenth of the cobalt now used will be needed in the next 5 to 8 years, even if the price of cobalt remains at its current level. This is because of the continuing rapid technological changes occurring in this industry as reflected in miniaturization, large-scale integration, digital signaling, and the advent of photonics.

Projected cobalt use in 1990, assuming the present price level, is given in Table 22 based on the estimates of category share and growth rate discussed here for RE-Co and the other magnetic alloys. Basically, the projection recognizes the small current market share of the RE-Co magnets combined with their high growth potential as contrasted with the high market share and low growth potential of the other magnetic alloys. If the price of cobalt were to increase by a factor of 3, projected cobalt use in 1990 in magnetic applications would drop by some 10 percent to 1.8 million pounds per year; if it increased by a factor of 10, projected cobalt use in 1990 would fall some 80 percent to 400,000 pounds per year.

Conclusions Pertaining to Magnetic Devices

1. Most of the significant substitution for cobalt in magnetic applications has already occurred, and it is estimated that only a further 10 percent or so reduction in cobalt use would occur even at 3 times the present price.

2. The one significant growth area identified for cobalt use in magnetic materials is in motors, particularly small motors employing rare earth-cobalt magnets.

3. An estimated 20 percent of current cobalt use in magnetic applications is essential and would continue even at ten times the present price.

4. The cobalt demand associated with amorphous magnetic alloys is expected to be insignificant through about 1990.

TABLE 22 Projected Cobalt Use in Magnetic Applications at Present Price (millions of pounds)

Category	1981 Cobalt Use		Re-Co Use and Growth			Other alloys Use and Growth			Total
	%	10^3 lb	%	%/yr	10^3 lb 1990	%	%/yr	10^3 lb 1990	10^3 lb
Loudspeakers	25	423	10	10	100	90	2.6	480	580
Motors	25	423	10	20	218	90	2.6	480	698
Indicating devices	25	423	10	10	100	90	2.6	480	580
Telecommunications	20	338	0	0	0	100	-22.0	35	35
Other	5	85	0	0	0	100	2.6	107	107
Total	100	1692			418			1582	2000

Source: U.S. Bureau of Mines projection using overall growth rate of 2.6 percent per year equals 2129.

CEMENTED CARBIDES

Cobalt forms the binding phase in the structure of cemented tungsten carbide, which in turn is the principal foundation of the products of the cemented carbide industry. The special phase relationships in the cobalt-tungsten-carbon alloy system allow the practical production of these materials by powder metallurgy processes employing liquid-phase sintering. Cemented tungsten carbide-cobalt alloys are characterized by exceptional combinations of hardness, temperature and abrasion resistance, high elastic modulus, strength, and toughness. They are widely used in tools for machining cast iron and nonferrous metals, metal forming, mining, oil and gas well drilling, and a variety of highly stressed structural applications. In machining ferrous materials, additions of titanium carbide, tantalum carbide, and niobium carbide are employed to improve the cutting tool's resistance to chip erosion or "cratering" and to the effect of high cutting-edge temperatures generated during the machining operation.

Tables 23 and 24 show representative properties and typical applications of commercial cemented carbides. Figure 10 shows the effect of varying cobalt content on the properties of these materials. In recent years, the cutting performance of cemented carbide tools has been markedly improved by thin surface coatings of titanium carbide, titanium nitride, and aluminum oxide, singly or combined. An estimated 40 to 50 percent of such tools are now coated, usually by chemical vapor deposition.

It is estimated that cemented carbide tools account for as much as 75 percent of the metal removed in U.S. metal-cutting operations. In mining, oil and gas well drilling, and construction, cemented carbides perform the cutting or crushing function in over 50 percent of these uses. In certain metal-forming, super-pressure processing, and other structural applications, the unique combination of properties available in the straight tungsten carbide-cobalt alloys makes them of critical importance.

Substitution of other binder metals and alloys in cemented carbides has received concentrated worldwide attention of researchers over the past 60 years. While some encouraging results have been reported (see patents in references), cobalt remains the superior binder from the standpoint of ease of production and general attainment of mechanical properties except in certain cemented carbide alloys designed to combat combined corrosion and abrasion. Nickel and iron have shown the most promise as substitutes, with chromium additions used to impart corrosion resistance. All such improvements in specific properties of the tungsten carbide-cobalt alloys are obtained at some sacrifice of the unique combinations of properties of the basic alloy system or in ease of production.

The use of cemented carbide cutting tool materials (based on the tungsten carbide-cobalt system) gained dominance during and after World War II. Realization of the productivity and economic advantages of their use required advances in machine tool design (rigidity, speed, power) as

TABLE 23 Properties of Representative Cobalt-Bonded Cemented Carbides

Nominal composition	Grain size	Hardness* HRA	Density		Transverse strength		Comprehensive strength		Proportional limit compression		Modulus of elasticity	
			Mg/m^3	lb/in^3	MPa	Ksi	MPa	Ksi	MPa	Ksi	GPa	10^6 psi
97WC-3Co	Medium	92.5-93.2	15.3	0.55	1590	230	5860	850	2410	350	641	93
94WC-6Co	Fine	92.5-93.1	15.0	0.54	1790	260	5930	860	2550	370	614	89
	Medium	91.7-92.2	15.0	0.54	2000	290	5450	790	1930	280	648	94
	Coarse	90.5-91.5	15.0	0.54	2210	320	5170	750	1450	210	641	93
90WC-10Co	Fine	90.7-91.3	14.6	0.53	3100	450	5170	750	1590	230	620	90
	Coarse	87.4-88.2	14.5	0.52	2760	400	4000	580	1170	170	552	80
84WC-16Co	Fine	89	13.9	0.50	3380	490	4070	590	970	140	524	76
	Coarse	86.0-87.5	13.9	0.50	2900	420	3860	560	700	100	524	76
75WC-25Co	Medium	83-85	13.0	0.47	2550	370	3100	450	410	60	483	70
71WC-12.5TiC-12TaC-4.5Co	Medium	92.1-92.8	12.0	0.43	1380	200	5790	840	1170	170	565	82
72Wc-8TiC-11.5TaC-8.5Co	Medium	90.7-91.5	12.6	0.45	1720	250	5170	750	1720	250	558	81
64TiC-28WC-2TaC-2Cr$_2$C$_3$-4.0Co	Medium	94.5-95.2	6.6	0.24	690	100	4340	630	...	...	...	..
57WC-27TaC-16Co	Coarse	84.0-86.0	13.7	0.49	2690	390	3720	540	1170	170	441	64

* (Based on a value of 100 for the most abrasion-resistant grade)

Source: Metals Handbook, Vol. 3, 9th Ed.

TABLE 24 Typical Application of Cobalt-Bonded Cemented Carbides

Straight Grade	Grain size	Application
97WC-3Co	Medium	Machining of cast iron, nonferrous metals and nonmetallic materials; excellent abrasion resistance and low shock resistance; the most wear resistant of the straight WC-Co grades; maintains a sharp cutting edge and makes long finishing cuts to close tolerance possible; also used for fine wire dies and small nozzles.
94WC-6Co	Fine	Machining nonferrous and high-temperature alloys.
94WC-6Co	Medium	General-purpose machining of work materials other than steel; also used for small and medium size compacting dies, coating dies, burnishing rings and nozzles.
94WC-6Co	Coarse	Machining of cast iron, nonferrous metals and nonmetallic materials; also used for small wire-drawing dies, compacting dies, small drawing dies and caps and rings. The hardest grade used in mining applications where impact is encountered, as in rotary percussive bits.
90WC-10Co	Fine	Machining steel and milling high-temperature metals (including titanium and its alloys) at low feeds and speeds; face mills, end mills, form tools, cutoff tools and screw-machine tools.
90WC-10Co	Coarse	Primarily used for mining roller bits and percussive drilling bits.
84WC-16Co	Fine	Primarily used for mining and metal-forming components.
84WC-16Co	Coarse	Metal-forming and mining components: medium and large dies where great toughness is required, blanking dies for punch presses, and large mandrels.
75WC-25Co	Medium	Metal-forming components for heavy impact applications, such as heading dies, cold extrusion dies, and punches and dies for blanking heavy stock.

TABLE 24 continued

Complex Grade	Grain size	Application
71-74.5WC-10-12.5TiC-11-12TaC-4.5Co	Medium	Finishing, semifinishing and light roughing operations on plain carbon and alloy steels and alloy cast irons.
72-73WC-7-8TiC-11.5-12TaC-8-8.5Co	Medium	Tough, wear-resistant grade for heavy-duty roughing cuts. Successfully withstands high temperatures encountered in heavy-duty machining, interrupted turning, scale cuts and milling of plain carbon and alloy steels and alloy cast irons.
64TiC-28WC-2TaC-$2Cr_3C_2$-4Co	Medium	High-speed finishing of steels and cast irons.
57WC-27TaC-16Co	Coarse	Cutting hot flash formed in the manufacture of welded tubing; also used to make dies for hot extrusion of aluminum wirebar and tubing.

Source: Metals Handbook, Vol. 3, 9th Ed.

well as intelligent application. Titanium carbide-base cemented carbides commonly containing nickel as a binding metal have been the subject of lively interest from the earliest days of the carbide industry, particularly during times of critical material emergency. They have found an important but small and specialized field of use. The same is true of aluminum oxide-base ceramics and titanium carbide-aluminum oxide "cermets." Silicon nitride as a base compound for cutting tool materials is receiving current attention by the industry. Polycrystalline diamond and cubic boron nitride cutting tools are being increasingly applied to specialized areas of metal and composite material cutting. Growth in use of these alternate cutting tool materials will continue with the increasing use of newer materials of construction, with further advances in machine tool design, and with the "near net-shape" trend. They are not, however, considered capable of mass replacement of cobalt-bearing cemented carbides without unacceptable loss of productivity and economy in metal cutting. This is attributable to their relative brittleness and low cutting-edge strength.

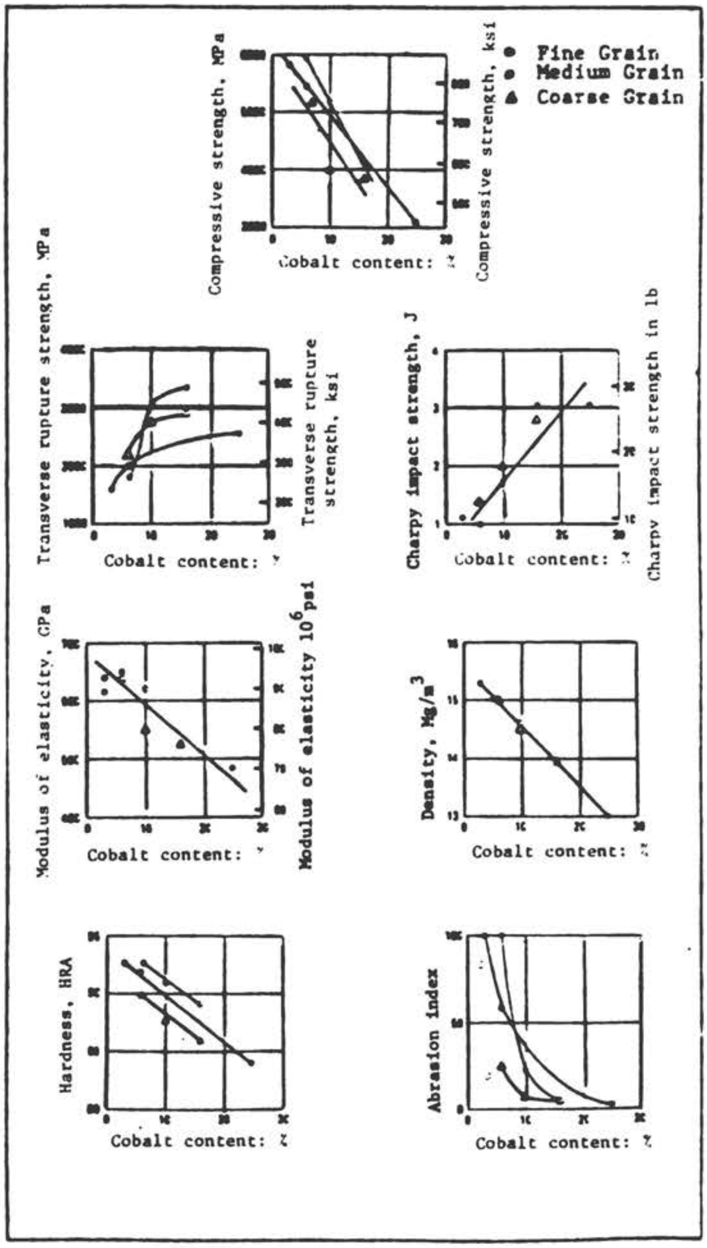


Figure 10 Variation of properties with cobalt content and grain size for straight grades of cemented carbides.
Source: Metals Handbook, Vol. 3, 9th edition.

Coal and hard-rock mining and oil and gas well-drilling applications depend on the unique combinations of strength, toughness, and abrasion resistance possessed by the tungsten carbide-cobalt alloys. There are no apparent practical alternates available or in sight today. The same is true for certain metal-forming and super-pressure applications.

About 80 percent of the cobalt powder used by the cemented carbide industry is of the "extra-fine" type; the balance is of somewhat coarser particle size but of similar purity. A typical cobalt powder specification is as follows:

Chemical Composition (percent):

Cobalt, min.	98.50
Oxygen, max	1.00
Nickel, max	0.10
Iron, max	0.10
Carbon, max	0.05
Calcium, max	0.05
Silicon, max	0.03
Sulfur, max	0.02
All others combined, max	0.10

MANUFACTURE:

Material--Shall be uniform in composition and free from dirt and other contamination

Particle size--The average particle size shall fall within 1.1-1.5 microns as determined by the Fisher Sub-Sieve Method (ASTM B330)

Sampling--Use ASTM B215

Particle size analysis (F.S.S.S.)--ASTM B330

The United States has the capacity to produce this extra-fine powder from cathode cobalt of 99.9 percent purity in sufficient quantity to supply the ongoing needs of the domestic cemented carbide industry (NMAB 1982).

In 1981 the U.S. industry produced about 8,300 tons of cemented carbide containing an estimated 830 tons of cobalt that consumed approximately 550 tons of "new" cobalt and 280 tons obtained from recycled scrap. About 220 tons of "new" cobalt went into metal-cutting tools and about 280 tons is judged to have gone into tools for mining, construction, oil and gas well drilling, and for certain very demanding metal-forming and super-pressure industry applications.

These estimates are based on the following assumptions:

- The Cemented Carbide Producers Association (CCPA) reported 7,111,000 kilograms sintered in 1981, which represents 95 percent of U.S. production.
- In 1981 metal-cutting applications used 45 percent of the U.S. cemented carbide sintered.
- The average cobalt content of cemented carbide used in metal-cutting applications was 8 percent by weight.
- Of the cobalt used in metal-cutting cemented carbides, 30 percent was obtained by recycling of scrap.
- Mining, oil and gas well drilling, metalworking, and other demanding applications used 45 percent of the U.S. cemented carbide sintered.
- The average cobalt content of cemented carbides used in demanding applications was 12 percent by weight.
- Of the cobalt used in demanding applications, 40 percent was obtained by recycling scrap.

The cemented carbide producers are expected to continue research on replacements for cobalt as a binding metal. Motivating factors include the desire for improvement in certain properties of the currently available alloys (e.g., corrosion resistance) and the well-known risks associated with dust exposure (Lichtenstein et al. 1975). The price of cobalt has been a relatively minor factor, but rapid increases, such as those experienced in 1978-1980, intensify the search. In a severe and prolonged cobalt shortage, the following would result:

- The metal-cutting industry could substitute non-cobalt-containing cemented carbides and other cutting tool materials, but with a significant loss in productivity.
- The mining, construction, and oil and gas well drilling and certain other industries with applications particularly dependent on the unique properties of the tungsten carbide-cobalt alloys would suffer the greatest impact of low efficiency.

There seems to be general agreement that the annual growth rate of U.S. cemented carbide production through the balance of the 1980s will approximate a compounded rate of 5 percent. The starting figures for 1981 reflect somewhat depressed conditions in metal-cutting use and a relatively strong mining and oil and gas well drilling tool market. Thus, it appears reasonable to assume that there will be no more than average growth in the latter area (which consumes higher cobalt-containing alloys) in the 1980s. The recovery and recycling of used cemented carbide is expected to gradually increase and thus will somewhat dampen the demand for "new" cobalt.

With these considerations in mind and in view of the purposes of this study, it seems reasonable to conclude that an estimated 3 percent long-range annual growth rate in total demand for cobalt should apply to the future demands of the U.S. cemented carbide industry (Reddy 1982, presentation of the survey of the cobalt supply and demand picture to the committee).

Conclusions Pertaining to Cemented Carbides

1. Cobalt in the form of extra-fine powder is a key requirement of the cemented carbide industry.
2. The use of cobalt-containing cemented carbides is critical to high productivity in metal cutting and forming, and in mining, oil and gas well drilling, and other important industrial operations.
3. Active and continuous carbide industry research on cobalt conservation measures and substitutes is principally driven by technical and supply considerations. Rapid price advances like those of the 1978-1980 period intensify this effort.
4. Other cobalt-free super-hard materials based on aluminum oxide, titanium carbide, silicon nitride, synthetic diamond, and cubic boron nitride supplement cobalt-containing cemented carbides principally in metal-cutting operations. These substitute materials cannot be considered as practical general alternates in major areas of industrial application but find extensive use in specific applications.
5. In view of the foregoing conclusions and an assumed annual long-range growth rate of 5 percent in domestic cemented carbide production, it is reasonable to plan for an annual growth of about 3 percent in carbide industry demand for "new" cobalt powder from the estimated 1981 figure of 550 tons.
6. There is adequate domestic capacity for producing extra-fine powder from cobalt of the quality recently added to the government stockpile.

WEAR-RESISTANT ALLOYS

Cobalt-base alloys have been used extensively as wear-resistant materials for over 60 years. Applications include automotive engine valves, fluid valves, knives, cutters, erosion shields, hot-working dies, and bearing surfaces that cannot be lubricated. The chemical composition of several of the most commonly used alloys is given in Table 25. It can be seen that the cobalt content of these alloys is on the order of 50 to 70 percent by weight. These materials are usually used as surface-weld deposits and are therefore commonly referred to as hardfacing alloys. In addition to hardfacing consumables, some of these materials are also produced as castings, powder metallurgy parts, and wrought forms. These materials generally possess not only excellent wear resistance, but also good high-temperature strength and resistance to corrosion and oxidation.

TABLE 25 Nominal Chemical Compositions of Several Cobalt-Base Hardfacing Alloys (percent)

Alloy	Co	Ni	Cr	Fe	W	Mo	C
STELLITE* No. 1	Bal	-	31	-	13	-	2.45
STELLITE No. 6	Bal	-	28	-	4.5	-	1.0
STELLITE No. 12	Bal	-	30	-	8.5	-	1.5
STELLITE No. 21	Bal	-	27	-	-	5.5	0.25
Substitute alloy [a]	Bal	23	26	29	4	3	1.1

* STELLITE is a registered trademark of Cabot Corporation.

[a] Gray, A. G., Substitution/Conservation Technology for Critical Materials, Metals Progress, December 1981, p. 18-27.

It is unclear how much new cobalt is consumed annually in cobalt-base cast, wrought, and powdered wear-resistant alloys (Metal Statistics 1981). The people reporting numbers to the Bureau of Mines may interpret differently the portions of this application category that fall under cutting and wear-resistant materials, welding and alloy hardfacing rods and materials, nonferrous alloys, or other alloys. If only the second item were used, the average for the years 1976 to 1980 is 3.2 percent. However, it is probable that some of the numbers submitted could add inflated amounts to wear-resistant materials, nonferrous alloys, or other alloys. If those numbers were subtracted and properly combined as cobalt-base wear-resistant alloys (exclusive of sintered carbides), the same average percentage could rise to 5 to 8 percent. This is of the same order of consumption as cobalt in catalysts and sintered carbides. Although wear-resistant alloys are not one of the biggest applications for cobalt, there still may be opportunities for many beneficial substitutions.

Cobalt Criticality and Alternatives

Studies conducted over the last several years have begun to shed some light on the criticality of cobalt in wear-resistant materials (Chandhok et al. 1962, Gulyaev and Kupalova 1970, Haswell et al. 1980, and Herth et al. 1982). This stems from the classification of wear into three basic modes:

1. Abrasive wear - material loss due to the sliding or rolling under pressure of hard, abrasive particles against a surface;

2. Adhesive wear - material loss due to the relative motion under pressure of metallic surfaces; and

3. Erosion and cavitation wear - material loss due to the action of solid particles or liquid droplets in a high-pressure fluid system, or material loss due to the collapse of bubbles within a liquid (cavitation erosion).

These wear modes permit the isolation of specific wear mechanisms that enable the role of cobalt to be assessed. However, there are many situations where several wear modes exist concurrently.

In abrasive wear, the volume fraction, size, morphology, and hardness of hard phases appear to control wear resistance. Attempts to develop nickel-base alternate alloys based on hard phase microstructural equivalency for abrasion resistance have been successful (Hickl 1966, Crook 1981). In most cases, alternate alloys demonstrated equivalent or superior abrasive wear resistance to the cobalt-base alloys currently used, at least at room temperature. At high temperature, the strength imparted by cobalt may be important. It should be noted that cobalt-base alloys are not usually selected in purely abrasive-type wear applications. Other materials, especially iron-base alloys, tend to dominate, so that cobalt is not an important issue in abrasive wear.

In metal-to-metal wear, the properties of the ductile matrix appear to control wear resistance. It has been shown that surface oxide films play an important role in low-load, metal-to-metal sliding studies conducted at room and elevated temperatures (Bhansali 1979). Thus, chromium content rather than cobalt content could be more important in certain metal-to-metal wear systems. Metal-to-metal wear at low loads, in the absence of galling, is an area where considerable progress has been made in substituting nickel-base alloys for cobalt-base alloys (Whelan 1980, Narasimham et al. 1981-82). At high loads, galling (gross damage) is promoted in metal-to-metal couples. In this situation, the cobalt-base alloys demonstrate superior performance in self-mating couples (e.g., valve and valve seat combinations). The experimental evidence points to the effect of cobalt in lowering the matrix stacking energy and the tendency for the cobalt base to twin and undergo the face centered cubic (fcc) to hexagonal close pack (hcp) allotropic transformation as the result of surface mechanical deformation in the wear couple. Attempts to develop nickel-base alloys with galling resistance equivalent to their cobalt-base counterparts have been less successful (Chandhok et al. 1962, Gulyaev and Kupalova 1970). However, it has been demonstrated that alloys with significantly less cobalt can be developed with comparable galling resistance (Haswell et al. 1980, Hirth et al. 1982).

There is some similarity between solid particle impingement erosion and abrasive wear. This similarity is most obvious at low impingement angles. One would assume, therefore, that alloy hard-phase characteristics play an important role in determining the rate of mechanical degradation. Nickel- and iron-base alloys may be viable alternatives to cobalt-base alloys using the same approach of hard-phase microstructural equivalency that was demonstrated for abrasive wear resistance. In the case of cavitation erosion, as in the case of galling, the matrix phase properties would appear to assume the dominant role. The cobalt-base alloys with their unique matrix characteristics demonstrate superior performance. However, alloys with reduced cobalt levels have been developed that possess comparable cavitation erosion resistance (Hirth et al. 1982).

In summary, the assessment of the role of cobalt wear-resistant materials has been facilitated through the classification of wear into specific wear modes. Experimental evidence indicates that cobalt could be substantially reduced or possibly eliminated in applications involving abrasive wear. This may be a moot point, however, since cobalt-containing alloys are not usually selected in abrasive wear applications. Under metal-to-metal sliding conditions, oxidation characteristics are the key to performance, and opportunities for alloys containing low or no cobalt exist. In high-load, metal-to-metal couples, galling is promoted. Because of its unique properties, cobalt provides important performance benefits. However, alloys with lower cobalt levels provide alternatives to the commonly used alloys. The same can be said for cavitation erosion wear. For particle impingement erosion, alloy hard-phase characteristics appear to be more important than matrix characteristics, and there should exist opportunities for alternate alloys containing low or no cobalt. One application (Narasimham et al. 1981-1982) where nickel-base wear-resistant alloys are gaining in substitution over cobalt-base alloys is hardfacing for automotive engine valves and valve-seat inserts. Here, extensive service testing has shown the nickel-base properties to be wholly comparable or better. A considerable cost reduction can be made in alloy content and method of deposition, since nickel-base hardfacing is more easily processed as powder.

Cobalt Savings as a Function of Price

At the 1982 price of cobalt relative to other suitable replacement alloys, there is only a small incentive to replace high-cobalt-content, wear-resistant alloys with alternate alloys. This stems not only from a reduced economic justification for alloy replacement, but also from the reluctance to substitute new materials for cobalt alloys that have a long and well-proved track record. With cobalt at 3 times the current price level and higher, relative to other alloying elements, such as seen in the cobalt crisis of 1978, a much greater economic incentive would be created, in addition to the availability incentive. Commercially available alloys containing greatly reduced levels of cobalt or no cobalt would be available as substitutes for the common cobalt-base alloys.

Depending on the application, a time interval for testing would be required to verify the properties of a substitute alloy. However, the evaluation expenditures incurred would be expected to be offset by the cost reduction represented by the substitute alloy. At a cobalt price of 10 to 15 times the 1982 price level, efforts to use substitute alloys would sweep all areas of wear application. It is believed that these efforts would be largely successful with alternative materials already commercially available, and it is estimated that up to half of the cobalt currently used in wear-resistant alloys could be conserved.

Conclusions Pertaining to Wear-Resistant Alloys

1. In wear applications requiring either resistance to galling or resistance to cavitation erosion, cobalt is a required alloying element.
2. If the price and availability of cobalt were to return to the situation experienced in 1978, a high incentive to replace cobalt in wear-resistant alloys would exist. Replacement alloys have been identified and would be available for immediate application.
3. Substitutional alternatives might conserve up to half of the cobalt currently used in wear-resistant alloys.

HIGH SPEED TOOL STEELS

Cobalt is added to high-speed steel to increase tool life. This is particularly true for applications that involve difficult-to-machine materials such as high-hardness and austenitic stainless steels, superalloys, and titanium alloys. In machining the difficult-to-machine materials, high heat is generated that results in softening of the tool steel so that performance deteriorates. The addition of cobalt in the range of 5 to 12 percent to high-speed steels increases the attainable hardness, temper resistance, and hot hardness so that performance is markedly improved in severe machining operations.

Tool steels have been grouped into eight major categories, and each commonly accepted group of tool steels has been assigned a letter symbol. These are as follows:

- o Standard high-speed tool steels: M--molybdenum types, and T--tungsten types
- o Intermediate high-speed tool steels: M50 to M59 molybdenum types
- o Hot-work tool steels: H series, H1 through H59

- Cold-work tool steels: D--high carbon, high-chromium types; A--medium-alloy air-hardening types; and O--oil hardening types
- Shock resisting steels: S
- Mold steels: P
- Special-purpose tool steels: L
- Water-hardening tool steels: W

Except for the high-speed tool steels, the only cobalt-bearing standard grades are hot-work tool steel, H19 (0.40 C, 4.25 Cr, 2.0 V, and 4.25 Co), and cold-work tool steel, D5 (1.5 C, 1.0 Mo, 12.0 Cr, 3.0 Co). The amount of cobalt involved in the hot- and cold-work steels is minor compared to that of high-speed tool steels, and therefore steels other than the high-speed steels will not be considered any further.

A recent listing of the high-speed tool steels made in the United States is shown in Table 26. Typical applications for these steels include broaches, chasers, cheeking tools, drills, end mills, hobs, lathe tools, milling cutters, planer tools, punches, reamers, grouters, saws, taps, woodworking tools and cold-work applications such as cold header die inserts, thread rolling dies, punches, and blanking dies. Half the molybdenum-type high-speed steels (M types) contain cobalt, whereas all but T1 of the tungsten-type high-speed steels contain cobalt.

The amounts of cobalt in cobalt-bearing high-speed steels produced in the United States from 1978 through 1981 are shown in Table 27. The M-type high-speed steels represent the major users of cobalt; however, the total high-speed steels contain some 600,000 to 800,000 pounds per year.

The effect of cobalt on the temper resistance and microstructure of tool and alloy steels was shown to be related to the increased amount and decreased size of carbide particles that form during tempering (Chandhok et al. 1963, Gulyaev and Kupalova 1970). The increase in carbide nucleation rate, which causes a large number of carbide nuclei to form, and the decrease in growth rate of the carbides are related to the increase in the activity of carbon in ferrite (Chandhok et al. 1962). Thus, cobalt increases the amount and slows down the coalescence of carbides to give greater temper resistance and hot hardness.

The manufacturing method for producing high-speed tool steel primarily involves melting in small electric furnaces (maximum size about 35 tons) and casting into relatively small ingots, (maximum size on the order of 20 by 20 inches). The primary reason for the limitation in furnace size is that small ingots are required because of the carbide segregation that occurs in the slow cooling process. When larger ingot sizes are used, the massive carbides are difficult to break up, so that difficulties are encountered in hot-working to finish size. Also, in the final microstructures, carbide segregations of various types are detrimental to tool performance.

TABLE 26 High-Speed Tool Steels

Type	UNS	Identifying Elements (percent)					
		C	W	Mo	Cr	V	Co
M1	(T11301	0.85*	1.50	8.50	4.00	1.00	-
M2	(T11302)	0.85;1.00*	6.00	5.00	4.00	2.00	-
M3 Class 1	(T11313)	1.05	6.00	5.00	4.00	2.40	-
M3 Class 2	(T11323)	1.20	6.00	5.00	4.00	3.00	-
M4	(T11304)	1.30	5.50	4.50	4.00	4.00	-
M6	(T11306)	0.80	4.00	5.00	4.00	1.50	12.00
M7	(T11307)	1.00	1.75	8.75	4.00	2.00	-
M10	(T11310)	0.85;1.00*	-	8.00	4.00	2.00	-
M33	(T11333)	0.90	1.50	9.50	4.00	1.15	8.00
M34	(T11334)	0.90	2.00	8.00	4.00	2.00	8.00
M36	(T11336)	0.85	6.00	5.00	4.00	2.00	8.00
M41	(T11341)	1.10	6.75	3.75	4.25	2.00	5.00
M42	(T11342)	1.10	1.50	9.50	3.75	1.15	8.00
M46	(T11346	1.25	2.00	8.25	4.00	3.20	8.25
T1	(T12001)	0.75*	18.00	-	4.00	1.00	-
T4	(T12004)	0.75	18.00	-	4.00	1.00	5.00
T5	(T12005)	0.80	18.00	-	4.00	2.00	8.00
T6	(T12006)	0.80	20.00	-	4.50	1.50	12.00
T8	(T12008)	0.75	14.00	-	4.00	2.00	5.00
T15	(T12015)	1.50	12.00	-	4.00	5.00	5.00

Note: Some of the types can be produced with sulfur addition to improve machinability.

* Other carbon contents may be available.

Source: Tool Steels, Steel Product, AISI, September 1981.

In 1970 a commercial process using particle (powder) metallurgy (PM) of gas-atomized induction-melted prealloyed high-speed steel followed by hot isostatic pressing was introduced to make a superior quality product. The primary advantage of the PM approach was to eliminate carbide segregation by the very rapid cooling of the individual particles or microingots. Rapid solidification technology in general is currently being widely investigated for various types of steels as a means of upgrading and developing entirely new alloys that can be made only using this process.

In addition to making improved, low-segregation, standard-composition high-speed steel grades, entirely new steels that can only be made by the particle metallurgy process are being introduced. Cobalt-free high-speed steels, CPM Rex 20 and CPM Rex 25, were developed as replacements for the cobalt bearing steels, M42 and T15 (Hirth et al. 1982) when the cobalt supply was disrupted in 1978. Because of the high tungsten equivalency (W + 2Mo), CPM Rex 20 and 25 steels can be made only by the particle metallurgy process. The chemical composition of these cobalt-free high-speed steels is shown in Table 28.

TABLE 27 Cobalt Contained in High-Speed Steel Ingots Produced for U.S. Consumption (tons except where indicated)

Category	1978	1979	1980	1981
U.S.A. shipped, M-type[a]	3018	2905	2941	2344
U.S.A. shipped, T-type[a]	575	639	552	476
Total U.S.A. shipped	3583	3544	3493	2820
Imports of mill products[b]	--	815	559	1072
		4359	4052	3892
At 65 percent, ingot production		6706	6234	5988
Cobalt contained in ingots[c]		563	499	479
Pounds contained cobalt (thousands)		1126	998	958

[a] AISI data of U.S. producers.

[b] Imports of high-speed steel bar, rod, and wire; data from the Department of Commerce. Same percent of total high-speed steel imports used for cobalt grades.

[c] Based on an average of 8 percent.

Table 28 Chemical Compositions

Steel	Composition (percent weight)						
	C	Cr	V	W	Mo	Co	Weq.*
CPM Rex 25	1.80	4.0	5.0	12.50	6.5	-	25.5
T15	1.55	4.0	5.0	12.25	-	5.0	12.25
CPM Rex 20	1.30	3.75	2.0	6.25	10.50	-	27.25
M42	1.10	3.75	1.10	1.50	9.50	8.0	20.5

* Weq. = percent W + 2 x percent Mo.

An increase in tungsten or molybdenum or both, so that the tungsten equivalency (Weq.) increases, produces retardation of tempering and hot hardness retention of the same order as cobalt. The effects of Weq. on nucleation, growth, and agglomeration of carbides appear to be parallel to those of cobalt (Hirth et al. 1982). A comparison of CPM Rex 20 with M42 shows that cobalt-free CPM Rex 20 is at least the equivalent of M42 in temper resistance, hot hardness, and toughness (Tables 29, 30, and 31).

TABLE 29 Temper Resistance of CPM Rex 20 and M42

	Hardness (HRc) After Indicated Exposures (°F)				
	As heat-treated hardness (HRc)	1100		1200	
Grade	2175/1025/3x2hr	2 hrs	2+2 hrs	2 hrs	2+2 hrs
CPM Rex 20	67.5	66.0	65.5	60.0	57.0
CPM M42	67.0	65.5	65.5	59.0	55.5
Conv. M42	67.5	65.0	65.0	59.0	55.0

TABLE 30 Hot Hardness of CPM Rex 20 and M42

	Hot Hardness (HRc) at Indicated Temperatures (°F)				
	Room Temp.	Test Temperature			Room Temp.
Grade	Before Test	1000	1100	1200	After Test
CPM Rex 20	67.5	58.2	56.0	47.5	63.8
CPM M42	67.0	58.4	56.0	48.0	63.0
Conv. M42	66.5	58.5	56.1	48.0	62.2

TABLE 31 C-Notch Impact and Bend Fracture Strengths of CPM Rex 20 and M42

		Response to Heat Treatment and Properties		
Grade	Aust.* Temp.(°F)	HRc	C-Notch Impact Strength (ft-lb)	Bend Fracture Strength (ksi)
CPM Rex 20	2175	67.5	12	581
CPM Rex M42	2175	67.5	12	581
Conv. M42	2175	67.5	5	372

* Minute soak in bath and oil quenched; triple tempered at 1025°F.

Results of extensive field testing by many tool manufacturers and users showed the cobalt-free high-speed steels to be as good as the most commonly used cobalt-bearing grades M42 and T15. The new steels CPM Rex 20 and 25 have been commercially adopted and their use is growing. Thus, cobalt is an element not critically needed for high-speed tool steels. The use of cobalt will be determined by economic considerations.

A relatively recent process to increase tool life in high-speed steel tools is hard-coating of finished tools. The prevalent current coating process is chemical vapor deposition (CVD) by which a thin, hard coating of TiN or TiC is applied. The use of coatings that increase tool life will decrease the needed volume of cobalt-bearing steels.

Conclusions Pertaining to High-Speed Tool Steels

1. Cobalt is an element that is not critically needed for high-speed tool steels. The use of cobalt will be determined by economic considerations.

2. Cobalts price over $20 per pound, resulted in price increase for cobalt-bearing high-speed steel sufficient to create a strong user interest in substitute grades and new cobalt-free grades. The user concern was both one of cost and availability of suitable high-speed steels for difficult-to-machine materials.

3. By using substitute grades, a cobalt use decrease in the United States of 600,000 to 800,000 pounds could occur if required by a critical shortage period.

MARAGING STEEL

To fill the aerospace industry's needs for ultra-high strength materials that have good toughness, the International Nickel Company developed 18 percent Ni maraging steels in the early 1960s (Decker et al. 1962; Magnee et al. 1974). Although the initial applications for these steels were in the aerospace industry, now they are used for tools and other structural applications as well. The numerical designations of the four different types of maraging steels (Table 32) indicate the strength level in the grade designation; i.e., 18Ni200 implies a strength level of 200,000 psi and 18Ni350 a strength level of 350,000 psi. The most commonly used grade by far is 18Ni250.

Maraging steels achieve full hardness and strength by a simple aging treatment, usually 3 hours at about 900°F (480°C). Hardening and strengthening do not depend on cooling rate, so that full hardness and strengthening can be developed uniformly in massive sections with almost no distortion. Also, decarburization is of no concern in these alloys because they contain very little carbon and aging temperatures are relatively low.

TABLE 32 Nominal Chemical Composition of Maraging Steels (weight percent)

Element	18Ni200	18Ni250	18Ni300	18Ni350
Nickel	18.50	18.50	18.50	18.50
Cobalt	8.50	7.50	9.00	12.00
Molybdenum	3.25	4.80	4.80	4.80
Titanium	0.20	0.40	0.60	1.40
Aluminum	0.10	0.10	0.10	0.10
Silicon	0.10 max	0.10 max	0.10 max	0.10 max
Manganese	0.10 max	0.10 max	0.10 max	0.10 max
Carbon	0.03 max	0.03 max	0.03 max	0.03 max
Sulfur	0.01 max	0.01 max	0.01 max	0.01 max
Phosphorous	0.01 max	0.01 max	0.01 max	0.01 max
Zirconium	0.01	0.01	0.01	0.01
Boron	0.003	0.003	0.003	0.003

A survey of the producers of maraging steel indicates that production ranges from 1,000 to 2,000 tons per year, so the amount of cobalt involved is 180,000 to 360,000 pounds per year. [Estimates supplied by Teledyne Vasco and International Nickel Company.] A cobalt-free 18Ni250 alloy was recently developed by INCO Research and Development Center. In a joint program with Teledyne Vasco, this new steel was scaled up to commercial production and application. Compositions of 18Ni250 and the cobalt-free 18NiT250 (T for titanium) are shown in Table 33. The cobalt-free grade also has less molybdenum, but substantially greater titanium than the original 18Ni250 alloy. Nominal mechanical property comparisons of the two steels are shown in Table 34. Tests by Teledyne Vasco and other firms have shown the cobalt-free grade properties to be consistent with those of the cobalt-bearing 250 grade.

TABLE 33 Nominal Chemical Compositions (weight percent)

Grade	Ni	Co	Mo	Ti	Al	Zr	B
18Ni250	18.5	7.5	4.8	0.40	0.10	0.01	0.003
Vasco Max T-250	18.5	-	3.0	1.40	0.10	0.01	0.003

Note: In addition, 0.10 max Si and Mn, 0.03 max C, and 0.01 S and P.

Source: Vasco Max T-250 1982.

TABLE 34 Nominal Mechanical Properties

Property	18Ni250	Vasco Max T-250
Tensile Strength, ksi	260	260
0.2% yield strength, ksi	255	255
Elongation, percent	11	10
Reduction of area, percent	58	52
Notch tensile strength (K_t 5.0), ksi	381	384
Charpy V-Notch, ft-lb	20	18
Hardness, R_c	48/52	48/52

Source: Vasco Max T-250 1982.

Conclusions Pertaining to Maraging Steel

1. A cobalt-free maraging steel has been developed to replace most of the volume of grade 18Ni250 used, so cobalt is not considered critical for these steels.
2. For critical aerospace applications, time-consuming and costly qualification testing will be required before substitution can be made.

CATALYSTS

There are many applications for cobalt as a catalyst in processes to produce chemicals and to alter petroleum feedstocks. This catalytic activity is associated with many of the elements in the transition series; other elements in Group VIII of the periodic table of elements are also extensively used as catalysts. Electron shell configuration is a fundamental reason for the difference in catalyst activity from one metal to another, but there is not enough information currently available to predict their relative behavior from this structure.

Cobalt is used as a catalyst in the following processes:

Process	Catalyst Types	Products
Hydrotreating	Cobalt and molybdenum oxides on alumina	Transporation and heating fuels, lube oils
Hydroformylation (Oxo process)	Soluble cobalt salts	C_4-C_{13} alcohols
Terephthalic acid dimethyl terephthalate production	Soluble cobalt salts	Fiber monomers
Pyrolysis gasoline hydrogenation	Cobalt and molybdenum oxides on alumina	Gasoline
Organic acids production (acetic, adipic, benzoic)	Various	Various organic compounds

Estimated U.S. annual use of cobalt (metal basis) in these processes over the last few years has ranged as follows (in thousand pounds per year):

Process	Amount Used
Hydrotreating	400 - 700
Hydroformylation	600 - 800
Terephthalic acid and dimethyl terephthalate production	200 - 300
Pyrolysis gasoline hydrogenation	20 - 30
Organic acids production	30 - 40
Total	1250 - 1870

Hydrotreating

Petroleum refiners remove sulfur, nitrogen, and metals from various streams in order to meet product specifications, satisfy environmental regulations, and protect the catalysts in other processes. These hydrotreating processes are shown in the simplified refinery flow-sheet of Figure 11.

Most hydrotreating processes are fixed-bed operations, in which the petroleum stream is fed down over a catalyst bed. Typical operating conditions are 200 to 2000 psig, 500°F to 800°F, and hydrogen partial pressures of 50 to 1200 psia; capacities range from 200 to 100,000 barrels per stream day (BPSD). Catalyst loading in a 44,000 resid BPSD unit typically is about 1.5 million pounds. Depending on the feedstock and the severity of the operation, the life of the catalyst ranges from 6 months to several years.

Typical hydrotreating catalysts contain either molybdenum and cobalt or molybdenum and nickel on an alumina support. The metals range in content from 8 to 11 percent for the molybdenum and 1.5 to 3.5 percent for either the cobalt or nickel (weight percents expressed as metal). For certain hydrocracking processes, the catalytic metals are nickel and tungsten in the feed pretreatment. Prior to use, the catalysts are pre-sulfided, so the actual chemical forms of the metals in use are sulfides.

During the process, the sulfur and nitrogen contained in complex organic compounds are catalytically reduced to hydrogen sulfide and ammonia while the metals in the oil, such as vanadium and nickel, are adsorbed on the catalyst. Concurrently, some saturation of the polynuclear aromatic compounds and cracking of these to lighter products is occurring. There is also a deposition of carbon on the catalyst together with other impurities. This contamination gradually decreases the activity of the catalyst.

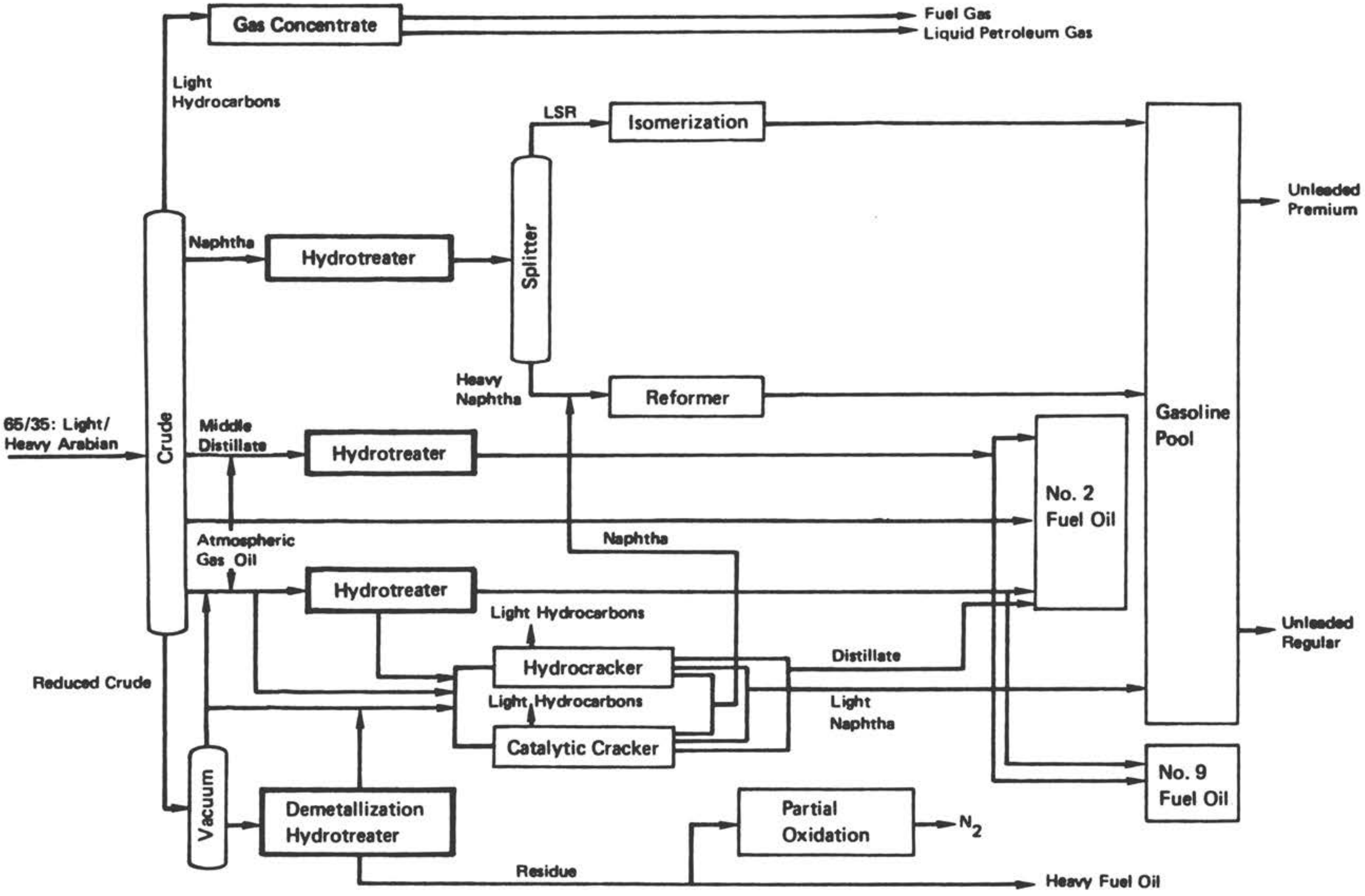


Figure 11 Crude oil refinery flow sheet.

Current refinery capacity in the United States for crude distillation is about 18 million barrels per day. There are about 9 million barrels per day of hydrotreating capacity. An estimated 40 to 60 million pounds of hydrotreating catalysts are installed in these units, of which about half are cobalt-molybdenum catalysts. In 1982, about 20 million pounds of hydrotreating catalysts will be installed. Approximately 8 to 10 million pounds of these will be cobalt-molybdenum types containing from 200,000 to 300,000 pounds of cobalt. Actual use of cobalt in these types of catalysts will be somewhat higher because of exports. The 1982 use is somewhat below previous years because of lower refinery utilization.

Catalyst Preparation

The steps to make the hydrotreating catalysts are as follows: Alumina powder is rehydrated and formed into tablets, beads, or extrudates. After drying and calcining, these substrates are impregnated with solutions of metals and then dried and calcined. Any fine particles coming off the calciners and driers are usually recycled in the process.

Catalyst Disposition

When the catalyst activity falls below some economically determined level, it is dropped out of the reactor. It may then either be regenerated (the coke that has accumulated is burned off) or sent out for disposal. Many of the spent hydrotreating catalysts have been purchased by metals reclaimers who recover molybdenum and vanadium but not cobalt.

Hydroformylation

Ten companies in the United States and one in Canada produce alcohols ranging from C_4 to C_{13} via the Oxo process or a Ziegler-type oligomerization. In the Oxo process, ethylene or propylene is reacted with CO and H_2 in the presence of a cobalt or rhodium catalyst to form a linear alcohol (hence hydroformylation). In the Ziegler-type process, triethylaluminum triggers a chain-growth mechanism with the olefins and is consumed in the course of the process. Of the estimated 3.2 million pounds capacity in place on January 1, 1981, about 95 percent was Oxo process. Of the Oxo process units, 73 percent were designed for cobalt catalysts; the balance use rhodium catalysts.

Estimates of U.S. production of alcohols from these processes are shown in Table 35. The C_4 and C_5 alcohols are used primarily as solvents while the higher alcohols are further processed to produce plasticizers, mainly phthalates. Some of the C_{12} alcohols are used to make detergents.

TABLE 35 U.S. Production of Plasticizer Alcohols (millions of pounds)

Product	1979	1980
n-Butanol	767	772
Isobutanol	143	140
Amyl alcohol	55	55
Hexyl alcohol (non-Ziegler)	15	15
2-Ethylhexanol	318	318
Isooctyle alcohol	70	70
Isononyl alcohol	155	145
Isodecyl alcohol	170	130
Linear C_6 - C_{11} alcohols	310	275
Tridecyl alcohol	50	50
Total	2053	1977

Source: Gibson et al. 1981.

Oxo Process

Propylene and synthesis gas (CO, H_2) are reacted with a cobalt catalyst (in the form of cobalt carbonyl) at 110°C to 160°C and 1,500 psig. A mixture of the normal and isobutyraldehydes is formed, and these are then hydrogenated to produce the alcohols. Where a higher normal and isobutyraldehyde mix is wanted, rhodium replaces the cobalt. A further modification of the process uses the cobalt or rhodium catalyst with trialkylphosphine ligands, giving a direct route to the alcohols with a higher n and iso ratio.

The first stage of the reaction, i.e., the hydroformylation, is a homogeneous catalytic process. The hydrogenation step may be carried out via heterogeneous catalysis where the catalyst metal has been impregnated on a support.

There is a continuous recycling of the catalyst in this process. There is also a withdrawal of catalyst, which is sent back to the chemical manufacturers for recovery of cobalt.

Production of Terephthalic Acid and Esters

Another major cobalt catalyst use in the United States is the production of terephthalic acid (TPA) and its esters from paraxylene. TPA and dimethyl terephthalate (DMT) are used primarily to produce fibers and films, with some TPA converted to poly(ethylene terephthalate). Table 36 shows U.S. supply and demand for these chemicals in 1979; estimated demand for DMT equivalents is expected to grow at an average annual rate of 4.5 percent through 1984.

TABLE 36 U.S. DMT and TPA Supply and Demand, 1979 (millions of pounds)

Category	DMT	TPA
Production	3540	2200
Imports	neg.	neg.
Exports	160	470
Domestic consumption	3380	1730
Domestic end-use markets		
Polyester fibers	2780	1510
Polyester film	340	70
Polyester terephthalate bottle resins	120	120
Thermoplastic PBT and PET resins	50	neg.
Miscellaneous	90	40
Nameplate capacity	4250	3080
Production to nameplate capacity ratio	84%	71%
Domestic demand to nameplate capacity ratio	80%	56%

Source: Gessler 1981.

Processes

The Witten process, or variations of it, is used to produce most of the world production of DMT. Paraxylene, in a liquid-phase reaction, is oxidized to p-toluic acid. This is then esterified to methyl p-toluate, which is next oxidized to monomethyl terephthalate. The latter is then further esterified to DMT. The oxidation steps are promoted by a cobalt-manganese catalyst.

In this process, quite similar to the Oxo process, the cobalt is used in the form of a soluble salt and is fed into a reaction zone, along with air and the paraxylene to be oxidized. The product is then separated and the catalyst is constantly recycled and used on site. Also, as in the Oxo process, there are some inevitable losses. Cobalt-containing residues are returned to chemical suppliers for reprocessing into fresh catalyst make-up material.

Pyrolysis Gasoline Hydrogenation

Pyrolysis gasoline is a by-product of the process used to make ethylene and propylene by thermal or steam cracking of hydrocarbon feedstocks. Pyrolysis gasoline is catalytically treated in two stages to saturate the olefins present and to remove sulfur. Cobalt catalysts are usually used in the second stage. There are about 25 such units operating at refineries in the United States, and estimated 200,000 pounds of cobalt-type catalysts are in place in these units. The catalysts are the same as those used in hydrotreating, with an estimated life of about 3 years.

Production of Organic Acids

Organic acids use relatively small quantities of cobalt catalysts. Acetic acid made by the BASF process (high-pressure methanol carbonylation) uses a 50 percent combination of cobaltous acetate and iodine as catalyts. In the conventional du Pont process to produce adipic acid, cobalt naphthenate or stearate is used as a catalyst in the first oxidation step of cyclohexane to cyclohexanol. It is believed that very small quantities of cobalt catalysts are also used in the production of benzoic acid.

Alternatives for Cobalt in Catalysts

(Neal 1982, private communication to the committee)

Hydrotreating Catalysts

Processing Practices

Three methods of approach may show material savings in the use of cobalt in refinery processing catalysts. The first is more effective use of the metal. As understanding of the fundamentals of catalysis improves and the quantifiable physical and chemical characteristics can be better correlated with measures of performance, the same results will be obtained with lower metals content. This kind of research will obviously be given highest priority when cobalt supply becomes tight again.

A more immediate means of saving cobalt is the recycling of spent catalysts. Reclaimers so far have taken out only molybdenum and vanadium; the latter, together with nickel, is present in the crude oil and deposits on the catalyst. With the rapid drop in molybdenum prices from 1980 and the fall in demand for molybdenum, these operations have become economically marginal. Furthermore, they did not produce metals that were fully recyclable in catalysts. Two companies have recently announced that they will build plants in the United States that will recover cobalt and the other useful metals. It is anticipated that, beginning in 1984, the United States will have the potential to recover essentially all of the cobalt from any type of catalyst.

A third step that will decrease overall demand for cobalt is an increased use of catalyst regeneration. Cleaning up spent catalyst and returning it to use increases its life. This has been a gradually increasing practice with U.S. refineries.

Substitution Alternatives

Nickel-molybdenum catalysts are currently widely used in a variety of hydrotreating processes. In general, they are more effective than cobalt-molybdenum types for denitrification and hydrogen uptake, whereas cobalt-molybdenum varieties show higher desulfurization activity. Research carried out by refinery laboratories indicates that a significant portion of the remaining cobalt-molybdenum catalyst applications might use nickel catalysts without any substantial process penalty. This is fortunate because the products of the refining processes are vital for the national economy and defense.

Oxo Alcohol Catalysts

Processing Practices

Oxo alcohol catalysts are recycled in the process but, over a period of time, there tends to be a build-up on the walls of the reactor and on the tower packing. This material is currently being sent to a reclaimer who recovers high-grade cobalt suitable for recycling. About 90 percent is now being reclaimed; the remaining 10 percent is lost in various handling steps.

Substitution Alternatives

Alternate routes to manufacturing oxo alcohols using catalysts other than cobalt are in commercial operation, but it is not apparent what could be substituted for cobalt in the processes now employing this metal. Thus, the best prospects for conservation in this area are to cut down on process losses and ensure maximum reclaiming of cobalt from process residues. The alcohols are available from the same process using rhodium catalysts and from other processes, and therefore cobalt is not critical for the production of these chemicals from this process.

TPA and DMT Catalysts

Processing Practices

A situation similar to the oxo alcohol catalysts exists for TPA and DMT; there is recycling of catalysts in the process. As the by-products build up, catalyst material is withdrawn from the reactors. This cobalt-containing sludge is incinerated and sent out for reclamation of the metal. Currently about 50 percent is being reclaimed, and this will increase to 90 percent in the near future as a major user installs incineration facilities.

Substitution Alternatives

The production of terephthalate esters for fibers and films in today's plants is highly dependent on cobalt, and there does not appear to be any alternative. However, there are fibers that could be substituted for those made from DMT.

Pyrolysis Gasoline and Organic Acids

Processing Practices

There is no reclamation today of cobalt from pyrolysis gasoline catalysts. The status of reclamation of the organic acid catalysts is unknown.

Substitution Alternatives

Nickel-molybdenum catalysts can be used for pyrolysis gasoline processes. Many other routes to organic acids are in commercial practice, so cobalt can effectively be substituted by using other processes.

Conservation Trends in Cobalt for Catalysts

Although there are always further opportunities to reduce catalyst use through tighter process controls, the amount that can be saved appears to be small since these are relatively mature businesses. A substantial amount of cobalt is now being reclaimed in two of the major processes--hydroformylation and terephthalate esters.

When new plants to recover cobalt from spent hydrotreating catalysts come into production, it is possible that fresh cobalt additions per year could fall as low as 200,000 to 400,000 pounds per year. More efficient use of cobalt in hydrotreating catalysts combined with greater regeneration could reduce this another 100,000 pounds.

Almost all of the hydrotreating catalysts and those for pyrolysis gasoline could ultimately be based on nickel-molybdenum rather than cobalt-molybdenum. Thus, with the conservation steps postulated under the discussion of processing practice, it is probably possible to reduce fresh cobalt metal requirements for catalysts to under 100,000 pounds per year.

Developing Uses for Cobalt Catalysts

The most significant possibilities for an increase in cobalt demand for catalyst preparation over the next 10 years are in hydrotreating, particularly the residual fractions, and in shale-oil processing. In both cases it is possible to use nickel in place of cobalt to achieve almost equal results. Thus, no marked increase in demand for catalyst applications is foreseen within this time period.

Conclusions Pertaining to Catalysts

1. Of the three major applications of cobalt in catalysts, only hydrotreating materials are amenable to substitution; there is a continuing trend toward replacing cobalt with nickel.
2. If cobalt supplies were totally cut off, most hydrotreating applications could be converted to nickel-molybdenum catalysts.
3. Additional regeneration of catalysts, will reduce annual requirements for cobalt to a small degree--about 5 to 10 percent.
4. Reclaiming metals from spent catalysts will soon reach about 90 percent recovery of cobalt in hydroformation and in TPA and DMT processes.
5. In about 2 years, some 85 to 90 percent of the cobalt in hydrotreating catalysts will be recovered.
6. More efficient use of other metals in catalysts is theoretically possible but will probably not be achieved in a substantial measure over the next 10 years.

PAINT DRIERS

Cobalt is of central importance to paint driers and other chemicals used in applications other than Oxo and related petrochemical synthesis reported in the preceding section. These represent approximately 12 percent of the total U.S. consumption of cobalt in recent years. Most of these uses involve cobalt concentrations of much less than 1 percent of the affected product in diverse billion dollar industries. Primary cobalt uses in these chemicals include: driers in paints (500,000 pounds), porcelain enamel frits (500,000 pounds), inorganic pigments (300,000 pounds), unsaturated polyesters [in plastics] (250,000 pounds), and cobalt soaps in petrochemical catalysts (250,000 pounds). [Amounts are estimates for 1980.]

Partial or complete replacement of cobalt in the applications cited above is possible, but only with significant disruptions in some major segments of the economy, including the military. In driers for paints, part of the overall replacement problem involves duplicating the complicated chemical interaction of cobalt with other transition metal additives in paint formulations, such as manganese, nickel, and perhaps zirconium. These complexities, coupled with the fragmentation of the industry, the diversity of paint products, and legal aspects (involving warranties, product liability, and government regulations) dictate against reduced use of cobalt except under emergency conditions. An additional complication is that cobalt replacements impinge on the price and supply of the other additives, (i.e., Mn, Ni, and Zr) which have their own logistic problems, as well as the hundredfold substrate or product systems that cobalt so strongly enhances.

The Function of Cobalt in Driers

Cobalt is the surface drier and while substitutions can be made in the form of manganese and other metals, there always will be some consumption of cobalt although it could be reduced significantly in an emergency. The $8 billion annual production of paints represents over 1 billion U.S. gallons, more than half of which is in architectural use where the paint is air dried and therefore, may require much cobalt. The other half-billion gallons are very diverse and is both baked and air dried. In a war economy some of these uses would have high priorities as with insignia, armor, and camouflage paints, and other coatings even more unique.

The following statistical information on cobalt in paint driers is noteworthy. About 2 billion pounds of nonvolatile binder (e.g., polymers and oligomers) are used in the one billion gallons of paints. Among these are the 700 million pounds of alkyds (see Apendix Table C-2), plus lesser amounts of drying oils per se, bisphenol A epoxy esters of drying oil acids, and similar organics. This gives a total of about one billion pounds of binders requiring drier catalysts of cobalt and other metals. The typical requirement of 0.05 percent of cobalt, if applied loosely to 1 billion pounds of paint media, amounts to only 0.5 million pounds of cobalt. This is far less than the 1.021 million pounds of cobalt content in the drier production in the Bureau of Mines cobalt report for 1980. It is also much less than the 1.501 million pounds in 1979. This discrepancy seems too big to ignore.

Paints as reported in the SIC 2851 category probably entail large reporting and sampling errors because of the industry complexities. Tracing cobalt use through the SIC 2851 route may be impractical and erroneous because of increasing use of cobalt soaps in other SIC categories. The 1.021 million pounds of cobalt in "driers (organic compounds)" in 1980 may likely have three major uses: 500,000 pounds as driers in paints; 250,000 pounds as promoters in plastic gel coats, etc., and 250,000 pounds as catalysts in petrochemical homogeneous catalysts.

In the application of cobalt in paint driers, the role of cobalt is that of a catalytic agent, much like in cobalt petrochemical catalysis. A brief summary of the chemical principles involved is given in Appendix D. The cobaltous-cobaltic valence transition catalyzes the appropriate chemical reactions, such as the transformation of unsaturated glyceride oils (e.g., linseed, fumaric acid, and styrene) in polyesters and also in various olefins. Manganese, cerium, zirconium, vanadium and iron have similar valence transitions and also act as catalysts. However, these have deficiencies not only in reaction rate but in product discoloration and other deleterious properties when used as a one-to-one replacement for cobalt.

Cobalt in paint driers is usually derived from 300-mesh (0.0018-in.) cobalt metal of 99.8 percent or greater purity that is reacted with an organic, e.g., 2-ethylhexonoic, acid in water for chemical reactivity, and dispersed in mineral spirits for physical solvency and convenient liquidity. There is a 6 to 24 percent cobalt concentration in the drier concentrate. Solution of the cobalt metal powder is effected by blowing air through the mixture for a few hours, with evolution of heat, in 2,000- to 10,000-pound batches. Coarser metal powder, such as 200 mesh (0.0029-in.), reacts far too slowly. An alternative to this direct metal reaction (DMR) process is the older double-decomposition process that uses cobalt hydrate or cobalt acetate, which react easily with the organic acid. These compounds are more costly, but they are an alternate method for producing driers by chemical cobalt recovery, particularly from cobalt alloy scrap. Organic acid alternates to 2-ethylhexanoic acid include linseed fatty acids (the oldest drier tradition), naphthenic acid mixtures, rosin and tall oil acids (by-products from wood pulping), neodecanoic acid, and 3,5,5-trimethylhexanoic acid. In each case, the function of the organic acid is to form a cobalt soap that is soluble in the diverse range of paint media with minimal concomitant detracting properties for the particular application.

Paint Formulations

Cobalt soap is usually preferred over manganese, cerium, iron, and perhaps zirconium soaps in the class of "top driers" in terms of speed of reduction and disappearance of surface tack as the paint, enamel, ink, or varnish dries. The drying process involves the conversion of the liquid to solid by a chemical oxidative mechanism. This contrasts with drying by physical evaporation of solvents as occurs in lacquers, or solidification from a melt, as with "hot lacquers" or hot-melt adhesives.

Top driers are complemented by the class of "bottom driers," usually soaps of lead, zinc, calcium, potassium, and perhaps zirconium. These hasten the solidification of a liquid coating down through the film to the substrate not only by promoting the oxidative process but also by physical gelation of the liquid. Cobalt alone can dry the surface of a film too rapidly, so that it will wrinkle the slide or sag over the still-liquid interior on a vertical substrate. Lead, or an alternate bottom drier, alone leaves the surface tacky too long for most practical uses. The development of 4-hour drying paints, widely advertised in the 1920s, was based on both an improved polymer chemistry and on a careful balance of top and bottom driers, particularly on the use of cobalt. Even now, the blending of the several drier metals with the chemical complexities of the polymeric media for paints is a highly developed art. It cuts across a large number of compositional and paint performance variables that can be controlled in science. An indication of the balances employed compositionally in paint driers used in commercial formulations is given in Table 37. Performance variables include temperature, relative humidity, light conditions, and shelf-stability; any one of these can dictate changes in formulation to meet a particular application.

TABLE 37 Examples of Drier Metal Combinations in Typical Paint Formulations (in weight percent)

Vehicle or Type	Pb	Co	Mn	Ca	Zn	Fe	Ce	Zr	Remarks
Exterior coatings									
Conventional oil vehicle	0.4-0.8	0.01-0.03	-	-	-	-	-	-	-
	0.4-0.8	-	0.02-0.04	-	-	-	-	-	-
	0.4-0.8	0.01-0.02	-	-	-	-	-	-	-
	-	0.02-0.04	-	0.1-0.2	-	-	-	-	Lead free
	-	-	0.02-0.05	0.1-0.2	-	-	-	-	Lead free
	-	0.02-0.03	0.02-0.05	-	-	-	-	0.1-0.3	Lead free
Blister-resistant alkyd vehicle	-	-	-	0.1-0.2	0.1-0.2	-	-	-	Minimizes wrinkling
Blister-resistant co-polymer oil vehicle	0.3-0.6	-	0.03-0.05	-	-	-	-	-	Fastest dry
	-	0.02-0.04	-	0.2	0.1-0.2	-	-	-	Lead free
Butadiene-styrene vehicles	-	0.1-0.25	-	-	-	-	-	-	Improves gloss and resistance to organic solvents such as gasoline
Trim paints									
Linseed alkyd base	0.02-0.05	0.02-0.06	-	-	-	-	-	-	Lead free
	-	0.02-0.06	-	0.1-0.2	-	-	-	-	Lead free
	-	0.020.06	-	-	-	-	-	0.1-0.3	Lead free
Soya alkyd base, tail oil, or safflower	0.4-0.8	0.04-0.08	-	-	-	-	-	-	Lead free
	-	0.4-0.8	-	0.1-0.2	-	-	-	-	-
	-	0.4-0.8	-	-	-	-	-	0.1-0.3	Lead free
Bodied fish oil base	0.2-0.4	0.04-0.08	-	0.1-0.2	-	-	-	-	Minimizes after tack
	0.2-0.4	0.04-0.08	-	-		0.04-0.15	-	-	
Bodied linseed oil	0.3-0.6	0.02-0.04	-	-	-	-	-	-	Lead free
	-	0.02-0.04	-	0.1-0.2	-	-	-	-	Lead free

TABLE 37 (continued)

Vehicle or Type	Pb	Co	Mn	Ca	Zn	Fe	Ce	Zr	Remarks
Oleoresinous									
Spar varnish									
Pure phenolic (5 parts tung: 3 parts linseed	0.3-0.5	0.02-0.04	-	-	-	-	-	-	
	-	0.02-0.04	-	-	-	-	-	0.1-0.3	Improves hardness
Pentaerythritol ester-linseed	0.5-0.7	0.04-0.07	-	-	-	-	--	-	Fastest dry
	-	0.3-0.5	-	-	-	-	-	0.1-0.3	Improves hardness
Floor Varnish									
Petroleum resin-linseed	0.5-0.7	-	0.4-0.8	-	-	-	-	-	
	-	0.3-0.5	-	-	-	-	-	0.1-0.3	Improves hardness
Congo-dehydrated caster oil	0.5	0.06-0.08	0.-3-0.05	-	-	-	-		
	-	0.03-0.05	-	-	-	-	-	0.1-0.3	Improves hardness
Pentaerythritol ester-linseed	0.3-0.5	0.5-0.08	0.03-0.05	-	-	-	-	-	
	-	0.03-0.05	-	-	-	-	-	0.1-0.3	Improves hardness
Baking									
Maleic-dehydrated castor oil	-	0.005-0.01	-	-	0.1-0.2	-	-	-	High gloss
Modified phenolic (4 parts tung: 1 part linseed	0.2	0.01	0.01	-	-	-	-	-	
	-	-	0.002-0.005	-	-	-	-	0.02-0.04	
Aluminum Vehicle									
Linseed-Coumarone	-	0.02-0.05	-	-	-	-	-	-	
	-	0.02-0.05	-	-	-	-	-	0.1-0.3	Improves hardness
Phenolic (1 part fish: 1 pt tung)	-	0.02-0.05	-	-	-	-	-	-	
	-	0.02-0.05	-	-	-	-	-	0.1-0.3	Improves hardness
Metal Primer									
Modified phenolic linseed	0.5-0.8	0.07-0.1	-	-	-	-	-	-	
Phenolic-dehydrated castor oil	0.5	0.05	0.2	-					Hardest film

Alternative Driers

Alternatives for cobalt in paint driers are mainly manganese and a few other metals such as iron, cerium, and zirconium. To attain the same drying speed, more manganese is usually needed, but this results in more discoloration and poorer durability because of enhanced oxidative disintegration of the film (weathering). Excess amounts of drier, whether cobalt or manganese, must be avoided and compromises can be made between drying speed and durability. Iron as a paint drier has long been used only in baked-on black or dark enamels, where its inherent brown hue is acceptable. Cerium is the principal element among several rare earth elements used in the so-called "rare earth driers." Moderate increases in their use developed in the 1970s as alternates to cobalt or manganese. Zirconium, with a di- and tetravalent transition, serves as top drier and also has strong gelation properties for bottom drying. However, none of the alternative elements replaces cobalt directly on a one-to-one basis. The long life expected, or often legally warranted, require a very thin paint film to provide over 5 to 25 years of service. This longevity depends critically on the delicate balances and amount of these top and bottom drier elements. Their reformulations because of scarcity of supply or other reasons cannot be undertaken hastily. The current use in the paint industry of diverse accelerated weathering devices, which attempt to simulate the many types of climatic conditions that can be encountered in various applications, do not reduce the importance of proper judgments for making such changes.

Formulation Variations

Table 37 shows that the amount of cobalt used in paints is typically 0.05 percent with a range of 0.01 to 0.05 percent depending on the paint medium. Cobalt soap solubility that will give complete dispersion throughout the paint medium is essential to drier efficiency. Extra amounts may be needed in the presence of pigments that have high surface areas, such as carbon black, which adsorbs the drier from solution, to make up for activity loss. Extra surfactants used in water-emulsified alkyds add to the difficulty of keeping the drier in the alkyd phase.

Substitution Problems

Complete cobalt drier replacement would be very difficult to achieve for all types of formulations. However, in a critical supply situation, any one paint formula could likely be made free of cobalt with the attendant sacrifices in quality and probable increased costs associated with use of alternative chemicals.

The replacement of cobalt as a paint drier is hampered not only by the complexity of the chemical mechanisms of paint film formation and degradation, but also by the vast diversity of types of paints. Added to this is the fragmentation of paint production that is divided among more than 1,000 producers that have perhaps 2,000 paint-making facilities. The U.S. Department of Commerce, Bureau of Census, Standard Industrial Code (SIC) 2851 1980 data show that of the $8 billion annual wholesale value of paints, the largest producer has sales of only $0.6 billion, and the 10 largest have a combined total of only $3 billion. Further, each large manufacturer is likely to have an active, ready-to-manufacture file of several thousand paint formulas. These consist of hundreds of specialized "lines" of paint for specific end use with each line of paint having 5 to 15 colors. Many of these require unique balances of cobalt with other top and bottom driers in a paint formula that typically may contain 5 pigments, 2 to 5 main media, 2 or more driers, several solvents, and various minor additives of surfactants and stabilizers, for a total of 12 to 20 ingredients. The paint formulator's art as well as science is used to achieve the careful balance of these ingredients.

In addition to the diversity caused by many scientific and technical advances in polymers and pigments in the past 50 years, recent changes have been caused by environmental restrictions imposed by the Environmental Protection Agency (EPA). Lead toxicity has long been recognized as an environmental problem. The Lead Based Paint Poison Prevention Act which legislates against the use of lead in residential paints, has had a dramatic impact on the paint industry and limits the effective total replacement of cobalt as a drier. VOC regulation by EPA and its enforcement by the states continues to be in a state of flux. Thus many new paint formulations have been developed, not only for technological improvements in coatings, but also to reduce considerably the volatile organic solvents in factory applied paints and in residential paints. Success has come in part through advances in polymer chemistry, which reduce or eliminate the use of cobalt, and in part by development of water-dilutable systems of either latex or emulsion types. Extreme changes to either powder coatings or non-melt coatings have not as yet had much acceptance. The practical middle ground for many high-performance coatings is the gradual increase from the use of approximately 40 percent nonvolatiles up to a range of 60 to 80 percent, characteristic of the so-called "high solids" formulations. These involve more sophisticated surface chemistry in the formulation and the use of advanced spray or roller applications equipment, sometimes robotized.

Drying oils and their derivative alkyds continue to be the major paint media in the industry despite recurring forecasts of their replacements by a variety of new polymer types. Resistance to change is partly polymer cost, partly the inertia against unknowns in the vast complexity of polymer chemistry and partly the resultant implied product liability. Some recent consumption trends of selected resins are shown in Tables 38 and 39. Most soybean and related drying oils are now used in paints in the form of alkyds. These are, by definition, combinations of the fatty acids of these oils with polyoils, such as glycerine and pentaerythritol, and polyacids or their anhydrides, such as orthophthalic, isophthalic, trimellithic, maleic, and fumaric. Since about 1930, the extreme versatility of these 3 classes of alkyd components has resulted in a vast array of specialized alkyds and polyesters. These are made by perhaps 20 independent producers, in addition to captive alkyd manufacture by many paint makers. The products continue to be used in many classes of solvent-dilutable enamels and are used as adhesion improvers in latex paints and in emulsifiables. They also find use in important anionic electrocoatings for automotive frames and bodies, and other corrosion-prone steel surfaces. Cobalt continues to be the necessary drier catalyst in many of these alkyd types and uses.

TABLE 38 Consumption of Selected Resins by the Paint Industry 1977-80 (million lbs)

Product	Quantity			
	1977	1978	1979	1980
Alkyds	700	705	705	710
Acrylics	425	440	455	470
Vinyls[a]	325	345	370	390
Epoxies	125	130	135	145
Aminos	80	80	85	85
Urethanes	70	75	80	85
Cellulosics	55	55	60	60
Styrene-butadiene	25	25	30	25
Phenolics	20	20	20	25
Total	1825	1875	1940	1995

[a] Includes polyvinyl chloride resins and vinyl acetate monomers for resins

Sources: Industry sources and estimates by C. H. Kline & Co.

TABLE 39 Consumption of Selected Raw Materials Used in Alkyd Resins 1980 (million pounds)

Material	Quantity
Phthalic anhydride	120
Pentaerythritol	65
Glycerine	40
Maleic anhydride	20
Fumaric acid	5
Total	250

Sources: Estimates by C. H. Kline & Co. based on data from Chemical Profiles and Chemical Products Synopsis.

Conclusions Pertaining to Driers

The major conclusions derived from this investigation are:

1. Cobalt is the single most effective surface drier additive in paints. Its effectiveness as a catalyst depends on its interaction with other additives in complicated ways.

2. Cobalt in most drier and other chemical applications could be eliminated or reduced substantially, but most often at significant cost in industrial convenience and product quality.

3. Relaxation of government regulations could ease these indirect costs to the industry and consumers, but this is unlikely to occur except under emergency circumstances.

4. The fragmentation of the industry, the diversity of the products and the legal aspects involving product liability and warranties dictate against reduced use of cobalt except at extreme price increases, supply cutoffs, and other emergencies.

5. Recycling of cobalt in these applications is essentially negligible.

OTHER CHEMICAL USES OF COBALT

In 1980, 2.2 million pounds of cobalt were used in chemicals, including driers in the United States. This figure represents 14 percent of the nation's cobalt consumption. Cobalt chemicals are utilized by a broad cross section of industry and in some instances consumption is in noticeable quantities. In some cases the consumption is so miniscule that the industry was not aware of its essential requirement until cut-backs occurred at the time of the Shaba invasion. In describing these uses, this discussion adheres to the listing used in the publications of the Bureau of Mines.

Pigments

The 200,000 to 300,000 pounds of cobalt used in recent years for the production of pigments was mainly in the form of cobalt aluminate and silicate and associated oxides of other transition metals. They provide a range of violet, blue, and green inorganic pigments in the crystalline form of spinels, found under such historic names as cobalt blue, cerulean blue, and Thenard's blue. Cobalt pigments were used primarily in ceramic colors in porcelain enamel wall tile, floor tile, decorative tile, dinnerware, and ceramic artifacts. Nearly half of these are used in porcelain enamels with a like amount in organic coatings and lesser amounts in plastics. They are used even in artists' colors for unsurpassed permanence. These pigments are scarcely replaceable where ultimate resistance to high heat, light, or bleeding (organic solubility) or special infrared reflectance is needed. Military insignia, camouflage, and similar applications can command high priorities for these cobalt colors.

Cobalt oxide would appear to be the dominant chemical consumed in these cases. There will always be a swing in the amount of cobalt consumed as styles and trends have a noticeable effect on the colors used. It should be pointed out that with the exception of the use of a camouflage pigment, all other uses could be generally classified as nonessential. Manganese and other transition metals are potential substitutes in several applications.

Ground-Coat Frit

Cobalt used by the porcelain enamel industry was mainly in the form of frit, i.e., cobalt oxide as a 0.1 to 1 percent additive to the usual alkali alumino-boro-silicate glasses, although there is some cobalt sulfate used for preheating the steel prior to applying the frit. The end uses include cookware, appliances, bath tubs, and sanitary ware. These glasses are ground into frits for fusion onto metal above 425°C. Adhesion of the frit to sheet metal is greatly enhanced by the small amount of highly colored cobalt oxide in the frit. When cobalt was sold at $3 per pound, the 100 million pounds per year of ground coat frit production would use an estimated 0.75 percent cobalt. However, at the recent cobalt price of $12 the cobalt use would be only 0.1 percent of the frit, with manganese, nickel, and other transition metal oxides replacing part but not all of the cobalt. The mechanisms for improved adhesion through chemical and physical interactions between the oxides of the metal substrates and of the frit are still under study.

Complete replacement of cobalt in ground coats seem unlikely, although major fractions can be replaced by the other metals when high prices persist. It should be emphasized that cobalt-based frit has been the preferred coating, but there has always been some nickel oxide used along with the cobalt oxide. When shortages have occurred, the cobalt oxide component has been diminished and the nickel oxide component increased in order to accommodate the situation. At first it was believed that cobalt oxide would be practically eliminated in frit; however, those made with very low cobalt oxide content and high nickel oxide content not only proved to be inferior from the standpoint of durability but particularly when applied to the interior of hot-water tanks. It also should be recognized that the high nickel oxide frits did not give the characteristic deep blue color that most people associate with a good enamel. There is no question, however, that heavy dependency on cobalt oxide in this use has been permanently reduced because of its cost. Substitution will be about 25 percent, and therefore cobalt oxide is expected to return to only 75 percent of its previous market.

Glass Decolorizers

Some 40,000 pounds of cobalt is consumed in the glass trade as a decolorizing agent used to neutralize the coloring of other impurities such as iron and chromium in the average glass batch. There will always be some need for cobalt for this purpose where glass has to be optically clear, but this area of use can be minimized in the event of serious shortages.

Miscellaneous Uses

A broad range of industrial and agricultural uses consumed in 1981 some 1,406,000 pounds of cobalt in various chemical forms in the United States.

Accelerators and Stabilizers (Plastics)

Another area of cobalt application similar to that of paint dryers is the use of cobalt in accelerators and stabilizers in plastics. Substitutes could be found although they would be inferior to cobalt, at least at this present state of the art.

The plastic industry's use of unsaturated polyesters, which require cobalt as a catalyst, has continued to grow from about 1950 into many variants such as glass-fiber laminates, gel coats, and compression molding. Much of their use remains proprietary; Table 40 shows one vendor's recommendation on the use of his proprietary product (Poly-Cure 503) which contains an unstated lesser amount of cobalt. Surveys of this industry might be justified if the use accounts for 1 percent of the total.

The plastics industry's use of unsaturated polyesters in gel coats, laminates, compression molding, and similar applications requires three synergistic additives:

1. Catalyst--a peroxide such as methylethyl ketone peroxide;
2. Promoter--usually 12 percent cobalt octoate solution; and
3. Accelerator--such as an amine or an acetoacetic ester.

The reduction-oxidation chemistry of these three small additives strongly influences the time of cure and related properties such as peak exotherm temperature and surface hardness. Cobalt as a promoter is almost universally used as about 0.2 percent of a 12 percent cobalt octoate solution--i.e., about 0.025 percent cobalt in a gel coat or lesser amounts in laminates and moldings. This 0.025 percent concentration is comparable to the 0.05 percent cobalt average in air-drying paints. It is much less susceptible to alternatives, although potassium soap has some very limited acceptance.

TABLE 40 Comparison of Gel Times and Costs Utilizing Poly-Cure 503 versus 12 Percent Cobalt Octoate[a]

Promoter Concentration (PHR) 12 Percent Octoate	Promoter Concentration (PHR) Poly-Cure 503	Gel Times (minutes)	Cost Efficiency (dollar savings)[b]
0.04	0.075	20.5	1.35
0.06	0.11	16.5	1.45
0.08	0.13	14.5	1.92
0.10	0.15	13.0	2.20
0.12	0.17	11.7	2.39
0.14	0.18	11.3	2.69
0.16	0.19	11.0	2.91
0.18	0.19	10.7	3.21
0.20	0.20	10.5	3.34

PHR = Parts per hundred resin; 12% cobalt octoate @ $5.61/lb; Poly-Cure 503 @ $2.27/lb (comparisons based on 7/9/79 prices).

[a] Tests were performed utilizing Cargill Chemical's HLU/SU Polyester Resin catalyzed with Lucidol's Lupersol DDM at 1 percent. When used in other resins, studies should be carried out to determine the effects of Poly-Cure 503 on activity, gel time drift, prepromoted resin stability, color, peak exotherm and other important properties.

[b] Dollar savings per pound of present 12 percent cobalt octoate usage, i.e., if 100,000 lbs of 12 percent cobalt octoate at 0.1 PHR were used, savings by using Poly-Cure 503 would be 100,000 x 2.20 or $220,000 per year.

The plastics industry's recent annual production of 3/4 to 1 billion pounds of these unsaturated polyester compositions accounts for the use of perhaps 200,000 to 300,000 pounds of cobalt per year. Gel coats and laminates, which cure at ambient or a little higher temperature, have a more critical need for cobalt than have compression moldings that are cured at higher temperatures. Alternate polymer types such as urethanes, and hybrids of these with unsaturated polyester, may grow in total volume along with the overall growth of the plastics industry. They would limit but not decrease needs for cobalt in plastics manufacture.

Animal Feeds

Cobalt has been used as a trace mineral diet additive for cattle, sheep, hogs, and poultry in the United States, Canada, Australia, New Zealand, and Argentina and to a lesser extent in Mexico. The purpose of the added trace minerals is to protect the health of the animal and also to increase growth. Cobalt is the nucleus of Vitamin B_{12}, the growth vitamin, and its presence in the animal's system in trace amounts enables the animal to generate its own Vitamin B_{12}. The spectacular growth results have attested to its effectiveness. This use has been reduced during supply shortages, but it has not been completely eliminated for obvious economic reasons.

Electronics

Soluble cobalt salts and cobalt oxide are used in some electronic applications. Typical examples are soluble salts for magnetic tapes, both audio and video, and cobalt oxide for varistors and thermistors.

Rubber Tires

Cobalt compounds are now used in the production of steel-belted radial tires. The presence of cobalt has brought about the adherence of the rubber to the steel and its use here seems to be a growing requirement. This would seem to be an area where substitution is unlikely.

Battery Manufacturing

Cobalt is used widely in the production of power cells and nickel-cadmium batteries. Cobalt imparts improved recharging characteristics, although, this use could be eliminated under dire necessity.

Other Minor Chemical Uses

Cobalt chemicals are also used in the following categories in smaller but significant quantities: electroplating and electrorefining, desiccant indicators, nucleating agents in investment casting, promoters in water treatment, chemical fuels, components in special oil drilling muds, etching tool steels; printing inks; and fertilizers.

Many of the minor uses would be suspended during an emergency or used in very specific cases where defense requirements are involved. Furthermore, few of the uses to which the cobalt is being put now can be minimized by the practice of thrift. The specification for the amount of cobalt in some of the applications listed could be cautiously reduced but the effectiveness, of course, would be altered. It is estimated that under extreme emergency the consumption of cobalt in the miscellaneous category would be reduced by 40 percent without serious consequences. As long as the price of cobalt remains high, substitutes will be sought by these users.

Conclusions Pertaining to Other Cobalt Uses

1. The 2.2 million pounds of cobalt used as chemicals other than catalysts during 1980, could without much difficulty, be cut by 20 percent. Some further reductions could come from rubber and battery manufacturing. However, defense-related products in certain fields such as ceramics, camouflage pigments, glass decolorizations etc. require cobalt to accomplish the required effect.

2. It appears that under the most severe emergency conditions, a reduction of 60 percent of the 2.2 million pounds could be realized.

CONCLUDING REMARKS REGARDING TECHNOLOGICAL ALTERNATIVES

Specific conclusions on the substitutability of cobalt in each of the end-use categories has been articulated in appropriate subsections of this chapter. Generally it appears that, in the event of a severe and prolonged cobalt supply disruption, many of the end uses can remain functional with little or no cobalt. These include tool and maraging steels, paint driers and other chemicals, and many of the catalyst applications. The magnetic materials sector could survive for prolonged periods with much less cobalt, but, there would be some economic penalties.

By contrast, it appears that the superalloy system, which is by far the single largest user of cobalt, will require cobalt at slightly increasing demand rates for the forseeable future. Significant substitutions for cobalt with other alloying elements are possible in theory, but in practice such action requires large-scale and prolonged engine certification programs. These will take place only under pressure of severe shortages or when the economic incentives are sufficiently high. A similar situation apparently exists for cemented carbides.

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Appendix A

BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

JAGDISH C. AGARWAL received his BS degree from Benares Hindu University in 1945, and his DChE (1951) from Polytechnic Institute of New York. He was senior process engineer at Blaw-Knox Co., 1951-1954; research associate in the Applied Research Laboratory of U.S. Steel Corporation, 1954-1964 and division chief for process analysis for U.S. Steel Corporation, 1964-1969; director of development at Kennecott Copper Corporation, 1969-1979; and group vice president, natural resource engineering at Charles River Associates, Inc. 1979-1982. He is currently vice president of technology at AMAX Specialty Metals Corporation. His areas of technical expertise include metallurgical process plant design and economics, materials substitution and cost-benefit analysis, resource development strategy, mineral economics and feasibility analysis.

JOEL P. CLARK received his BS degree in materials science and engineering from Florida State University in 1966 and an MS degree in 1968 and a ScD degree in 1972 from the Massachusetts Institute of Technology. In 1975 he received an MS degree from the M.I.T. Sloan School of Management. He has been consultant to Diagnos Ltd. of Switzerland, C.S. Draper Laboratories, Charles River Associates, the General Accounting Office, and the Erie County Industrial Development Agency. He is currently professor of materials systems in the Department of Materials Science and Engineering at M.I.T. His expertise is in engineering systems analysis, metallurgical systems, materials substitution, and economic trade-offs.

JOHN J. deBARBADILLO received his BS in 1963, MS in 1965, and PhD in 1967 from Lehigh University, all in metallurgy. He is manager of materials processing at INCO Alloy Products Company Research Center. He has worked in various metallurgical areas including the development of carburizing steels, ultra-high-strength corrosion-resistant alloys, cryogenic steels, wrought and cast high-strength steels and stainless steels, and metals reclamation. Reclamation of values from superalloy scrap is the area of his current technical contribution.

EDWARD J. DULIS received his BS degree at the University of Alabama in 1942 and an MS degree from Stevens Institute of Technology in 1950 in the field of physical metallurgy. He worked as assistant metallurgist at the U.S. Naval Air Station, 1942-1945; research metallurgist at the U.S. Steel Research Laboratory, 1945-1955, and has moved through various positions at the Crucible Steel Company since 1955 to his present position as president of the Crucible Research Center. His wide experience in metallurgical research includes the development of new stainless steels, valve steels, high-temperature alloys, powder metallurgy processing and products, and technical management.

TAKESHI EGAMI received his BEng degree from the University of Tokyo in 1968 and his PhD degree in 1971 from the University of Pennsylvania in metallurgy and materials science. He was a fellow in applied science at the University of Sussex, 1971-1972, and visiting scientist in physics at the Max Planck Institute of Metal Research 1972-1973. He is currently professor of metallurgy and materials science in the Department of Materials Science and Engineering at the University of Pennsylvania. His areas of expertise are magnetic, mechanical, and structural properties of metallic glasses, crystal field effects, and domain wall theory.

RONALD GIBALA received his BS degree from Carnegie Institute of Technology in 1960 and an MS degree in 1962 and a PhD degree in 1964 from the University of Illinois, all in metallurgical engineering. He has worked on numerous government-sponsored research projects, 1966-1975, was visiting professor at the Centre d'Etudes Nucleaires de Grenoble, 1973-1974, and is a research consultant for the General Motors Corporation. His areas of expertise are in physical metallurgy, defects in solids, internal friction, mechanical properties of solids, and critical materials in aerospace systems.

JAMES D. HALL received his BS in 1935 and his MS in 1937 from Case Western Reserve University in inorganic chemistry. He served as manager of the development department at the Harshaw Chemical Company, 1938-1946. He was the founder and president of The Hall Chemical Company since 1946. His fields of expertise are inorganic chemicals purification and preparation, chemical process development, and the reclamation of critical materials from chemical process wastes, spent catalysts, cemented carbides, and materials fabrication and machining scrap.

WARNE P. JOHNSON received his BS degree in 1942 and his MS in 1947 from Massachusetts Institute of Technology in chemical engineering, and a BS in accounting in 1974 from Fairleigh Dickenson University. He served as treasurer and president of Pettit Paint Company, 1963-1973; controller for Ingredient Technology, 1976-1979; and manager of business development and planning for American Cyanamid Company since 1979. He has been involved in the areas of metals recovery from spent catalysts and catalyst business analysis.

BERNARD H. KEAR received his BSc degree in metallurgy in 1954 and his PhD in 1970 from Birmingham University. He worked as metallurgist at Tube Investments Ltd., 1957-1959, a fellow at the Franklin Institute 1959-1963; was a staff member at Pratt & Whitney Aircraft, 1963-1976; and served as senior consulting scientist at the United Technologies Research Center, 1976-1981. He is presently scientific advisor at the Physical Science Laboratory of the Exxon Research & Development Company. He was elected to the National Academy of Engineering in 1979. His areas of expertise include rapid solidification technology, thin filaments, surfaces of materials, and laser processing of materials.

DWAINE L. KLARSTROM received his BS degree in 1965, MS degree in 1966, and PhD degree in 1970 from the University of Wisconsin--Madison, all in metallurgical engineering. He was assistant professor of materials science at the University of Wisconsin--Milwaukee. He worked on various metallurgical engineering programs at the Cabot Corporation since 1973 and is manager of the corrosion and high-temperature and alloys sections in Cabot's Technology Department.

JOSEPH B. MOORE received his BS degree in 1948 and an MS in 1955 from the University of Alabama in aeronautical and mechanical engineering. He worked as metallurgist on materials development at the General Electric Company, 1955-1957, manager of metallurgical development at Wyman-Gordon Company, 1957-1960, senior scientist at Southern Research Institute, 1960-1961; and at various engineering tasks at Pratt & Whitney Aircraft Group of United Technologies Corporation since 1961 and is presently director of materials engineering and technology. His wide professional expertise include turbine blade alloy developmment, materials selection and test, pilot and production-line vacuum melting and casting, and mechanics of materials and structures.

THOMAS J. O'KEEFE received his BS degree in 1958 from the Missouri School of Mines and his PhD degree in metallurgical engineering in 1965 from the University of Missouri--Rolla. He worked as process control metallurgist at Dow Metal Products, 1959-1961, and as research director at Air Products and Chemical Company, 1977-1978. He has been at the University of Missouri--Rolla since 1965 and now holds the position of professor of metallurgical engineering. His materials expertise is in electrodeposition processes for nonferrous metals and dental materials, and extractive metallurgy.

EDWARD L. PEPPER received his BS degree in 1942 from the Massachusetts Institute of Technology in metallurgy and attended the Advanced Management Program at the Harvard University School of Business Administration. He has been with A. D. Little, Inc., since 1946 and is now vice president, resource consulting. He is also a director of Copperweld Corporation. His technical expertise is in the fields of production and marketing of iron and steel, specialty steels, and alloys (Ni, Al, Mg, Co), and feasibility studies of metals and minerals.

PAUL E. QUENEAU received his BA degree in 1931, BSc degree in 1932, and EM degree in mineral engineering and extractive metallurgy in 1933 from Columbia University. He pursued postgraduate studies at Cambridge University, England and Delft University of Technology receiving his DSc degree in 1971 for his thesis on cobalt. He worked for INCO in various capacities since 1934, advancing to vice president of engineering and assistant to the chairman when he retired in 1971. He is presently professor of engineering in the Thayer School of Engineering at Dartmouth College. He was elected to the National Academy of Engineering in 1981. His expertise is in utilization of mineral resources, extractive metallurgy, and plant design.

WILLIAM A. REICH received his BS degree in 1938 in metallurgy from the Carnegie Institute of Technology. He has been with the General Electric Company since 1938 engaged in technical management, research, development, and applications of a wide variety of metallurgical materials and processes. He is presently manager of technical resources of the Carboloy Systems Department of General Electric. His areas of expertise are in powder metallurgy, and hard metals related tooling materials.

STEVEN H. REICHMAN received his BS degree in 1965 and an MS in 1967 in physics and metallurgy from the Polytechnic Institute of New York. In 1979 he participated in the executive development program at the University of Michigan. He was an NSF fellow, 1965-1967; research metallurgist at Battelle Columbus Laboratories, 1967-1969; research director at Federal Mogul Corporation, 1969-1975; and since 1975 has been with Special Metals, Inc., where he is now director of research, development, and new products. His areas of expertise are physical metallurgy, superalloy design, dental materials, and powder metallurgy.

TOM D. SCHLABACH received his BS in chemistry from Baldwin-Wallace College in 1948 and his PhD in physical chemistry from Michigan State College in 1952, where he was Parke-Davis fellow (1949-1950) and Hinman fellow (1950-1951). He has been a member of the technical staff of the Bell Laboratories since 1952 and is now head of the Department of Metallurgical Engineering. His areas of expertise include alloy development, mechanical properties, composites, and surface chemistry.

MARION SEMCHYSHEN received his BS degree from Wayne State University in 1941, an MS degree from the University of Michigan in 1942, and a PhD degree from Wayne State University in 1959, all in metallurgical engineering. In 1970, he studied research management at Harvard University. He has been with Climax Molybdenum Company of Michigan since 1942, serving in various metallurgical areas, and is presently vice president of development. His areas of expertise include physical ferrous metallurgy, molybdenum and molybdenum-base alloys, stainless steels, wrought construction steels, superalloys, low-alloy steels, and critical materials substitution.

ROBERT A. SPRAGUE received his BME degree in materials science and engineering from the General Motors Institute in 1957, and an MS degree in metallurgy from Rensselaer Polytechnic Institute in 1968. He was research metallurgist in the New Departure Division of General Motors Corporation, 1962-1964; was supervisor in the materials and research laboratory of Pratt & Whitney Aircraft, 1964-1980; and has been with the Aircraft Technology Operation Division of the General Electric Company since 1980, where he is now manager of the Materials and Process Technology Laboratories. His areas of expertise are materials and process research, development of critical alloys for high-pressure turbine airfoils, and superalloys for high-temperature use in commercial and military gas turbine engines.

WILLIAM L. SWAGER received his BS degree in chemical engineering from Purdue in 1942. He held various (technical and supervisory) positions at Baker and Adamson Division, General Chemical Company, 1942-1948. Since 1948 he has been with the Battelle Columbus Laboratories, where he is now manager of materials economics. His areas of technical expertise are technical economic analysis, strategic planning, technological forecasting, technology assessment, and materials policy analysis.

JOHN K. TIEN received his BSME degree in 1962 from Worcester Polytechnic Institute in mechanical engineering, an ME degree in 1964 from Yale University, and an MS degree in 1967 and a PhD degree in 1969 from Carnegie-Mellon University in metallurgy. He worked as project supervisor at Chase Brass & Copper Company in 1964-1965 and as research associate in metallurgy and materials science at Pratt & Whitney Aircraft, 1967-1971. In 1971 he joined the faculty of Columbia University where he is now professor and head of the department of metallurgy and materials science. He is a consultant to many high materials technology corporations. His areas of expertise include effects of solidification and heat treatment on the microstructure and properties of materials, migrational characteristics of interfaces, stress effects on particle coarsening, section processes, creep fatigue, oxidation, and alloy design, especially with respect to superalloys.

Appendix B

ESTIMATED FLOWS OF COBALT IN MAJOR PROCESSING AND MANUFACTURING OPERATIONS

This appendix provides background data and estimates on the flows of cobalt in major processing and manufacturing operations. The data and estimates presented below were summarized in Figure 3 in the body of the report. Some introductory data from Chapter 2 are repeated here for ease of reference and to make this discussion more complete.

INITIAL RECONCILIATION OF DATA ON COBALT CONSUMPTION

The Bureau of Mines (Kummer 1980) provides data on cobalt consumption under two headings, "reported consumption" and "apparent consumption." Table B-1 gives Bureau of Mines data on "reported consumption" of cobalt in the United States in 1980 of 15.32 million pounds. "Apparent consumption" is calculated from imports, net exports, changes in industrial and government stocks, and purchased scrap. The total "apparent consumption" of cobalt in the United States in 1980 was, according to the Bureau of Mines, 16.96 million pounds as shown in Table B-2.

TABLE B-1 Reported Consumption of Cobalt in the United States, 1980 (million pounds of contained cobalt)

Category	Amount
Superalloys	6.29
Magnets	2.27
Cemented Carbides	1.37
Hard Facing Alloys	0.62
Steel	0.50
Other Metals	0.45
Catalysts	1.66
Other Chemicals	2.21
Total	15.32

TABLE B-2 Apparent Consumption of Cobalt in the United States, 1980 (million pounds of contained cobalt)

Category	Amount
Imports	16.30
Exports	-1.37
Industrial Stock Release	0.85
Scrap Recycled	1.18
Total	16.96

Neither "reported" nor "apparent" consumption necessarily represents actual consumption of cobalt in 1980. "Actual consumption" is in excess of "reported consumption" because some companies, by policy, do not report such data to the Bureau of Mines. "Actual consumption" of cobalt may be greater or less than "apparent consumption" because there appear to be stock increases and decreases not reported to the Bureau of Mines, perhaps by traders or speculators. Mineral Facts and Problems (Sibley 1980) presents data on "reported consumption" and "apparent consumption." The letter on a three-year running average is about 7 percent in excess of reported consumption. The general trend can be explained by improved coverage of reporting.

The "reported consumption" of cobalt in 1980 in this analysis was assumed to represent only 93 percent of "actual consumption," and thus the "estimated consumption" of cobalt by major product in 1980 was calculated as given in Table B-3. Instead of prorating the additional 7 percent to all major uses, it was allocated to "other metal" and "other chemicals" in proportion to the amounts reported.

TABLE B-3 Estimated Consumption of Cobalt by Major Product Class, 1980 (million pounds of contained cobalt)

Category	Amount
Superalloys	6.3
Magnets	2.3
Cemented Carbides	1.3
Hard Facing Alloys	0.6
Steels	0.5
Other Metals	0.6
Catalysts	1.7
Other Chemicals	3.2
Total	16.5

Source: (Kummer 1980)

ESTIMATED FLOWS OF COBALT IN THE PROCESSING AND FABRICATION OF PRODUCTS

The data and estimates in Tables B-2 and B-3 provided the starting point for these calculations. Data from other sources and committee judgments were used as explained below.

Superalloys

The flows of superalloys in the manufacture of aircraft engine disks and other parts fabricated from wrought shapes are shown in Figure B-1. The flows of cobalt in the manufacture of turbine blades and other parts fabricated by investment casting are shown in Figure B-2. A composite of the flows of cobalt in superalloys is shown in Figure B-3. In estimating the flows of cobalt in Figures B-1, B-2, and B-3, a number of conditions had to be satisfied:

- It was assumed that 1.1 million pounds of the cobalt scrap consumption reported to the Bureau of Mines was used in superalloys manufacturing.
- Of the reported 6.3 million pounds of cobalt consumed in superalloy production, 1.1 million pounds was purchased scrap and 5.2 million pounds was new cobalt.
- The ratio of primary cobalt consumed in wrought products to that consumed in cast products is 2.0.

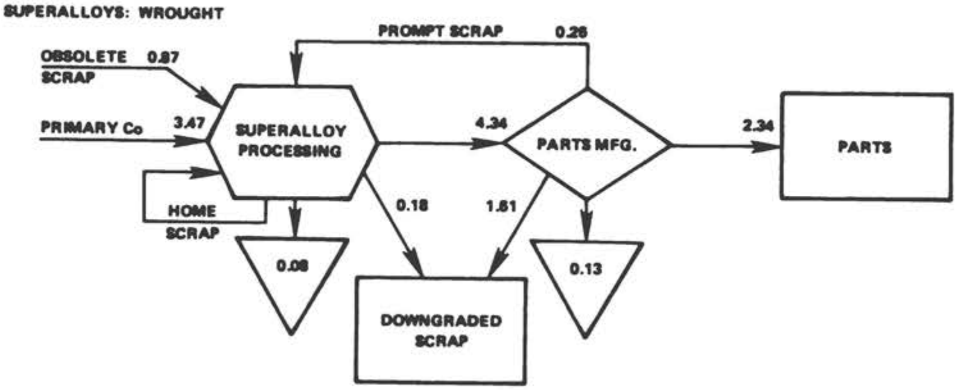

Figure B-1 Flow of superalloys in the manufacture of aircraft engine discs and other parts fabricated from wrought shapes (quantities in million pounds).

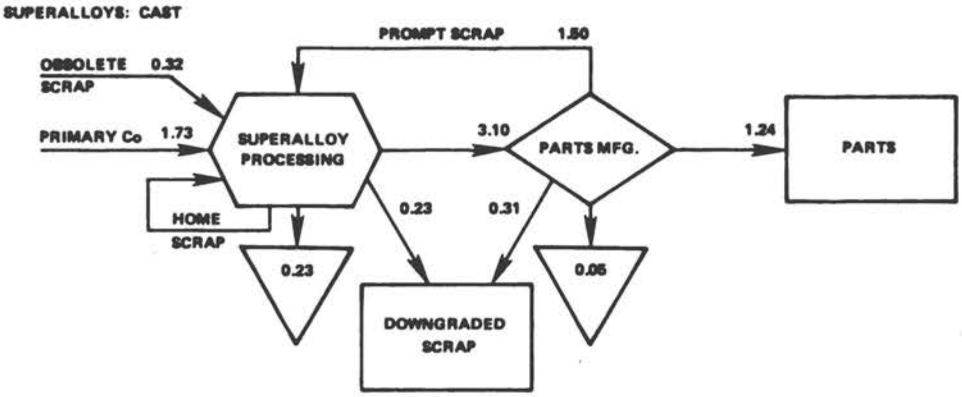

Figure B-2 Flow of superalloys in the manufacture of turbine blades and other parts fabricated by investment casting (quantities in million pounds).

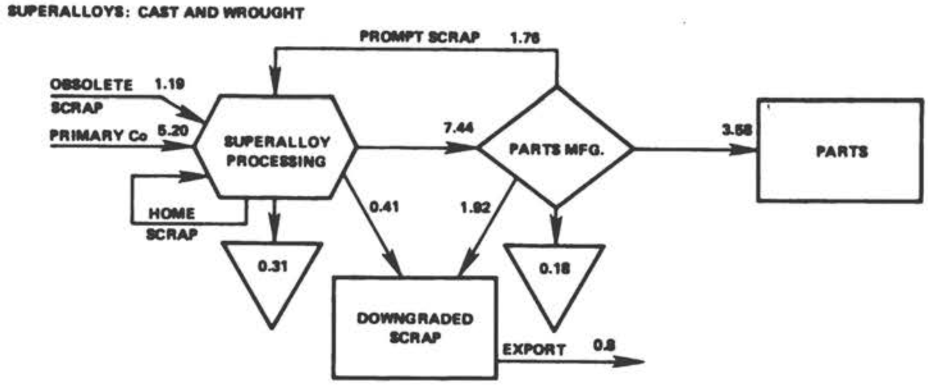

Figure B-3 Composite flow of cobalt in superalloys (quantities in million pounds).

Magnets

As in the case of superalloys, the manufacture of magnets involves two major processes, ductile alloy processing and casting. The flows of cobalt in the manufacture of magnets by production and processing of ductile alloys are shown in Figure B-4. The flows of cobalt in the manufacture of magnets by casting processes are shown in Figure B-5. A composite flow of cobalt in the manufacture of magnets is shown in Figure B-6. The flows were estimated judgmentally based in part on Curwick et al. (1980) and in part on general knowledge of ingot processing and direct casting processes. Figure B-5 indicates that about 2.05 million pounds of cobalt was embodied in magnets in 1980.

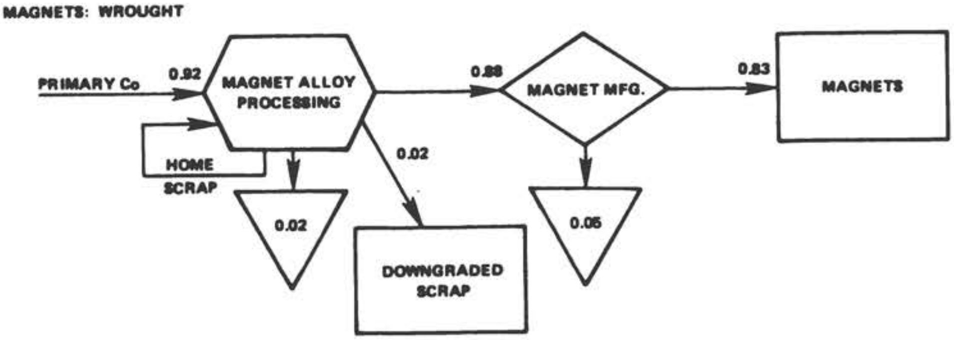

Figure B-4 Flow of cobalt in the manufacture of magnets by production and processing of ductile alloys (quantities in million pounds).

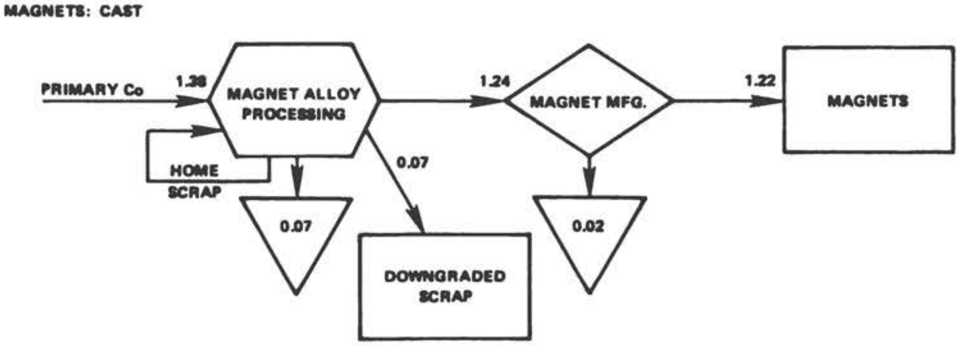

Figure B-5 Flow of cobalt in the manufacture of magnets by casting processes '(quantities in million pounds).

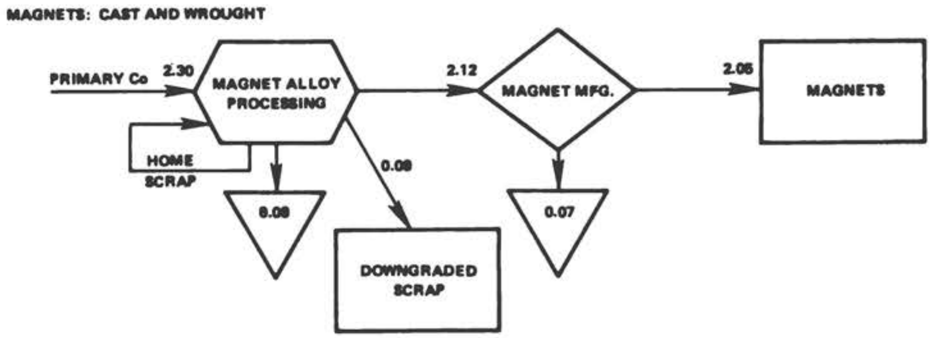

Figure B-6 A composite flow of cobalt in the manufacture of magnets (quantities in million pounds)

Cemented Carbides

Figure B-7 indicates that about 1.3 million pounds of primary cobalt was used in the manufacture of cemented carbides. According to a committee member (Reich), nearly 0.5 million pounds of cobalt is currently being recovered from obsolete cemented carbide scrap. It is assumed that the cobalt content of tungsten carbide scrap is not reported to the Bureau of Mines. Therefore, in 1980, 1.3 million pounds of primary cobalt and 0.5 million pounds of cobalt contained in obsolete scrap went into cemented carbide manufacture. This results in the use of 1.77 million pounds of cobalt in cemented carbide parts.

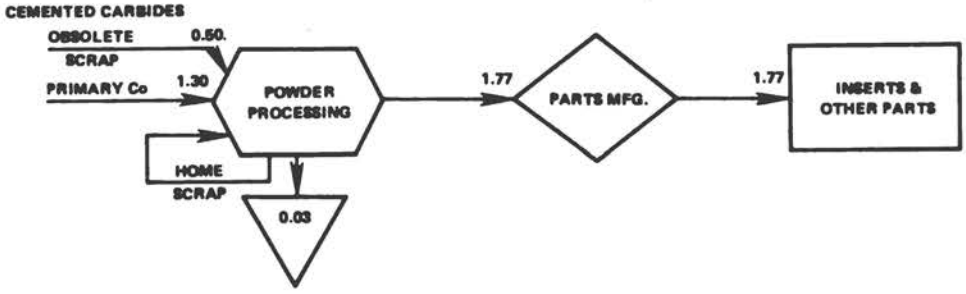

Figure B-7 Flow of cobalt in the manufacture of cemented carbides (quantities in million pounds)

Hardfacing Alloys

The estimated flows of cobalt in the production of hardfacing alloys are shown in Figure B-8. The flows are based on those reported by Curwick and co-workers (1980). It was assumed that 0.1 million pounds of the total reported scrap consumption was used in hardfacing alloy manufacturing. Therefore it is estimated that 0.5 million pounds of primary cobalt is included in the 0.6 million pounds consumed in hardfacing alloys that was reported to the Bureau of Mines.

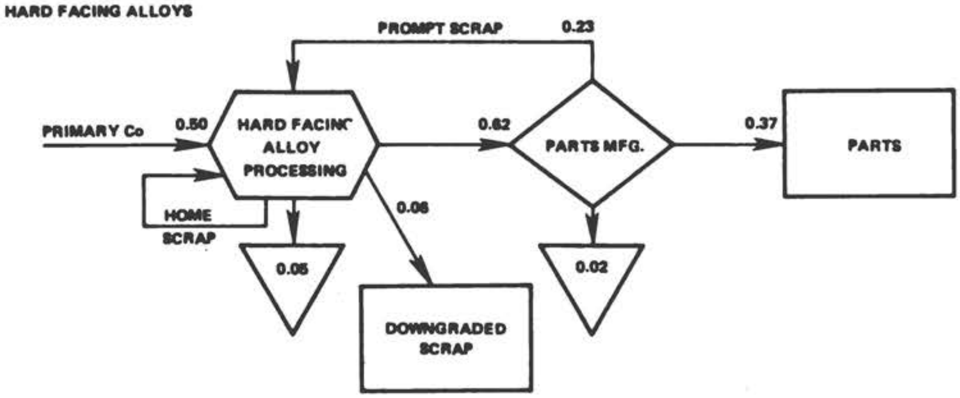

Figure B-8 Flow of cobalt in the production of hardfacing alloys (quantities in million pounds)

Steels

The flows of cobalt in the production of tool steels are shown in Figure B-9. About 0.41 million pounds of cobalt were embodied in tool steels in 1980. The flows and losses were based on those found in specialty steel operations.

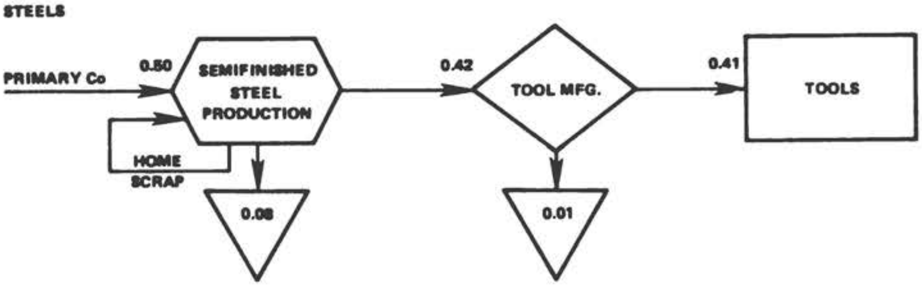

Figure B-9 Flow of cobalt in the production of tool steels (quantities in million pounds).

Other Metallic Uses

The flows of cobalt for other metallic uses, given in Figure B-10, are based on an input of 0.6 million pounds of primary cobalt. The various flows are proportional to those in a composite of all of the major metallic uses.

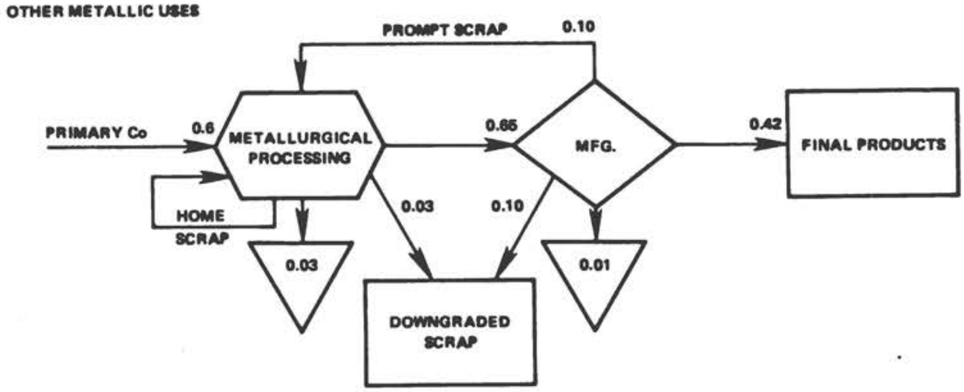

Figure B-10 Flows of cobalt for other metallic uses (quantities in million pounds).

Metallic Uses: Total

Figure B-11 presents a composite of the flows of cobalt for all metallic uses as previously shown in Figures B-1 through B-10. The detailed data may not add to totals due to rounding. The flows in Figure B-11 are the flows presented in the metallurgical section of Figure 3.

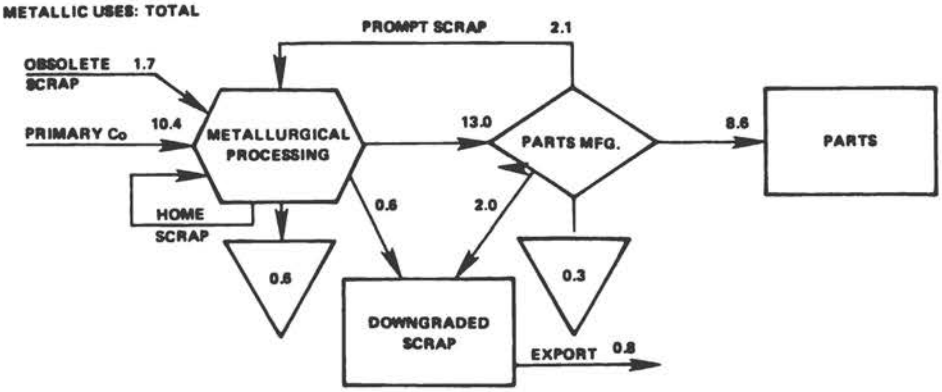

Figure B-11 Composite of the flows of cobalt for all metallic uses (quantities in million pounds).

Catalysts

The flow of cobalt in the manufacture of cobalt catalysts (Figure B-12) is rather simple and efficient. About 1.6 million pounds of contained cobalt in the form of catalysts is produced from 1.7 million pounds of input cobalt from all sources.

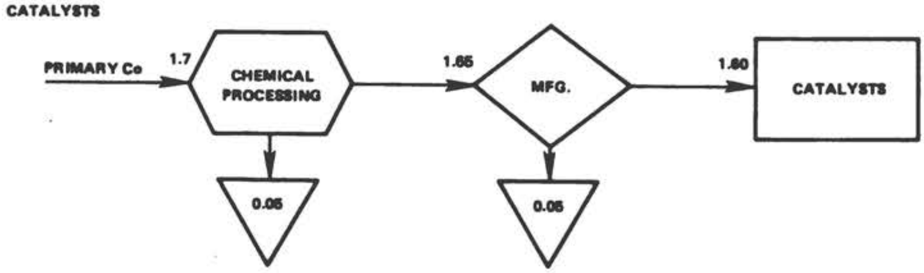

Figure B-12 Flow of cobalt in the manufacture of cobalt catalysts (quantities in million pounds).

Other Chemicals

The flow of cobalt in chemical processing and subsequent chemical use is shown in Figure B-13. Chemical processing is completed with yields of about 97 percent. In subsequent processing, yields are lower--of the order of 95 percent. It is estimated therefore that about 2.95 million pounds of cobalt is embodied in chemically related products in 1980, based on an input of about 3.2 million pounds of primary cobalt material.

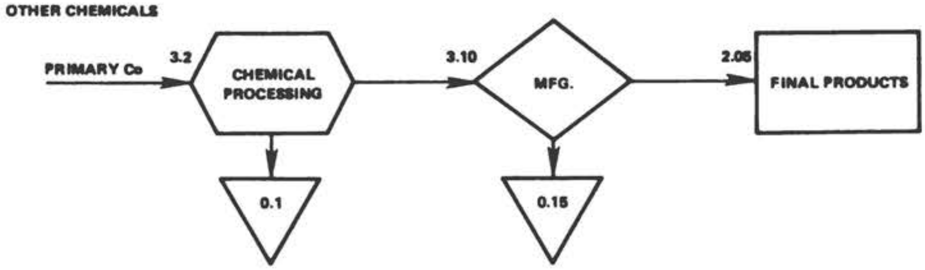

Figure B-13 Flow of cobalt in chemical processing and subsequent chemical use (quantities in million pounds).

Chemical Uses: Total

The flow of cobalt in chemical processing and various chemical uses given in Figure B-14, is a composite of the flows of cobalt in the manufacture of catalysts and other chemicals shown in Figure B-12 and Figure B-13. The detailed data may not add to totals due to rounding. The flows in Figure B-14 are the flows presented in the chemical section of Figure 3.

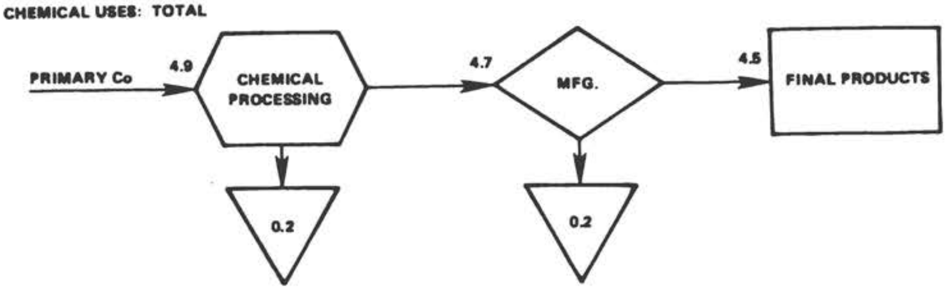

Figure B-14 Composite flow of cobalt in chemical processing and various chemical uses (quantities in million pounds).

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Appendix C

PAPERS PRESENTED AT THE INTERNATIONAL COBALT CONFERENCE

Brussels, November 10-13, 1981

This appendix contains two technical papers presented at the Brussels conference. These papers were used by the committee as background information on specific topics from knowledgeable experts, and the committee drew on these inputs where appropriate in its deliberations.

These papers are the views of the authors and are presented substantially as they appeared in preprints at the conference. The committee gratefully acknowledges the contributions of the authors and of the conference officials (R. Nonon, Director, Cobalt Development Institute, Brussels, Belgium) for permitting the papers to be reproduced here.

EXTRACTIVE METALLURGY OF COBALT

P. Lenoir, A. Van Peteghem, and C. Feneau
Metallurgie Hoboken-Overpelt
Hoboken, Belgium

Although cobalt is still considered as a minor metal, the cobalt content of the earth's crust (about 25 ppm) is of the same magnitude as that of the three traditional metals, lead (15 ppm), copper (45 ppm), and zinc (65 ppm). But the cobalt content of most of the ores is too low and does not allow economic extraction.

Nevertheless, small quantities of a specific cobalt-arsenic mineral are found in Morocco, presently the only primary source of the metal. However, most of the cobalt is obtained today as a co-product of copper and as a by-product of nickel extractive metallurgy.

In comparison with the production of the three traditional metals mentioned above, the production of cobalt is very modest. The quantities produced in 1980 were about 26,000 tons. It is worth mentioning that this cobalt was mined in only eleven countries, cobalt being only present in appreciable amount in a very limited number of deposits.

Although beneficiation of cobalt bearing ores is very straightforward, the extraction of the metal is seldom easy and cobalt production flow-sheets make use of a combination of pyro and hydrometallurgical processes.

The aim of this paper is to give a general view of the operations governing the extractive metallurgy of cobalt. This implies a short look at the basic metallurgy of copper and nickel, which we will try to limit to what is really specific to cobalt extraction. It will of course not be possible to enter into detailed flow-sheets which are sometimes very particular or specific to local operating conditions.

The literature of cobalt extraction is very abundant and this paper should, by no means, be considered as an exhaustive survey. Furthermore, many processing details are proprietary and not published. We cannot therefore accept responsibility for any possible errors and wish to apologize to some companies in case of reporting incorrect data, which we would appreciate to be put straight at the occasion of this meeting.

COBALT FROM COBALT ARSENIDE MINERALS

As mentioned above, cobalt arsenic minerals from Morocco are the only true primary source of this metal. The cobalt content of the ores is about 1 percent. After beneficiation it is possible to obtain concentrates with about 10 to 12 percent cobalt but also 50 to 55 percent arsenic.

Figure C-1 shows two possible routes for processing these concentrates. The first route, shown at the left, is the one which is used at present.

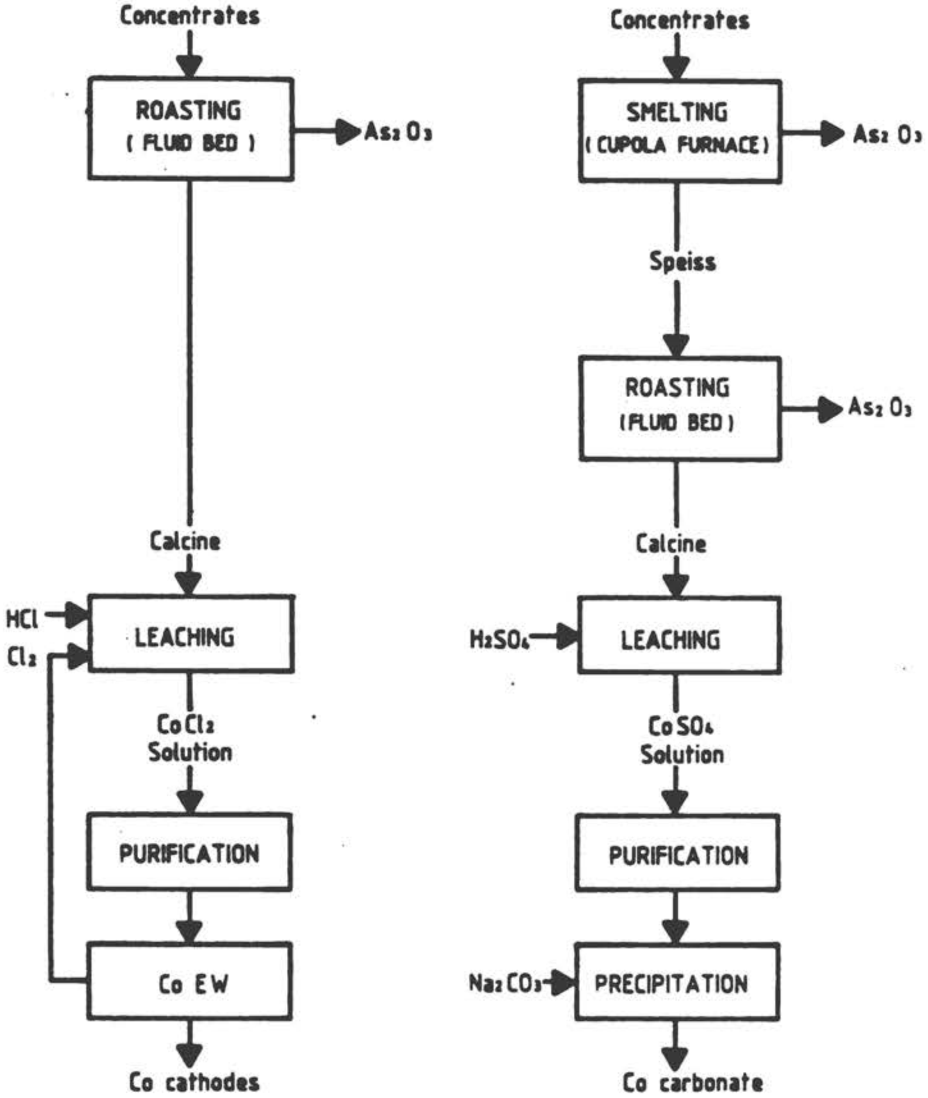

Figure C-1 Processing of cobalt-arsenic concentrates.

The concentrates are processed in France, first at the Estaque plant of Penarroya near Marseille where they are roasted in fluid bed at 600-700°C. This operation removes about 60 to 70 percent of the arsenic as saleable trioxide. The roasted concentrates, about 17 to 18 percent cobalt, 17 to 18 percent arsenic and 13 percent iron, are sent to the Metaux Speciaux plant at Plombieres, which has a total capacity of 1,500 tons of cobalt per year. The roasted concentrates are leached with hydrochloric acid and chlorine and, after several purification steps, the purified solution is electrolysed, producing cobalt cathodes and chlorine which is recycled to the leaching step. Few details are known about this process but, quite luckily, a paper will be given here by the Metaux Speciaux people so that we will be able to take a closer view at their operations.

The second route, shown at the right of Figure C-1, was followed some years ago by our company. The concentrates were smelted to speiss in a Cupola furnace with volatilization of nearly 75 percent of the arsenic. The resulting speiss at 40 percent As and 34 percent Co was then roasted in a fluid bed furnace at 850°C. The calcine with 5 percent As and 40 percent Co was leached in sulfuric acid and, after different purification steps, the cobalt was recovered as a pure carbonate--the starting material for the production of salts, oxides, and metal powders.

A lot of work is at present done on developing new ways for the treatment of cobalt arsenide or cobalt sulfo-arsenide ores. A good paper has been given on this topic by Ritcey and Ashbrook (1980).

Noranda Mining, Inc. is very active in establishing a flow-sheet for the treatment of the Black Bird Mine (Idaho) arsenical ores which should be processed by a pressure leach route to cobalt electrowon cathodes. A plant, with a capacity of 1800 tons of cobalt per year, could be in operation in 1984.

COBALT FROM COPPER-COBALT CONCENTRATES

Copper deposits from Zaire and Zambia are the most important sources of cobalt since these two countries assure more than 70 percent of the total world production of the metal. Minerals are mostly sulphides although some dolomitic oxides are also processed.

The basic flow-sheet is a roast-leach electrowinning process as shown in Figure C-2. The sulphide concentrates undergo a sulphate roast operation in a fluid bed furnace where copper and cobalt are transformed into soluble oxides and iron in an insoluble hematite. The calcine is leached with copper spent electrolyte. Oxide concentrates are also introduced at this leaching step and help to maintain the acid balance of the circuit. After purification for iron and aluminum the solution is electrowon to copper cathodes. Part of the copper spent electroylte is sent to the cobalt circuit. In this circuit solutions are further purified and then concentrated in cobalt. This concentration step involves the precipitation of cobalt hydroxide and then leaching out the precipitate with the cobalt electrowinning spent electrolyte to obtain a cobalt solution amenable to cobalt electrowinning.

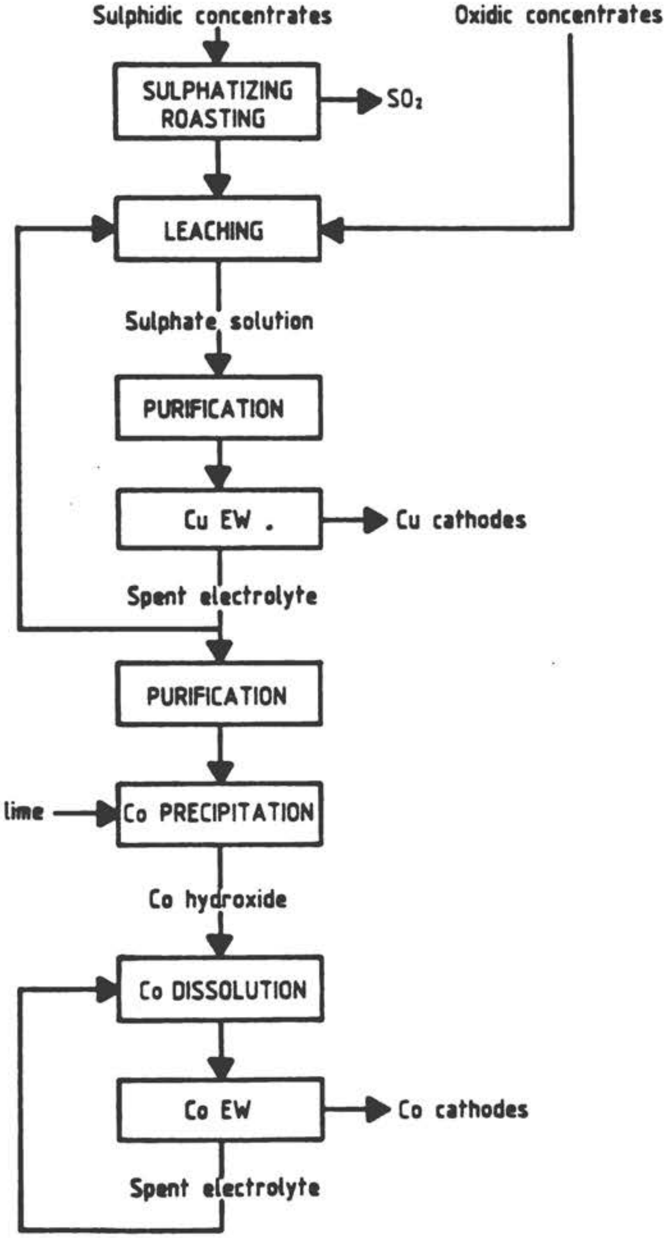

Figure C-2 Processing of copper-cobalt concentrates.

This basic roast-leaching electrowinning flow-sheet is used by GCM in Zaire at the Shituru and Luilu plants, by Roan Consolidated Mines Ltd. (RCM) at the Chambisi plant and by Nchanga Consolidated Copper Mines Ltd. (NCCM) at their Rhokana plant, both in Zambia. I might at this stage mention that these two Zambian companies will be joined in a single company called Zambian Consolidated Copper Mines (ZCCM).

As an example of operations we would like to show the Luilu cobalt flow-sheet of GCM in some details and then briefly comment on the operations of the other plants. The GCM Luilu flow-sheet is given in Figure C-3 (Wyllie 1970, Thoumsin 1969, and White November 1979).

The main feed to the plant is sulphide concentrates with 43 percent Cu and 2.5 percent Co and oxide concentrates with 24 percent Cu and 2 percent Co. The bleed stream of copper electrowinning at (gpl) 32 Cu, 40 Co, and 3.5 Fe, 5.0 Al, 16.0 MgO, 60 H_2SO_4 and at a flow rate of 25 m^3/h is neutralized with a slurry of lime at pH 3.3-3.7 for removal of Fe and Al. Copper is then removed in two steps. In the first step 80 to 90 percent of the copper is selectively precipitated with lime at pH 5.0 and the resulting copper hydroxide is recycled to the copper circuit. In the second step, copper is reduced from about 1 gpl to 0.14 gpl with lime at pH 6.2 and the copper-cobalt hydroxide slurry is recycled just before the iron-aluminum precipitation.

Nickel is then removed as a mixed Ni-Co sulphide (1 Ni/1 Co) by Co shots and NaHS and zinc as a sulphide with H_2S and Na_2CO_3 as a pH buffer.

Cobalt from the purified solution is then precipitated by lime at pH 8.2. This cobalt slurry is leached out with spect electrolyte from the cobalt tankhouse. Leaching is carried out at pH 6.5 in order to avoid solubilization of the zinc introduced as impurity with the lime. The cobalt rich residue from the pH 6.5 leaching is recycled to the iron-aluminum removal step where it acts as a neutralizer. The liquor from the pH 6.5 leaching now contains about (gpl) 45 Co., 0.01 Cu, 17 MgO, 4 Mn and is electrolyzed, after clarification, to cobalt cathodes.

Electrowinning is carried out at 70°C, at a current density of 350 to 400 A/m^2 and 14 kA/cel on stainless steel cathodes in a 4 day cycle. The current efficiency is 80 percent and energy consumption lies between 5000 and 6000 kWh/t cobalt deposited. In order to avoid lead contamination of the cobalt cathodes, special anodes of CoMnSi alloy (82-4-14) are used. Cobalt is reduced only to 39 gpl during electrolysis in order to control acidity. The cobalt is stripped from the blanks and traces of hydrogen and removed by vacuum degassing at 820°C and 200 torr.

A typical composition of cathodic cobalt is:

percent	99.9 Co
ppm	300 to 400 Ni, 10 to 30 Zn, 30 Fe, 20 S, 8 Cu, 50 C, 1 to 2 Pb, 2 H_2.

The capacity of the Luilu plant is 8000 tons of cobalt per year.

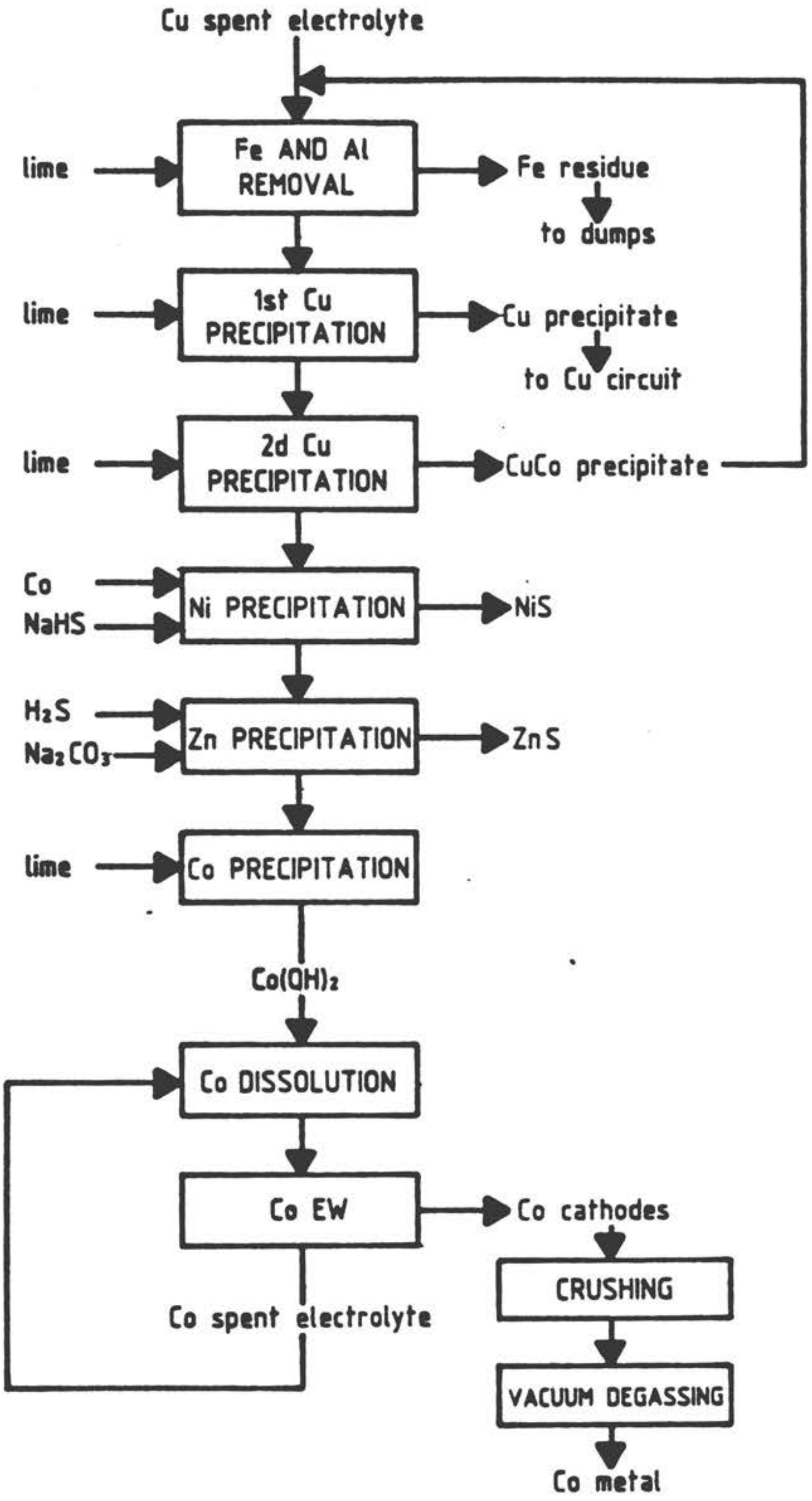

Figure C-3 Cobalt flow-sheet of the GCM's Luilu plant.

At the Shituru plant of GCM, with a capacity of 7000 tons of cobalt per year, the cobalt flow-sheet is somewhat different. The copper tank house bleed is first decopperized by electrolysis. The same purification scheme then applies for iron-aluminum and copper removal although remaining traces of copper are eliminated by cementation of cobalt granules. But the major difference lies in the fact that the precipitated cobalt hydroxide is not fully leached out and that cobalt electrowinning is carried out on the pulp at pH 7.0 in air agitated cells. Acid generated in the cells dissolves additional cobalt hydroxide, ensuring a constant 25 gpl cobalt concentration in the electrolyte. The cathode blanks are made of stainless steel, the anodes of a lead-antimony alloy and electrolysis is carried out at 10 kA per cell. After electrolysis the pulp is leached at pH 3.0-3.5 and the cobalt solution enters nickel purification with cobalt cathode shot and elemental sulphur and then returns to the repulping of the precipitated cobalt hydroxide. Cobalt cathodes have a purity of 95 percent and are further refined in electric furnaces to 99.5 percent purity, and then granulated in water.

Let us now take a look at Zambian operations (World Mining 1979, White 1979, and Brummit 1980). In 1978 RCM started a new cobalt plant at Chambisi with a capacity of 2400 tons of cobalt per year (Eng. Min. Journal 1980, Aird et al. 1980). In this new plant the bleed-off of the copper circuit is first decopperized by electrowinning to 0.5 gpl Cu and then further purified before cobalt hydroxide precipitation. However the iron removal is done with limestone instead of lime in a cascade where the pH is controlled from 1.8 at the start to 4.3 at the end. The long residence time related to the use of limestone, which reacts not as fast as lime, promotes the formation of large gypsum crystals with better settling rates. All the solids produced in the plant are recycled to this iron removal stage for recovery of the associated cobalt. The overflow from the iron removal thickener contains (gpl) 15 Co, 0.5 Cu, 0.5 Fe and 0.4 Zn and is sent to a clean up precipitation stage with slaked lime at 40°C and a pH 6.9 to 7.1 which brings the impurity levels down to 1-2 ppm. About 35 percent of the cobalt also precipitates, giving a precipitate at 15 percent Co which is recycled to the first iron removal step at pH 1.8.

The purified solution contains (gpl) 7 Co, 0.3 Mn and 3 Mg. Cobalt hydroxide is precipitated with slaked lime at pH 8.5 and the precipitate is sent to the dissolution stage at pH 5.8 - 6.4, ensuring a dissolution of 87 percent of the cobalt. The composition of the dissolution thickener overflow is:

gpl 30-40 Co, 2 Mn, 10 Mg
ppm 3 Cu, 2 Fe, 0.5 Zn, 1500 Ni.

This solution is clarified to 10 ppm solids, treated with activated carbon to remove sulphide ions and organics and then electrowon at pH 1.9 and 70 to 75°C at a current density of 280 to 400 A/m^2. Cathode blanks are of 316 L stainless steel and 6 percent antimonial lead is used for the anodes (RCM however plans to introduce Luilu type anodes). The cathode cycle is 4 to 5 days and the energy consumption amounts to 6500 kWh/ton deposited. The nickel content of the cathodes is 0.5 to 0.7 percent. Hydrogen is reduced to less than 1 ppm by heating the crushed cathodes in vacuum to 860°C.

The NCCM Rhokana division plant at Kitwe has a capacity of 1200 tons of cobalt per year from its own mines. The bleed off from the copper tank house is decopperized by electrowinning to 0.2 gpl Cu and purified by stepwise additions of lime from pH 5.7 to 7.2. The cobalt electrowinning is carried out on a 40 gpl cobalt solution with stainless steel blanks and Luilu type anodes during 4 days. Cobalt cathodes are crushed and vacuum degassed.

A new NCCM cobalt plant will start up in 1982 with a capacity of 2500 tons of cobalt per year (World Mining 1979, Cocquerel 1980). After a first iron removal step at pH 2.0 with limerock, the copper will be electrostripped at 500 A/m^2 as a copper powder. The following purification scheme will then be very similar to the one used by RCM's new plant in Chambisi and electrowinning will make use of Luilu type anodes.

In this important chapter on cobalt winning from copper concentrates we feel that some possible pyrometallurgical operations need be mentioned. GCM has treated dolomitic copper concentrates in the electric furnaces of their Panda plant. Smelting and reducing in these furnaces yield two distinct metallic phases which may be separated in the tapping ladles. The heavier phase called "red alloy" with about 90 percent Cu and 5 percent Co was converted by blowing to blister copper and the copper--cobalt convertor slag recycled to the electric furnaces. The lighter phase called "white alloy" with about 40 percent Co and 15 percent Cu was shipped to the Olen plant of M.H.O. to be processed via sulphuric acid route with the production of cobalt salts and oxides (Theys 1962).

Work has also been done by NCCM and RCM on cobalt recovery from copper convertor slags with 2.5 percent Co (White et al. 1977). These slags are subjected to a carbothermic reduction with production of an alloy containing iron, 20 to 25 percent Cu, and 10 to 15 percent Co. The alloy is pressure leached, iron is removed as hematite, copper by solvent extraction, and cobalt recovered as sulphate crystals to be fed to a cobalt electrowinning plant. However, this process has never been operated on an industrial scale.

Finally, it should be pointed out that MHO has also made some industrial trials on cobalt recovery from complex slags. These slags, averaging 20 percent Cu and 7 percent Co were decopperized in the copper blast furnace of the Hoboken plant to about 2.0 percent Cu. The decopperized slag was then processed to a cobalt white alloy with 20 to 25 percent either in an electric furnace or in a Cupola type furnace used in the steel industry.

COBALT FROM NICKEL SULPHIDE CONCENTRATES

Figure C-4 shows three different ways to process nickel sulphide concentrates (Gill 1980).

1. In the first method, the concentrates are roasted in a fluid bed reactor, the roasted concentrates are smelted for matte in an electric furnace and the matte is blown in convertors, giving a converted matte at e.g., 50 percent Ni, 20 percent S and varying amounts of Cu and Co depending on the feed source. The system is used by INCO in Thompson, Manitoba, by Falconbridge in Sudbury, Ontario, by Mathey Rustenburg Refiners Ltd. (MRR) in South Africa and in the fussion plants of Pechanganikel at Pechanga and of Severanikel at Monchegorsk. It is also used by INCO at Copper Cliff, Ontario although roasting is done in multihearth furnaces and matte smelting in reverberatory furnaces.

2. In the second system, concentrates are dried to less than 1 percent water and injected in a flash smelting reactor, giving a matte which is, as in the first case, blown in Pierce-Smith convertors. This scheme is used by Outokumpu at Harjavalta in Finland, by Western Mining (WM) at Kalgoorlie in Australia, by Bamangwato Concessions Ltd. (BCL) at Selebi Pikwe in Botswana and in the russian plant of the Norilsk Combine at Norilsk. In all these plants there is a slag cleaning operation of the flash and converter slags in an electric furnace. In the case of WM however, cleaning of the flash slags is achieved in an electric furnace installed in the settler of the flash reactor and the cleaning of the converter slags is done in a separate electric furnace.

3. A third possibility for processing nickel sulphide concentrates is the Sheritt Gordon Mines Ltd. process which was used by this company at their Fort Saskatchewan plant in Alberta when processing Lynn Lake concentrates (Mackiw and Veltman 1980).

It is difficult to have an idea of the amount of cobalt which is recovered in the nickel mattes of these different plants. A recent paper from Matousek (May 1981) gives the approximate cobalt distributions between matte and slag in different nickel smelters (see Table C-1). One should mention the good recovery, about 60 percent of the cobalt in the INCO's Thompson matte. Following Matousek this is partly due to the presence of naturally occuring graphite in the concentrates and partly to a program of continuous attention in the plant operations. Cobalt recovery in the BCL plant is rather low although they operate a slag cleaning operation. All these nickel mattes are refined to nickel and cobalt by hydrometallurgy (See Production of Cobalt from Matte and Mixed Sulphides).

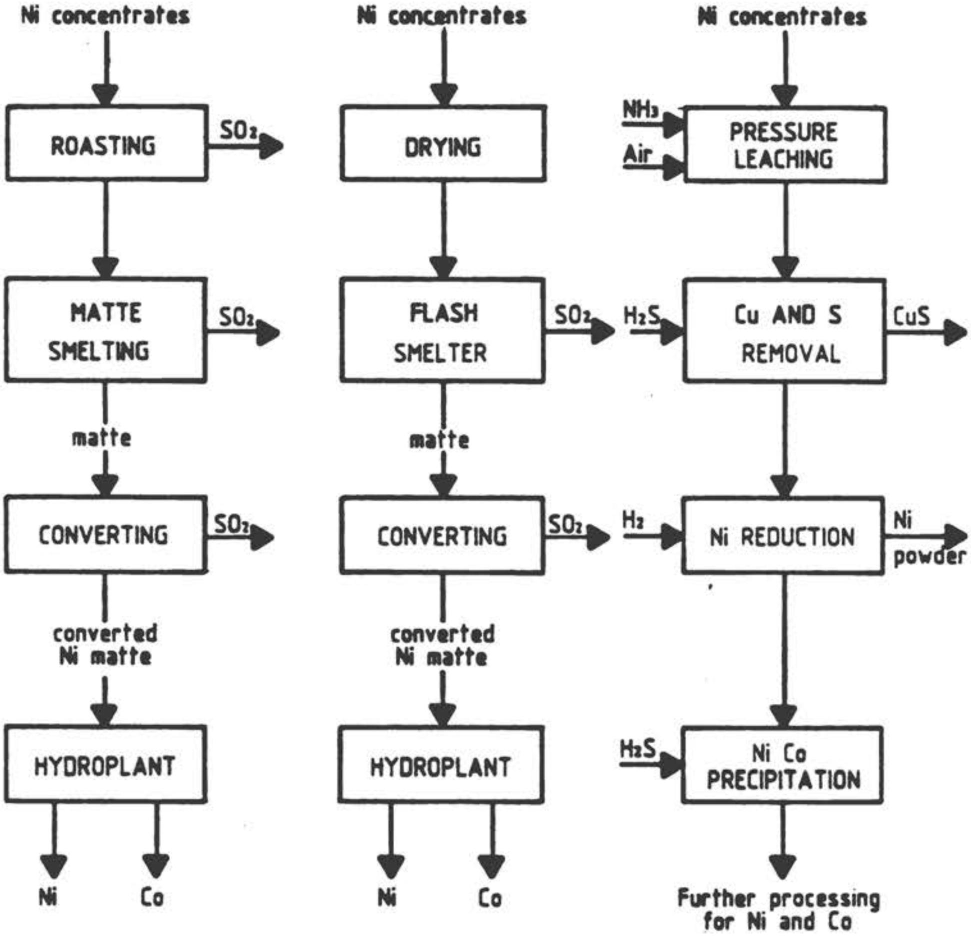

Figure C-4 Processing of nickel sulphide concentrates.

TABLE C-1 Cobalt Distribution Between Matte and Slag (percent)

Plant	Matte	Slag
INCO, Copper Clif	45	55
INCO, Thompson	60	40
Falconbridge, Sudbury	55	45
Outokumpu, Harjavalta	50	50
BCL, Selebi Pikwe	30	70
Western Mining, Kalgoorlie	60	40

One should also mention the special case of INCO at Copper Cliff. the nickel-copper mattes are slowly cooled and, after crushing, magnetic separation allows to isolate a magnetic Ni-Co-Cu alloy. This alloy is smelted in a top blown rotary converter (TBRC), desulphurized by oxygen lancing and granulated. The granules are sent to the carbonyle plant to recover the nickel. The residue of this process, containing a few percent of cobalt is leached and the cobalt is precipitated from the leached solution as an impure cobalt (nickel) carbonate which is further refined at other INCO's plants. This impure cobalt carbonate, as well as the cobalt residues coming from the purification of the anolyte of the nickel electrorefining operations at Thompson (matte anode) and Port Colborne (metal anode) will probably be the feed of the new INCO's cobalt electrowinning plant. This plant should be in operation at Port Colborne in 1982 with a capacity of about 900 tons of cobalt per year.

PROCESSING OF NICKEL OXIDE MINERALS

Nickel oxide minerals are formed by atmospheric weathering of rocks. During this process the rocks have been progressively enriched in nickel to laterites with 1 to 1.5 percent Ni and 0.1 to 0.2 percent Co and, to a lesser extent, to garnierites where the nickel content may be as high as 3 to 5 percent. Since it is assumed that about 75 percent of the world nickel resources are oxide one realizes that the problem of processing these ores is very important. Depending on the magnesium oxide content of the deposits, these oxide minerals are either transformed into ferro-nickel or matte by pyrometallurgy or treated hydrometallurgically yielding mixed nickel-cobalt sulphides.

Matte Production

Societe le Nickel (SLN) is a big producer of ferro-nickel in their Doniambo plant in New Caledonia (S. Roume, May 1976). The oxide nickel minerals are first dried, calcined at 859°C and then reduced in electric furnaces to a ferro-alloy with about 21 percent Ni. Part of this ferro-alloy is blown in convertors at 1650°C by injecting sulphur through the tuyeres in order to transform the nickel in a matte. The matte is then further blown with air in order to oxidize most of the iron. A typical analysis of the converted matte is:

percent 75 Ni 2.5 Fe 1 to 2 Co and 20 S

This matte is shipped to the SLN plant near Le Havre in France where it is further processed by hydrometallurgy.

A similar process is used by INCO in Guatemala and Indonesia where the sulphuration of the nickel is achieved in rotary furnaces and the matte production in electric furnaces. The nickel matte is then converted in Pierce Smith convertors (Guatemala) or the TBRC convertors (Indonesia) before hydrometallurgical treatment. The Guatemala plant however will have been mothballed early next year (Metal Bulletin 1981).

Hydrometallurgical Processes

This section concerns hydrometallurgical treatment of the oxidic materials which have been calcined in a reducing atmosphere.

1. The first plant to adopt this processing route is the Nicaro plant in Cuba. Calcination is being done in multiple hearth furnaces at 700°C to 900°C where the nickel, and to a lesser extent the cobalt, are selectively reduced to metal versus the iron. The calcine is leached with an aerated solution of ammonium hydroxide and carbonate (Caron process) (Rey 1972). Nickel and cobalt are leached out while the iron remains insoluble. Cobalt is however not recovered.

   The Moa Bay plant, also in Cuba, has a feed of oxidic material poor in magnesium oxide. In this case a sulphuric acid pressure leach is applied and nickel and cobalt are recovered as mixed sulphides (Carlson and Simons 1961). These mixed sulphides of Moa Bay are further processed in Russia to recover nickel and cobalt. The total cobalt content of these sulphides is about 1600 tons per year.

2. Queensland Nickel Pty. Ltd. (Greenvale) operates a Nicaro type ammonia leach process in Australia from which mixed nickel-cobalt sulphides are also produced (International Laterite Symposium 1979).

3. The pressure hydrometallurgical process of Sheritt Gordon Mines Ltd. developed for sulphidic nickel concentrates, can also be employed for the recovery of nickel and cobalt from lateritic ores. It is presently used at the Marinduque Mining and Industrial Corporation (MMIC). Lateritic ores are reduced in multiple hearth furnaces. This converts nickel and cobalt to the metallic state and renders these metals soluble in ammoniacal ammonium carbonate solutions by pressure leaching. The leach solution is treated with hydrogen sulphide to precipitate the bulk of the cobalt as a sulphide. This precipitate contains about 1 part of cobalt to 2 parts of nickel and is presently shipped to Japan for refining at the Sumitomo Metal Mining Co (SMMC). It is however expected that MMIC will build a refinery in the Philippines, using the Sherritt pentammine Co. recovery process.

4. A lot of research work is still being done on nickel and cobalt recovery from laterites. One should mention the AMAX process, an acid leach process applicable to a broad range of oxidic nickel ores, and the UOP process, a modified ammonia leach process. Details on these processes as well as a comparison of already existing processes are available (International Laterite Symposium 1979). One should also mention that P. T. Pacific Nikkel Indonesia, a consortium of U.S. Steel Corporation, Amoco Mineral Cy, Hoogovens, the Indonesian Government and Sheritt are undertaking a feasibility study to plan the construction of another laterite refinery using Sheritt's processes (Mackiw and Veltman 1980). The tonnage of cobalt to be recovered, when these projects will go on stream, is however very difficult to evaluate.

PRODUCTION OF COBALT FROM PYRITE CONCENTRATES AND OTHER FEEDS

The case of the cobalt plant of Outokumpu at Kokkola should be treated separately because this refinery process has many different cobalt bearing feeds (Ojanen 1980, Metal Bulletin Monthly, November 1980). The flow sheet of the Kokkola plant is given in Figure C-5. This refinery has produced about 1400 tons of cobalt i.e., about 30 percent from pyrite concentrates with 0.7 percent Co from the Keretti mine; 50 percent from roasted calcines with 0.9 percent Co; 10 percent from Co concentrates; 10 percent from mixed sulphates coming from the treatment of the Mansfeld ferro-alloy (see below).

This mixed feed is submitted to a sulphate roasting operation in a fluid bed furnace at 680°C. The calcine is leached and the solution is purified by precipitating iron as jarosite, copper, and zinc as sulphides and finally mixed nickel cobalt sulphides at a pH 4.5. The mixed sulphides are pressure leached at 140° and 10 bar in a sulphate media. The Sheritt pentammines process is then used to separate the cobalt which is further reduced by hydrogen to cobalt powder.

The Manfield alloy is a residue from a copper blast furnace and contains about:

percent - 75 Fe, 1.5 Co, 1.5 Ni, 10 Cu, 1.5 Mo, 3 S

This alloy is granulated at the Manfield plant in German Democratic Republic and shipped to Kokkola in Finland where the granules are processed since 1978 at a rate of 30,000 to 40,000 tons per year (Parviainen and Fugleberg 1980). The granules are reduced to less than 5 mm and are leached with sulphuric acid at a pH 1.5 and at 60°C. Iron is removed from the leach solution by blowing air at a pH 3.0 and the residue, containing the copper and molybdenum is treated separately for the recovery of these elements. The leach solution is concentrated to a level of:

gpl 180 Fe, 4.5 Co, 10 Ni, 150 H_2SO_4

and mixed FeCoNi sulphate is crystallized. These crystals are then, as mentioned above, introduced in the fluid bed roast reactors.

The cobalt flows throughout the different plants of Outokumpu Oy is given (Ojanen 1980). It is stated that the total recovery of cobalt in finished products is about 45 percent.

It should also be mentioned that Kilembe Mines Ltd. in Uganda are looking at the recovery of cobalt from cobaltferrous pyrites at 1.4 percent cobalt. A plant could be in operation in 5 years from now treating 300 tons of pyrites per day, using a Sheritt Process and producing cobalt carbonate.

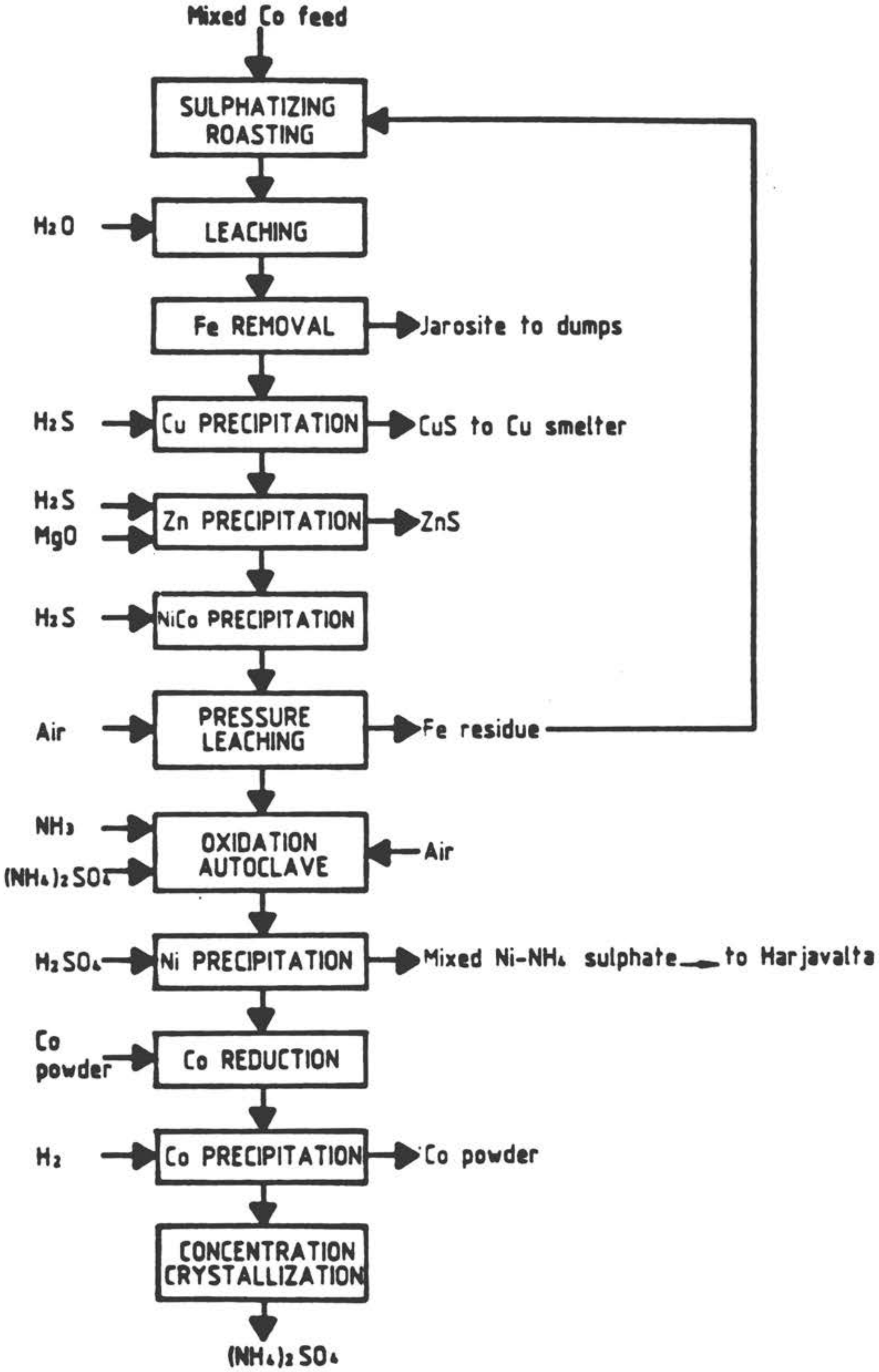

Figure C-5 Flow sheet of the Outokumpu's Kokkola plant.

PRODUCTION OF COBALT FROM MATTE AND MIXED SULPHIDES

As mentioned above the metallurgical treatment of sulphide or oxide nickel concentrates gives as final product a nickel matte or mixed nickel-cobalt sulphides from which the two metals can be recovered. Cobalt is in this sense really a by-product of nickel. Table C-2 shows the different ways used in plant practice.

The Sulphuric Acid Route

Let us first take a look to the AMAX plant at Port Nickel, Louisiana. This plant was originally built in 1959 by the Freeport Sulphur Company in order to process mixed nickel-cobalt sulphides from Moa Bay in Cuba. Due to political changes in that country, there resulted a curtailment in the supply of this raw material to this plant and the site in the U.S.A. remained idle until it was taken over by AMAX in 1972 and converted for the treatment of mattes. The feed of the plant is presently:

- BCL matte from Botswana (Percent: 42 Ni, 37 Cu, 0.5 Co, 48.5 S)
- Agnew matte from Western Mining in Australia.

The mattes are crushed, wet milled and blended to a mixture of:
Percent: 47 Ni, 35 Cu, 20 S, 1.2 Fe, 0.5 to 1.2 Co

The process flow-sheet is given in Figure C-6 (Hoppe 1977, Nikolic et al. 1980, Llanos et al. 1973). The $CuSO_4$-$NiSO_4$ spent electrolyte from the copper electrowinning tank house is used to perform the atmospheric leaching of the matte. During leaching half of the nickel and the cobalt from the matte go into solution, while the copper from the leaching solution is cemented and the iron is kept insoluble by close pH control. Solids from this first leaching step are sent to a two step pressure leaching process. The atmospheric leach solution at 75 gpl Ni and 1 gpl Co is treated with ammonium persulphate to precipitate the cobalt. The cobalt free solution is sent to the nickel recovery (Sheritt process). The cobaltic and the solution is further purified for nickel by the pentammine process (SGM process). After nickel removal the cobalt solution is further depleted in nickel by ion-exchange and cobalt is then reduced with hydrogen to cobalt powder. The cobalt powder is dryed under hydrogen at 540°C and then sintered to cobalt briquettes also under hydrogen at 960°C. The plant capacity is 545 tons of cobalt per year.

It was mentioned very recently (Metal Bulletin, November 1981) that AMAX plans an extension of the Port Nickel refinery to process cobalt-bearing ores through solvent extraction and electrowinning to cobalt cathodes.

Sulphate pressure leaching is also used by MRR in South Africa on a nickel matte rich in the platinum group metals. The leach solution contains about 100 gpl Ni and 1 to 2 gpl Co. Cobalt is removed with nickelic hydroxide (Outokumpu process) into a cake at 3 Co/1 Ni. The cake is leached in sulphuric acid, in the presence of formaldehyde to reduce the cobalt to its second oxidation state. The cobalt is then extracted with DEHPA, stripped and crystallized as $CoSO_4 . 7 H_2O$. The capacity of the plant is about 100 tons of cobalt per year (Clemente et al. 1980).

TABLE C-2 Production of Cobalt from Nickel Matte and Mixed Nickel-Cobalt Sulphides

Company	Leaching		Ni/Co	Outlet	Capacity
	Pressure	Media	Separation	Co	+ Co/yr
AMAX, Port Nickel	Atm+pressure	H_2SO_4	Amax process	powder	545
MRR, South Africa	yes	H_2SO_4	SX process	$CoSO_4.7H_2O$	100
NM, Hitachi	yes	H_2SO_4	SX process	Co cathodes	1300
Outokumpu, Kokkola	yes	H_2SO_4	Sherritt process	Co powder	230
SLN, Le Havre	no	$FeCl_3Cl_2$	SX process	$CoCl_2$ solution	600
Falconbridge, Kristiansand	no	HCl	SX process	Co cathodes	2000
	no	Cl_2	SX process	Co cathodes	2000
SMMC, Niihama	yes	H_2SO_4	SX process	Co cathodes	1410
Sherritt, Fort Saskatchewan	yes	NH_4O_4	Sherritt process	Co powder	600

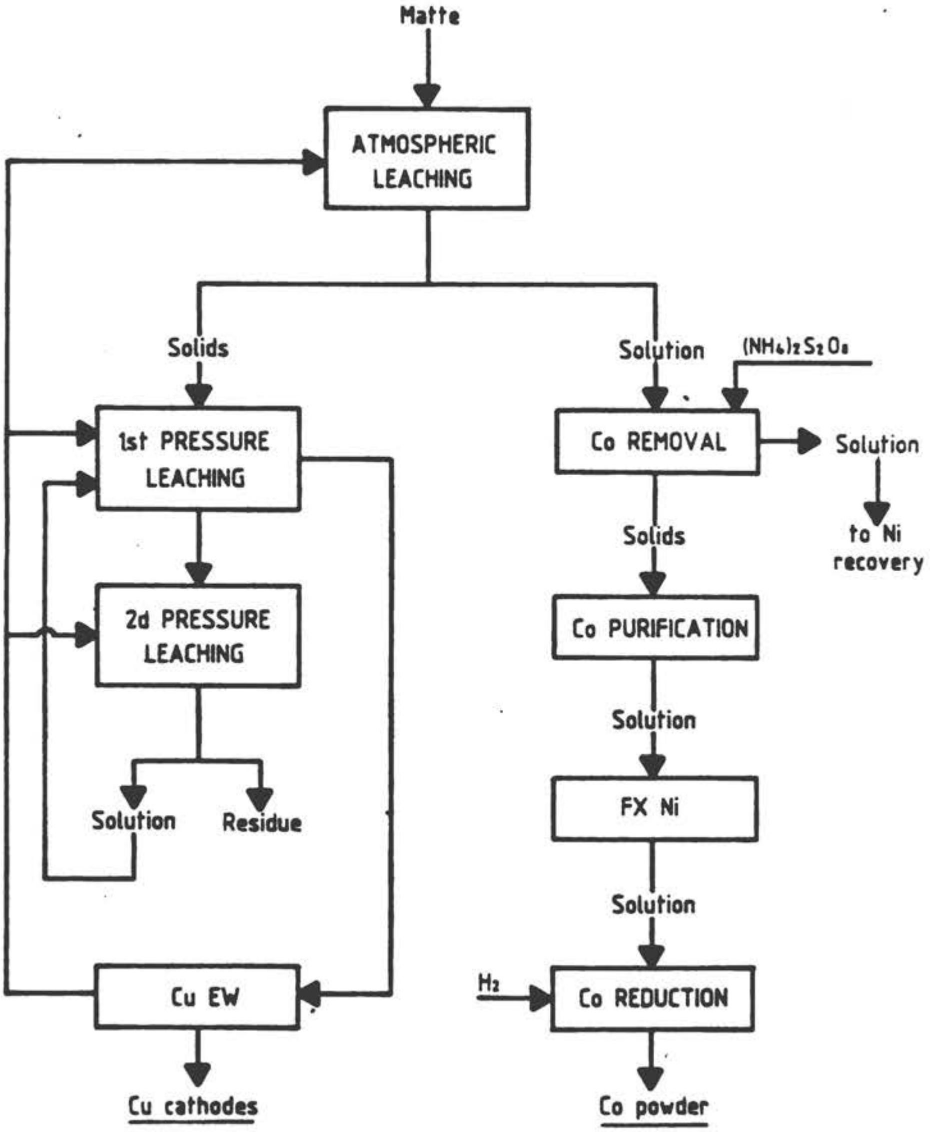

Figure C-6 AMAX Port Nickel refinery.

The Nippon Mining Plant at Hitachi in Japan also makes use of a sulphuric acid pressure leach to treat about 4,000 tons per year of mixed sulphides at 37 percent Ni and 15 percent Co from the Greenvale operations in Austrialia. The flow sheet is given in Figure C-7 (Kasai et al. 1980, Nishimura 1981). The mixed sulphides are pressure leached at 170° and 50 kg/cm^2 with sulphuric acid and air. Iron is removed by NaHS to 1 mgpl and zinc is extracted with DEHPA at pH 2.0 - 3.0 to 1 mgpl. Cobalt is then extracted with an alkyl phosphonic acid and electrowon in sulphate media at 100 gpl Co, 60°, 200 A/m^2 using lead anodes and stainless steel cathodes. After cobalt extraction to less than 0.5 mgpl the nickel raffinate is contacted with LIX64N to extract the nickel which is also electrowon. The remaining solution is treated with a slurry of lime to recover NH_3. The capacity of the plant is 1300 tons of cobalt per year. The analysis of the cobalt cathodes is as follows:

(percent) 99.97 Co
(ppm) 20 Ni, 0.1 Zn, 0.1 Pb, 5 Fe, 2 Cu.

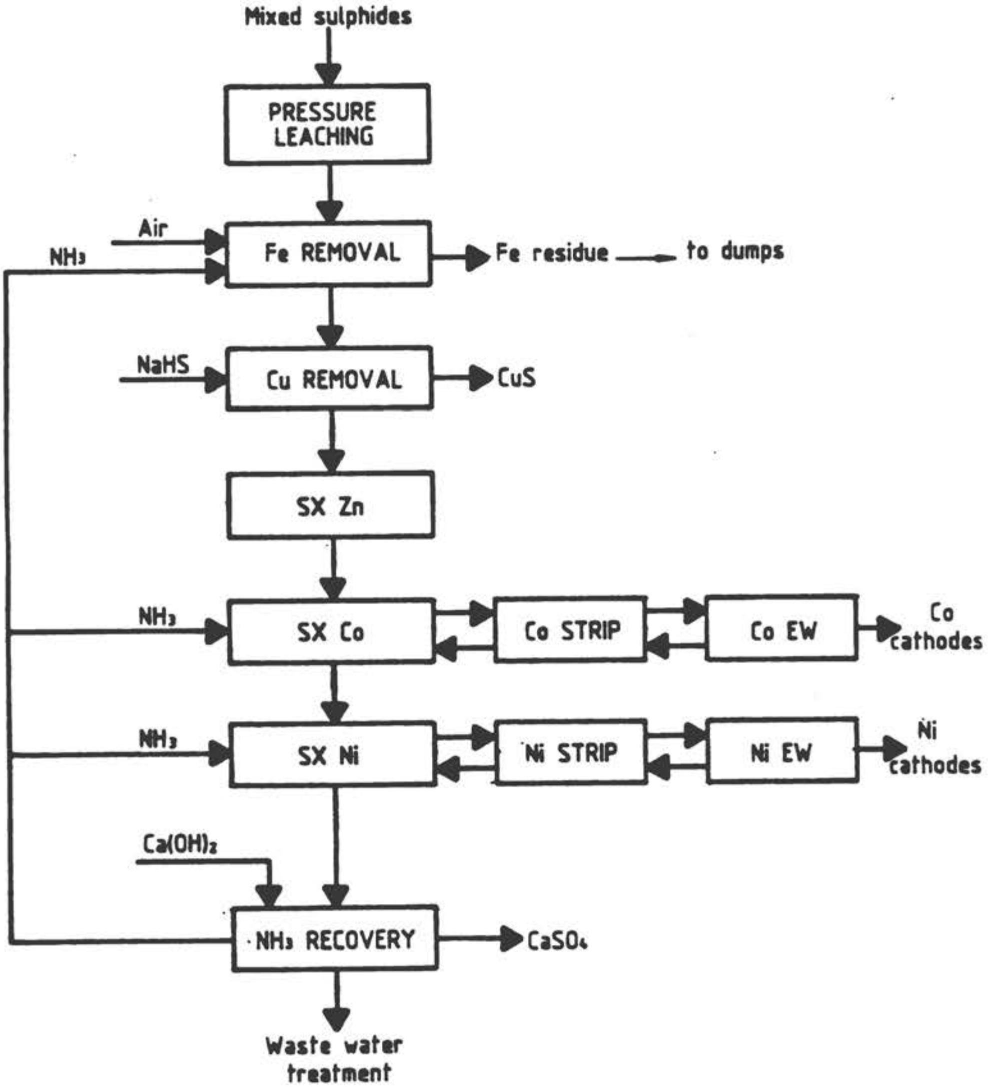

Figure C-7 Nippon Mine's Hitachi flow-sheet.

Regarding Outokumpu Oy we already mentioned the cobalt plant of Kokkola. But we have to include a short description of the processing of the nickel matte which is produced at the Harjavalta flash smelter (Ojanen 1980). The matte is granulated, crushed, and milled to 90 percent minus 270 mesh and leached at atmospheric pressure in three counter-current steps with the nickel electrowinning spent electrolyte. The matte is in fact a mixture of Ni_3S_2, Cu_2S and a Ni-Cu alloy. During the H_2SO_4 leaching the alloy is dissolved as well as one third of the nickel sulphide, the copper sulphide remaining unattacked. The leach residue is recycled to the smelter, the solution is purified by copper electrowinning and cobalt is finally precipitated with nickelic hydroxide to a cobalt cake (230 t/y Co) which is sent to the Kokkola plant. Nickel is recovered from the solution by electrowinning. The overall yield of the Harjavalta smelter is about 47 percent cobalt.

The Chloride Route

Two plants use a chloride route: Falconbridge and SLN.

The Falconbridge plant in Kristiansand, Norway, treats the nickel matte from the company's operations in Sudbury, Ontario, some matte from Western Platinum in South Africa and other sulphide materials. About 15 percent of the feed is handled by the matte-leach process in which nickel and cobalt are selectively leached at 70°C in a 280 gpl HCl solution (Thornhill et al. 1971). The other 85 percent are processed by direct cholrine leach. The cobalt from both circuits is extracted with TIOA and recovered by electrowinning in chloride media. Nickel is electrowon in a mixed chloride-sulphate electrolyte. The capacity of the plant is about 2,000 tons of cobalt per year and the purity of the cobalt cathodes is about 99.90 percent cobalt.

As already mentioned the nickel matte from the SLN's Doniambo plant in New Caledonia is shipped to the Sandouville plant near Le Havre in France. The matte with 75 percent Ni and 1 to 2 percent Co is leached with $FeCl_3$ and chlorine at atmospheric pressure, giving a solution with

(gpl) 210 Ni, 4.6 Co, 9-10 Fe

and a residue from which elemental sulphur is recovered (Hupper and Ries 1980). Iron is extracted from the leach solution with TBP and $FeCl_3$ is stripped from the organic phase with water. Part of the $FeCl_3$ is recycled to the leaching, part is concentrated and sold as a concentrated $FeCl_3$ solution. Cobalt is then extracted with TIOA and the $CoCl_2$ solution sold for cobalt recovery. The remaining nickel chloride solution is electrowon on nickel starting sheets and the recovered chlorine is sent back to the leaching.

The capacity of the plan is 16,000 tons Ni cathodes, 600 tons Co in $CoCl_2$ solution, 1,000 tons Fe in $FeCl_3$ solution and 4,000 tons per year of elemental sulphur.

The Sulphate-Chloride Route

This route was chosen by Sumitomo Metals Mining Company (SMMC) for the treatment of the mixed sulphides from Marinduque Mining and Industrial Corporation (MMIC) in the Philippines, in combinaton with the cobalt hydroxide cake from SMMC's nickel refinery. The capacity of the Niihama refinery is about 2,400 tons of nickel and 1,400 tons of cobalt per year (Nishimura 1981, Fujimoro et al. 1980).

The mixed sulphides are pressure leached with sulphuric acid. Manganese, iron, copper and zinc are removed and cobalt and nickel are co-extracted with versatic acid. Stripping of the organic phase is done with hydrochloric acid. Cobalt is then extracted from the mixed nickel-cobalt chloride solution with TNOA, stripped and electrowon with chlorine evolution.

The chlorine from the cobalt and nickel electrowinning operations is burned with hydrogen to hydrochloric acid which is recycled to the nickel-cobalt stripping step. No further details will be given now because this process will be more fully described in another paper.

The Ammoniacal Route

This process was developed during the 1950s by Sherritt-Gordon Mines Ltd. in their Fort Saskatchewan plant in Alberta for the treatment of nickel sulphidic concentrates from their Lynn Lake mine in Manitoba (Mackiw and Veltman 1980). As this mine is exhausted, the Fort Saskatchewan refinery now handles a lot of different materials, e.g., mixed sulphides from INCO, granulated matte from Western Mining (10Ni/1Co), a cobalt cake from Marinduque (1 Ni/1 CO) and so on. The average feed contains about:
percent 10 Ni, 2 Cu 0.4 Co, 33 Fe, 30 S.
The installed capacity is 14,600 tons of nickel and 600 tons of cobalt per year but an expansion of the refinery to 800 tons of cobalt is now completed.

The flow-sheet is given in Figure C-8. Matte and sulphides are leached with air in autoclaves at 83°C and 7 bar in ammoniacal media. Most of the copper from the leaching solution is removed in the so-called "Cu boil pots" where unsaturated sulphur compounds are destroyed, giving a mixture of CuS and Cu_2S and enabling NH_3 recovery. The solution still contains 0.1 gpl Cu and is further decopperized by H_2S in autoclaves, giving a mixed nickel-copper sulphide which is recylcled to the leaching. The solution now contains about 50 gpl Ni and 1 to 1.5 gpl Co and is sent to an oxyhydrolysis step in an autoclave at 65 bar where, by injection of air, the remaining sulphamates and thiosulphates are converted to ammonium sulphate. The solution then enters reduction autoclaves where nickel is precipitated by hydrogen at 36 bar as a powder. The resulting solution containing 1 to 1.5 gpl Ni and the same amount of cobalt is treated with H_2S in an autoclave to precipitate mixed nickel-cobalt sulphides which are the feed to the cobalt plant. The remaining solution is concentrated and saleable ammonium sulphate is obtained.

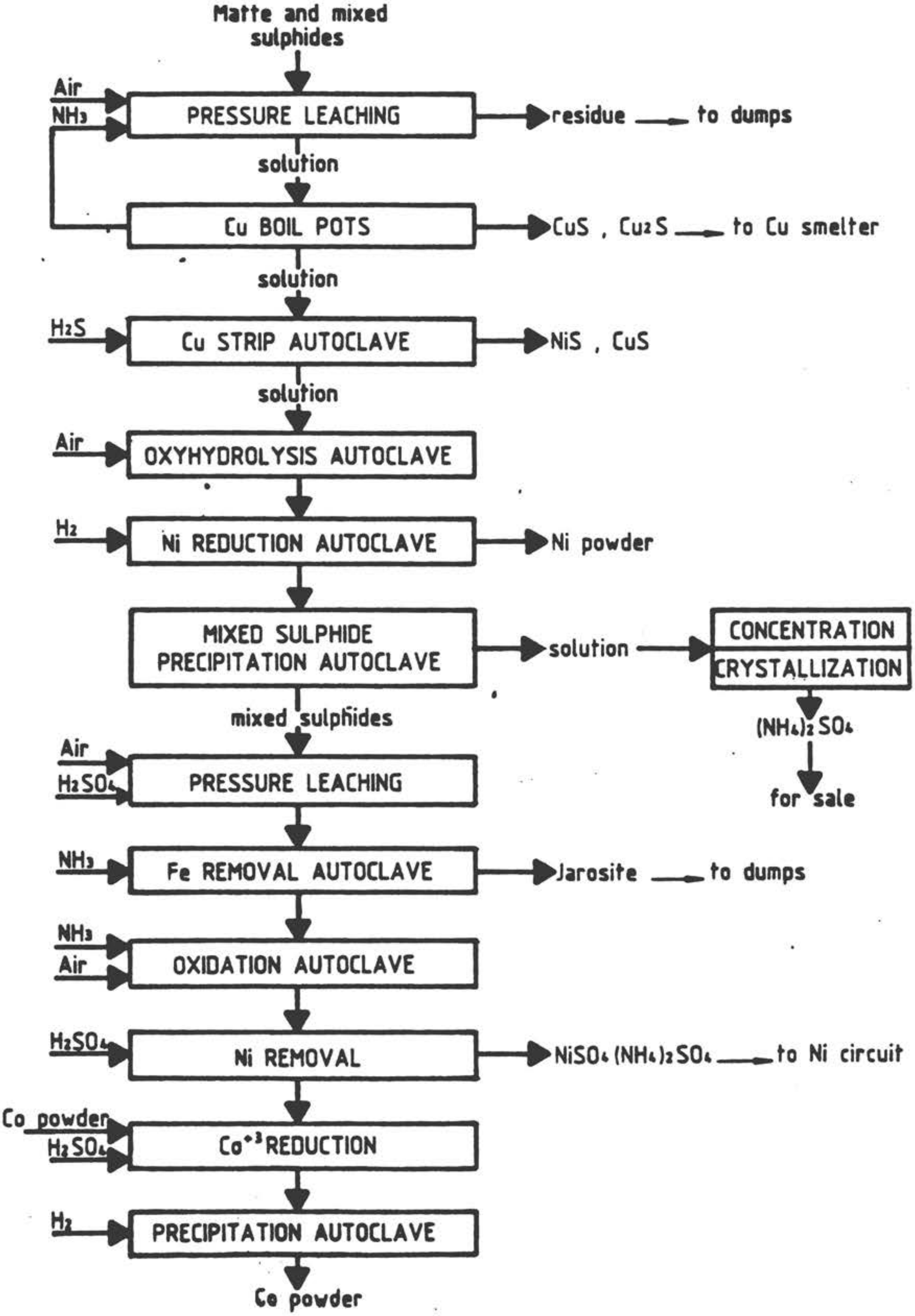

Figure C-8 Sherritt's Fort Saskatchewan's flow-sheet.

At the cobalt plant the mixed sulphides are repulped and autoclave leached with sulphuric acid at 140°C and 64 bar. Iron is subsequently removed at pH 2.5 to 3.0 with ammonium hydroxide as a jarosite and the solution now contains:

gpl 40 Ni, 30 Co, 15 Zn, 0.008 Fe, 0.01 Cu.

Cobalt in solution is oxidized by air in autoclave and in the presence of ammonium hydroxide to the tervalent state as a soluble cobalt pentammine complex (Mackiw and Benx 1961). Nickel is then removed from solution in two steps by adding sulphuric acid which gives a precipitate of a double sulphate nickel-ammonium salt which is recycled to the nickel refinery. After removing the crystals the solution now contains:

gpl 45 Co, 0.015 Ni.

The solution is treated with cobalt metal powder and sulphuric acid in order to reduce the cobalt to the bivalent state and the cobalt solution is then reduced in autoclaves with hydrogen at 46 bar and 120°C to cobalt powder. This powder is washed and then dried in hydrogen. The overall cobalt yield of the plant is about 80 percent.

The Sherritt technology is also used by Impala Platinum in South Africa since 1969 to treat a nickel-copper matte containing PGM's. They intend to produce now small amounts of cobalt powder as a by-product of platinum by the end of 1982 (Metal Bulletin October 1981).

Near Perth, Australia, Western Mining Corporation's Kwinana Refinery uses a Sheritt process to treat nickel sulphide concentrates and matte.

COBALT RECOVERY FROM OTHER MATERIALS

The problem of cobalt recovery from copper convertor slags has already been discussed. The distribution of cobalt between matte and slag in nickel smelters was also given according to Matousek's estimations. The author emphasizes also that cleaning of reverberatory or electric furnace slags should improve the overall cobalt recovery.

Turning to recycling, it is evident that due to high cobalt prices, a great number of cobalt consumers attempt to recycle this metal. This is already on the way for the recovery of cobalt from spent catalysts (e.g., CoMo and CoMn), from residues of hard metals and from superalloys. It is expected that recovery of cobalt will be more and more practised in the future.

A possible new source of cobalt could be the deep sea manganese nodules which contain about 0.25 percent Co and which may be regarded as the major potential cobalt source.

CONCLUSIONS

Cobalt extractive metallurgy made important steps forward in the last decades. Several improvements were made in cobalt purification processes for extraction of cobalt from copper concentrates by the sulphuric acid route, producing high quality electrowon cobalt.

Due to high cobalt prices, more attention has been paid to this metal by the nickel smelters and the potential of recovering cobalt from this source has already increased and could still be enhanced.

Major technical improvements were introduced in the processing of nickel mattes and mixed sulphides. Although the Sherritt technology for separation of nickel and cobalt is still mostly used, solvent extraction looks promising.

It is also expected that cobalt recovery from spent catalysts, hard metals, superalloys, and deepsea nodules could well become more and more important.

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CONCENTRATION OF COBALT ORES

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Cobalt is not found native except in meteorites, but occurs as sulfides, arsenides, sulfo-arsenides and oxidized minerals (carbonates, arsenates and complex hydrated oxides). More than 60 different cobalt minerals have been described (R. S. Young 1960), with cobalt contents running up to 60 percent. These cobalt minerals are associated in cobalt deposits with other valuable minerals and with the gangue, forming cobalt ores with cobalt contents varying from a trace to a few percent.

Like for other base metal ores, physical concentration processes, which do not modify the chemical characteristics of the minerals, should be applied in order to permit to supply the metallurgists with higher grade material. Cobalt concentrates are thus produced, however seldom assaying more than 10 to 15 percent cobalt. This indicates the limitations offered by physical concentration when applied to cobalt ores.

The aim of this paper is to explain the difficulties encountered in concentrating cobalt ores and to show that improvements are still going on in this field. We will of course limit our survey to typical cobalt ores and will thus not consider the cobalt which may be present in very minor amounts as solid solution in sulfide minerals such as galena, sphalarite or chalcopyrite.

COBALT ARSENIDE ORES

The principal cobalt arsenide minerals are either diarsenides (CoAs) such as smaltite (cubic) and safflorite (orthorhombic), or triarsenides ($CoAs_3$) such as skutterudite (cubic). These minerals characterize the primary cobalt ore deposits of the Bou-Azzer are in Morocco, where they are associated with a calcite-dolomite-talc-chlorite paragenesis.

Since the cobalt arsenides have specific gravities ranging from 6.5 to 7.2 and since a large proportion of the gangue can be separated as nearly free gangue at rather large grain sizes, gravity methods of concentration using jigs, spirals and shaking tables give successful results, as shown in Table 1.

TABLE 1 Typical Results of Cobalt Concentration at Bou-Azzer, Morocco

		Percent		
		Weight	Cobalt	Recovery
Jigs	Feed	100	1.928	100.0
	Concentrate	10	14.32	76.0
	Tail	41	0.05	1.1
Spirals	Feed	49	0.91	22.9
	Concentrate	2	12.29	13.9
	Tail	31	0.068	1.1
Tables	Feed	15	0.99	7.9
	Concentrate	1	11.47	5.9
	Tail	14	0.269	2.0
Total	Feed	100	1.928	100.0
	Concentrate	13	13.777	95.8
	Tail	87	0.093	4.2

Concentrates containing 13 to 14 percent cobalt have thus been produced in Bou-Azzer from 2 percent cobalt ore, with cobalt recoveries as high as 94 to 96 percent. Composition of various other cobalt arsenides flotation and table concentrates has been given by G. M. Ritcey and A. W. Ashbrook (Ritcey and Ashbrook 1981). Their cobalt contents vary from 6.4 to 16.8 percent with Co/As ratios of 0.16 to 0.29. The major cobalt minerals in these concentrates were safflorite and skutterudite.

As mentioned on the flow-sheet shown in Figure 1 (Formanek and Lauvernier 1964), flotation has been introduced for treating the <40 µm fraction from the spirals tails and tables. However, successful cobalt flotation appeared to require previous elimination of the talc by flotation, followed by desliming at 10 µm and conditioning the pulp with copper sulfate as activating agent and with sodium sulfide, amylxanthate being used as collector. The activation was considered as a necessary step in this process when the cobalt arsenides contain more than 3 to 4 percent iron.

Concentrations of Cobalt Ores

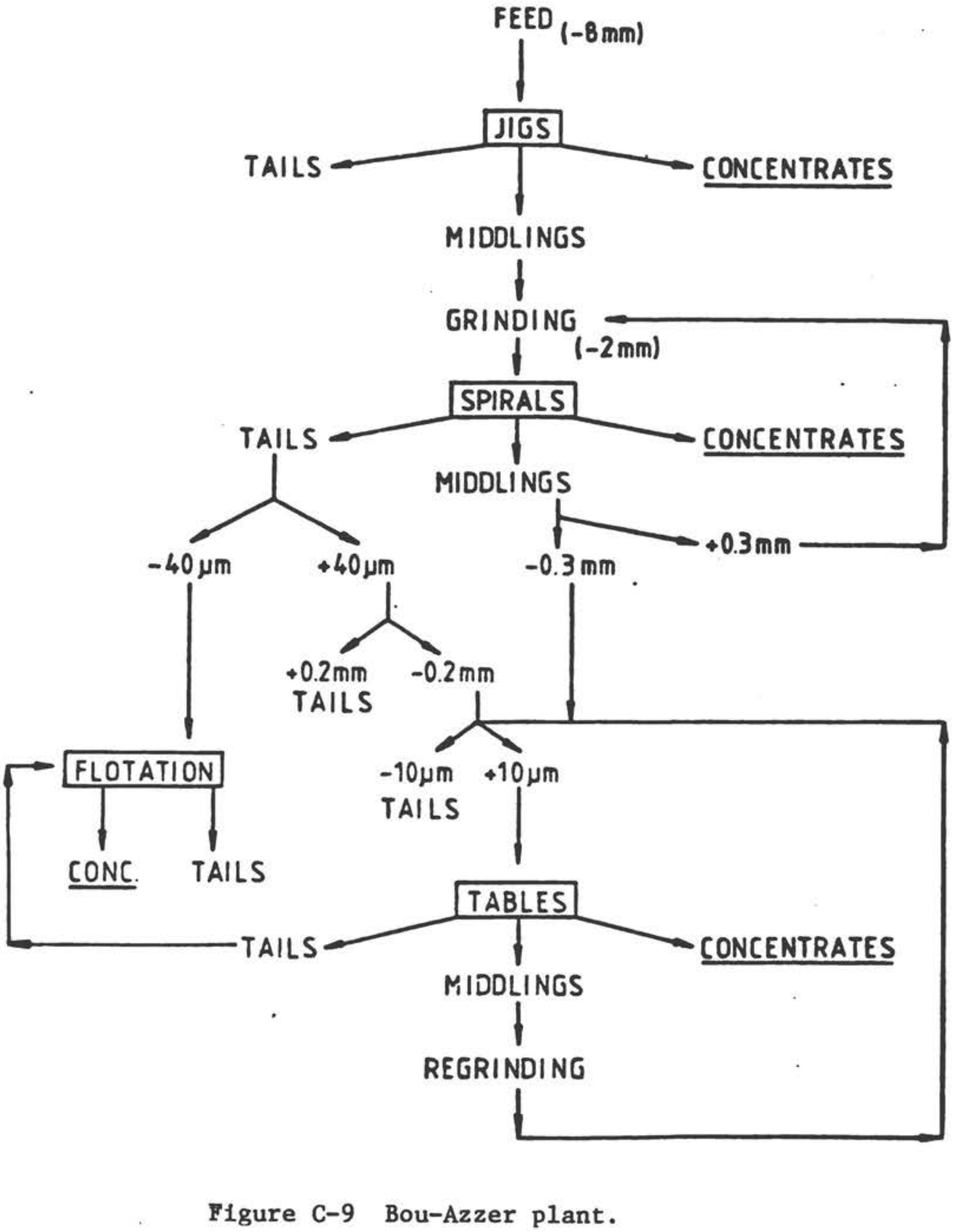

Figure C-9 Bou-Azzer plant.

On account of the critical conditions related to the cobalt flotation, this operation is limited to those ores which would give too low cobalt recoveries by the gravity methods. This would be the case where alteration of the ore becomes important and erythrite (a hydrous cobalt arsenate of specific gravity 3) is present.

There is undoubtedly a great need for further research studies in this field, particularly in view of retreating old tailings dumps. Such studies should not exclude magnetic separation since erythrite shows a relatively high magnetic susceptibility (53.2×10^{-6} cm^3/g) (Smith et al., 1976). One should also take advantage of the fact that these oxidized compounds have a strong tendency to form very fine slimes.

COBALT SULFO-ARSENIDE ORES

The main cobalt sulfo-arsenide mineral is cobaltite (CoAsS). This mineral is able to be floated effectively with xanthate at low pH values. According to the observation made by L. K. Smith, K. N. Han, and F. Lawson (Smith et al. 1976), maximum recovery is obtained at pH 4-5, while on both acidic and alkaline sides of this range, the recovery decreases very rapidly.

Unfortunately, the concentration of cobaltite is made complicated by the fact that the cobaltite ores also contain chalcopyrite and iron sulfides such as pyrite and pyrrhotite.

Chalcopyrite can be readily recovered as a high-grade copper concentrate by selective flotation at high pH (10.2 - 10.4) using any one of several copper collectors such as those belonging to the alkyl dithiophosphates group, while depressing the cobaltite and the iron sulfides with lime and sodium cyanide. But, the separation of the cobaltite from the iron minerals presents many more problems, since chemical reagents that depress iron minerals also depress cobaltite and, conversely, reagents that activate cobaltite also activate iron minerals.

Several methods have been proposed to solve these difficulties. Cunningham (1946) treats the copper tailing pulp with sulfuric acid and makes an acidic bulk flotation of the iron sulfides and cobaltite from the gangue; this bulk concentrate can subsequently be treated with a monocalcium aryl sulfonate or sodium cyanide in order to depress the cobaltite, while the iron sulfides are floated with xanthate after addition of an activator such as copper sulfate.

As reported by the American Cyanamid Company (1951), the following treatment has also been found effective: the copper sulfides are selectively floated at pH 10.2 after a long and strong aeration of the pulp at a temperature of 35°C, so that the cobaltite is depressed while the iron sulfides might still be floated with amylxanthate. The cobaltite is finally floated at pH 5 with secondary butylxanthate, after activation by sodium sulfide.

This favorable effect of sodium sulfide has been recently studied (Abeidu 1976) on a more scientific basis by adsorption measurements and electrokinetic potential determinations. This study which used free natural crystals of cobaltite, chalcopyrite and pyrite has shown that with sodium diethyl dithiophosphate, best selectivity between cobaltite and the other two sulfides should be expected in the pH range between 4 and 5, and in the presence of sodium sulfide, which under these conditions acts as an activator of cobaltite while depressing chalcopyrite and pyrite.

At the time Calera Mining Company was operating his concentrating plant for treating the cobaltite ore from the Blackbird mine in Idaho, the flow-sheet used was very similar (Douglas 1956), however, it started with a bulk flotation of all the sulfides using sodium sulfide and amylxanthate, the copper-cobalt-iron bulk concentrate being then heated to 40°C and subjected to a long conditioning treatment with lime at pH 10.4 in order to float selectively the copper sulfides. More sodium sulfide and xanthate were added for floating part of the iron sulfides, the residual part being floated with the cobaltite after activation of the latter with sodium sulfide and sulfuric acid at pH 3.5. The final cobaltite concentrate produced contained 15 percent Co, 20 percent Fe, and 24 percent As. The iron sulfides flotation was regulated so as to maintain the As/Fe ratio of the final cobalt concentrate between 1 and 1.2 in order to facilitate the removal of arsenic as iron arsenate during the pressure leach treatment.

The Blackbird mill tailings pond which has an average content of 0.23 percent Co and 0.29 percent Cu has been considered as a potential source for cobalt recycling (Rule and Siemens 1976). By direct flotation at natural pH of 3.7 and without regrinding, bulk concentrates were obtained with cobalt contents around 1 percent, using a combination of dithiophosphate and xanthate.

Finally, another method for obtaining rich cobaltite concentrates should still be mentioned, which has been proposed by S. R. Zimmerley and S. F. Ravitz (Zimmerley and Ravitz 1950). After the selective separation of the copper sulfides, a cobalt-iron bulk concentrate is produced, which is partially roasted in order to form an iron oxide coating on the iron sulfide particles. By subjecting the calcine to flotation, cobaltite concentrates assaying more than 20 percent Co were obtained.

Of course, the possibility of producing high grade cobaltite concentrates depends on the liberation size of this mineral: in some cases (such as in Mount Isa, Australia), this can be as low as a few microns, so that cobalt grades above 0.5 percent cannot be obtained.

COBALT SULFIDE ORES

Cobalt sulfide ores may be divided into four groups: Copper-cobalt sulfide ores, nickel-copper-cobalt sulfide ores, copper-zinc-cobalt ores, and cobalt-iron sulfide ores.

Copper-Cobalt Sulfide Ores

Cobalt occurs with copper as a double sulfide, carrollite ($CuS. Co_2S_3$), which is characteristic of the cobalt sulfide mineralization of the copper-cobalt ore bodies found in the Shaba province of Zaire and in Zambia. However, in the latter country, other cobalt-bearing minerals may also be present in substantial proportions, namely cobaltiferous pyrites, which at some places may contain up to 22 percent cobalt. Another big difference between the copper-cobalt sulfide ores of the Shaba deposits and of the Zambian Copperbelt lies in the associated copper minerals: while chalcocite is predominant in Shaba, chalcopyrite and bornite are the major copper sulfides present in most of the Copperbelt sulfide ores. Therefore, we shall consider these cases separately.

The Chalcocite-Carrollite Ores of Shaba

These ores are generally mixed oxide-sulfide ores, with average contents of 4 to 5 percent copper and 0.1 to 0.35 percent cobalt. The gangue presents a strong dolomitic character, which will impose the flotation procedure to be used for concentrating the oxide minerals as we shall see later. But let us consider here the way the carrollite is recovered (White 1979).

Chalcocite and carrollite are floated together at pH 9.2 using lime, a 1:1 mixture of ethyl and isopropylxanthates as collector and triethoxybutane as frothing agent. The bulk copper-cobalt concentrates thus produced contain 43 to 53 percent Cu and 0.5 to 3.5 percent Co, with a copper recovery of 85-90 percent while that of cobalt has a lower average value which does itself much fluctuate according to the wide variations in cobalt sulfide content and to the fineness of dissemination of the ores.

Since a part of the feed of the Gecamines Lubambashi smelter must derive from copper-cobalt sulfide concentrates, and since this plant does not have facilities for cobalt extraction, a selective separation between chalcocite and carrollite had to be realized. According to the literature (American Cyanamid Report, September 1951), such separation could be obtained by depressing carrollite by cyanide. Nevertheless, systematic studies (Van Belle 1975, Van Belle and Iyolo 1976) have been made by Gecamines' Research Department on laboratory and pilot scale, using lime, sodium cyanide, sodium sulfhydrate and calcium hypochlorite. Hallimond tests were also made in our laboratory, respectively on chalcocite and carrollite specimens coming from these African deposits and which we first purified to 96 to 98 percent purity by a combination of tabling, superpanning, and magnetic separation. Some observations derived from our tests, at pH 9 with 8 mg/l potassium amylxanthate, are summarized in Table 2.

TABLE 2 Hallimond Tests on Chalcocite-Carrollite Separation

Modifier	Percent Recovery Chalcocite	Carrollite
	86	80
$KMnO_4$(1 mg/l)	27	70
$FeCl_3.7H_2O$(10 mg/l)	15	70
NaSH (20 mg/l)	85	0

The separation has been introduced on a commercial scale in the Gecamines concentrating plants since 1970 with sodium cyanide. However an important parameter appears to be the pH, which should be brought up to 12.3 to 12.4 by addition of lime. Two concentrates are thus produced: a high-copper one assaying up to 65 percent Cu and a maximum of 2 percent Co,. and a low-copper concentrates which assay 35 to 38 percent Cu and up to 4 percent Co.

Some ores are of course lower in copper and on the high side for cobalt but the same process is followed. Table 3 shows the results currently obtained by Gecamines in such a case. By applying the chalcocite-carrollite separation process to these bulk copper-cobalt concentrates, the following concentrates were finally produced:

- a copper-rich concentrate assaying 63.7 percent Cu and 2.5 percent Co;
- a cobalt-rich concentrate assaying 38.2 percent Cu and 5.3 percent Co.

TABLE 3 Results of Copper-Cobalt Sulfide Ores Flotation at the Kambove Mill of Gecamines

		Copper		Cobalt	
	Percent Weight	Percent	Percent Recovery	Percent	Percent Recovery
Bulk Cu-Co conc.	5.9	44.80	90.9	4.33	77.4
tail	94.1	0.28	9.1	0.08	22.6
feed	100.0	2.94	100.0	0.33	100.0

Source: Personal communications given by the Management of Gecamines, Zaire, October 1981.

The Copper-Cobalt Sulfide Ores of Zambia

As already mentioned, these ores differ from their Zairian equivalents by two important aspects: nature of the cobalt mineralization and nature of the associated copper minerals. The predominance of chalcopyrite and bornite in comparison to chalcocite and the frequent presence of cobaltiferous pyrite as cobalt mineral besides carrollite will modify the flotation conditions and permit a more selective separation between copper and cobalt. Thus, in the Baluba and Chibuluma concentrators, differential flotation has become the common practice; the copper minerals are selectively floated at pH 10.5 - 11 and with the aid of sodium cyanide to depress the cobalt minerals, which are subsequently activated by sulfuric acid and floated at pH 8.5 - 9 with sodium isopropyl xanthate. Typical metallurgical balances are shown in Tables 4 and 5, respectively for the Baluba and Chibuluma sulfide ores concentrating plants.

TABLE 4 Results of Copper-Cobalt Sulfide Ores Flotation at the Baluba Plant, Zambia

Baluba Sulfide Plant	Percent Weight	Copper		Cobalt	
		Percent	Percent Recovery	Percent	Percent Recovery
copper concentrate	3.5	32.49	60.5	0.25	6.0
cobalt concentrate	4.4	13.42	31.9	2.25	67.9
tailing	92.1	0.15	7.6	0.04	26.1
feed	100.0	1.85	100.0	0.15	100.0

Source: Personal communications given by the Management of Nchanga Consolidated Copper Mines Ltd. and Roan Consolidated Mines Ltd. Mining Industry Technical Services, Zambia, October 1981.

TABLE 5 Results of Copper-Cobalt Sulfide Ores Flotation at the Chibuluma Plant, Zambia

Chibuluma Sulfide Plant	Percent Weight	Copper		Cobalt	
		Percent	Percent Recovery	Percent	Percent Recovery
copper concentrate	6.0	29.41	73.2	0.25	8.8
cobalt concentrate	8.0	6.98	23.3	1.82	85.4
tailing	86.0	0.08	3.5	0.009	05.8
feed	100.0	2.41	100.0	0.17	100.0

Source: Personal communications given by the Management of Nchanga Consolidated Copper Mines Ltd. and Roan Consolidated Mines Ltd. Mining Industry Technical Services, Zambia, October 1981.

Substantial difference can be observed between these two flotation performance tables, particularly in the losses of cobalt to the final tails and in the amount of copper remaining in the cobalt concentrate. They are accounted for by the differences in the mineralogical characteristics of the ores; in the Baluba feed, there is a higher relative abundance of chalcocite and carrollite, while pyrite is relatively less abundant but at the same time richer in cobalt; moreover, the gangue of the Baluba ore seems to present a more complex composition and to contain some unrecoverable cobalt in silicates and in wad.

In the Rokana sulfide concentrating plant (White 1979; Cocquerel 1980), present practice does not make use of differential flotation, but consists in a bulk copper-cobalt sulfide flotation, followed by a selective separation of the copper sulfides from the recleaned bulk concentrate, by depressing cobalt sulfides with sodium cyanide and lime at pH 11.5. Cobalt is finally refloated with a cationic collector at pH 7.5-8 in the presence of a gangue depressant. Typical results are given in Table 6.

TABLE 6 Results of Copper-Cobalt Sulfide Ores Flotation at the Rokana Plant, Zambia

Rokana Sulfide Plant	Percent Weight	Copper		Cobalt	
		Percent	Percent Recovery	Percent	Percent Recovery
copper concentrate	4.5	28.5	86.4	0.55	25.2
cobalt concentrate	1.5	6.4	6.5	3.19	48.7
tailing	94.0	0.11	7.1	0.028	26.1
feed	100.0	1.47	100.0	0.10	100.0

Source: Personal communications given by the Management of Nchanga Consolidated Copper Mines Ltd. and Roan Consolidated Mines Ltd. Mining Industry Technical Services, Zambia, October 1981.

These results indicate that a rather high proportion of the cobalt present in the bulk concentrate reports to the final copper concentrate, most probably due to extremely fine mineral-locking and intergrowth.

Nickel-Copper-Cobalt Sulfide Ores

Nickel-copper sulfide ores, such as those mined in the Sudbury district of Ontario and in the Lynn Lake area of northern Manitoba, Canada, do contain minor amounts of cobalt, generally lower than 0.10 percent.

Cobalt occurs in these ores mainly as a solid solution in pentlandite $(Ni,Fe,Co)_9\ S_8$, so that no attempt is made to separate cobalt by physical concentration methods. Almost all the cobalt recovered within the nickel sulfide concentrate, although part of it might be lost in the pyrrhotite which is generally the predominant associated sulfide and may itself contain nickel and cobalt as substitutes for iron.

There is consequently no problem of cobalt concentration as such, and we should rather refer to the concentration of copper-nickel sulfide ores. Without going into the details of this treatment, it is worth mentioning that the copper-nickel sulfides separation is a very complex problem, due mainly to the fact that in most cases pentlandite and, to a lesser extent, chalcopyrite are extremely finally divided in the pyrrhotite. Such dissemination may even take the form of ultra-fine exsolution lamellas. The nature of the gangue may also complicate the separation by the presence of naturally floating minerals such as talc or by the presence of olivine which may itself contain over 0.05 percent Ni.

Therefore in many cases, the concentration problem is limited to the separation of a bulk chalcopyrite-pentlandite concentrate, sufficiently freed from pyrrhotite and silicate gangue minerals. In favorable cases, this bulk concentrate can be retreated for selective separation between the copper and nickel sulfides. Such retreatment may include regrinding and several cleaning stages, before final separation at high pH (around 12) with addition of some colloid such as starch or guar gum to depress the nickel.

When the Cu/Ni ratio of the ore is high, there should be no difficulty in floating first the chalcopyrite while depressing the nickel and iron sulfides with the use of lime and, if necessary, of small amounts of cyanide. After separation of most of the chalcopyrite in a rich copper concentrate, the nickel and iron sulfides can be floated after activation by copper sulfate and be further retreated to give, together with the cleaner tails of the copper circuit, a combined nickel-copper low grade concentrate.

A similar procedure can be used for other copper-nickel-cobalt sulfide ores, such as those containing chalcopyrite, linnaeites $(Co,Ni)_2(Co,Ni,Fe,Cu)S_4$ and cobaltiferous pyrite (Tveter and McQuiston 1962). Chalcopyrite is floated first in an alkaline circuit, at pH 11 regulated by the addition of lime. If necessary, selectivity can be enhanced by small amounts of cyanide. This is followed by floation of low grade copper-cobalt concentrate after activation of the copper tailings with copper sulfate and lowering of pH with acid to pH 9.

Copper-Zinc-Cobalt Sulfide Ores

The problem of treating copper-zinc sulfide ores by selective flotation is, in most cases, one of the most difficult ones for mineral dressing engineers. There is indeed a strong tendency for sphalerite to contaminate the copper sulfide concentrate, due to its activation by copper ions present in the pulp. The degree of alteration of the ore contributes therefore directly to the complexity of the problem, besides the extremely fine dissemination which characterizes some of these ores (exsolution phenomena of chalcopyrite, pyrite and pyrrhotite in sphalerite, leading to inclusions of grain size as small as a few microns).

Typical examples of such complex ores are found in the Outokumpu deposits in Finland. These may also contain some cobalt, like at Keretti and Vuonos (Heinonen and Anttonen 1981). This cobalt is present in these ores, mainly as cobaltiferous pentlandite, and also partially in the pyrite which itself contains up to 5 percent Co, and, as extremely fine exsolutions, in pyrrhotite.

At Keretti, where the ore contains 0.6 percent Co, the standard practice of selective flotation of copper-zinc sulfide ores is used, i.e., copper sulfides flotation under conditions which would keep the sphalerite and pyrite non-floatable (high pH and addition of sodium cyanide), followed by zinc sulfides flotation and finally by cobalt flotation at lower pH (around 9), similarly to the procedure already mentioned for copper-nickel-cobalt sulfide ores.

At Vuonos, where the ore contains only 0.12 percent Co which is partially bound to pyrrhotite, better results have been obtained by starting with a bulk copper-cobalt flotation at pH 9 with addition of zinc sulfate to depress sphalterite and ending with the zinc flotation after activation by copper sulfate and addition of lime and cyanide to depress pyrrhotite. The copper-cobalt separation from the bulk concentrate consists in floating the copper selectively at pH 11.5 in the presence of cyanide.

Cobalt-Iron Sulfide Ores

A number of pyrites have been reported as bearing cobalt in solid solutions. Some may be very rich as we have seen in the copper-cobalt sulfide ore deposits of the Copperbelt in Zambia, where cobalt contents of several percent in the pyrite are very common values. But we shall now consider the low grade cobaltiferous pyrites, i.e., with cobalt contents lower than 2 percent. This is for instance the case of the Kilembe ores in Uganda.

In these ores, the pyrite occurs as octahedral crystals and in massive form containing over one percent cobalt in solid solution. It is associated with chalcopyrite and a silicate gangue (principally amphiboles) (Bird 1968).

The problem thus consists in the selective separation of the ore between three products: a chalcopyrite concentrate, a cobaltiferous pyrite concentrate and the gangue. At first sight, one might expect to solve it following a procedure similar to the one already suggested for copper-nickel-cobalt ores containing chalcopyrite, linnaeites and cobaltiferous pyrite. Nevertheless, at Kilembe, the preference has been given to a bulk flotation of all the sulfide minerals, followed by a differential flotation during which the pyrite is depressed. The reason for this choice has to be related with the very fine interlocking of the sulfide minerals, as confirmed by the fact that, between the two flotation stages, a very fine regrinding of the bulk concentrate was introduced. The regrind ball mill discharge which finally reports to the differential circuit is above 95 percent - 200 mesh. The pH in the bulk flotation is kept at 10.8, whereas in the differential circuit it is raised to 12.2 to 12.5. A rather complex combination of several collectors such as xanthates, dithiophosphates and thiocarbamates is used in the bulk flotation, but no collecting agent is added to the differential circuit. Average results obtained at the Kilembe mill for the last twenty years of operation are given in Table 7.

TABLE 7 Average Results of Copper-Cobalt Ore Flotation at the Kilembe Mill, Uganda

Kilembe Mill	Percent Weight	Copper		Cobalt	
		Percent	Percent Recovery	Percent	Percent Recovery
copper concentrate	6.2	28.4	92.7	0.19	09.1
cobalt concentrate	7.1	0.40	1.5	1.36	61.3
tailing	86.7	0.13	5.8	0.07	29.6
feed	100.0	1.90	100.0	0.17	100.0

Source: A. G. Mfite Basaza: Personal communication, October 1981.

COBALT OXIDE ORES

Cobalt oxide ores may be subdivided into three groups:

1. Cobalt-arsenate;
2. Copper-cobalt oxide ores; and
3. Nickel-cobalt oxide ores.

Cobalt Arsenate Ores

Erythrite ($3CoO.As_2O_5.8H_2O$) is the main alteration product of cobalt arsenides and sulfo-arsenides. Its potential commercial importance would therefore be related to these last cobalt minerals deposits and particularly to the tailings dumps from old mining and milling operations such as those of the Bou-Azzer area in Morocco.

The technical literature remains silent about the floatability of erythrite. This mineral was found to remain negatively charged over the entire pH range 3 to 11. Some flotation response was observed with amyl xanthate in the pH range 4 to 7 but was interpreted as due to the presence of some non-oxidized cobalt arsenide in the erythrite sample (Smith et al. 1976).

Copper-Cobalt Oxide Ores

The cobalt oxide minerals are essentially represented by the heterogenites. These are hydrated cobalt oxides, which present wide variations in crystallization degreee, from well crystallized species such as stainierite, to amorphous species, such as trieuite, which do also contain various amounts of copper, nickel, iron, and manganese.

The heterogenites are the main cobalt minerals found in the copper-cobalt oxide ores of the Shaba province of Zaire. They are associated in these ores with copper oxide minerals, mainly malachite, and, in the case of the mixed oxide-sulfide ores, carrollite and chalcocite are of course also present.

Two methods are used on a commercial scale for concentrating these ores. The first one is the so called "palm oil flotation process," which uses as collector a 3:1 mixture of hydrolized palm oil/gas emulsified in slightly carbonated hot water, with addition of soda ash for alkalinity and of sodium silicate for gangue dispersion and depression. Application of this process is limited to the treatment of siliceous ores which contain only traces of carbonate gangue minerals.

The concentrates produced by this process assay 23 to 25 percent Cu and up to 2 to 3 percent Co with respective copper and cobalt recoveries up to 80 to 85 percent and 50 to 70 percent. The reasons for getting such wide variations of the cobalt recovery may be related to the strong variations of the cobalt content of the ores, the higher sensitiveness of the heterogenites towards the depressing effect of sodium silicate (Theys 1947), their slower floatability and the higher palm oil consumption they require in comparison with malachite. Of course, the flotation process is controlled with the purpose of getting the best results from copper and no attempt is made to produce a separate cobalt-rich concentrate, but according to their cobalt content, the copper concentrates are dispatched to the appropriate metallurgical plant. Table 8 shows a recent monthly balance obtained on one of these ores at the Kolwezi plant.

Mineralogical investigations made in our laboratory by L. Evrard on concentrates and tailings coming from the palm oil flotation of copper-cobalt oxide ores have shown that the well crystallized varieties of heterogenites tend to float more completely than the amorphous ones. These observations were confirmed by Hallimond tests performed on heterogenite samples of various crystallization degrees.

TABLE 8 Results of Copper-Cobalt Siliceous Oxide Ores Flotation at the Kolwezi Plant

Kolwezi Plant	Percent Weight	Copper Percent	Copper Percent Recovery	Cobalt Percent	Cobalt Percent Recovery
copper-cobalt concentrate	18.0	23.07	77.2	1.64	49.5
tailing	82.0	1.50	22.8	0.37	50.5
feed	100.0	5.39	100.0	0.60	100.0

Source: Personal communications given by the Management of Gecamines, Zaire, October 1981.

The other process used by Gecamines for floating the copper and cobalt oxide minerals is the "sulfidization process." It offers the advantage over the palm oil process of being more selective and no more limited to the treatment of ores containing only traces of carbonate gangue minerals. In the case of mixed oxide-sulfide ores, which always contain a dolomitic gangue, this process is a must. After the sulfides flotation, the tails are conditioned with sodium sulfhydrate before the oxides flotation where amyl xanthate is used as collector and were multistage addition of sodium sulfhydrate is still made. Gasoil or an emulsion of gas oil and palm oil is generally added to the collector in order to strengthen its effect and to obtain best frothing characteristics.

The concentration produced by this process assay 18 to 20 percent Cu and up to 1 to 2.5 percent Co. The cobalt recovery is generally lower than with the palm oil flotation process.

Here again, detailed statistical microscopic analyses were made in our laboratory (Evrard, Evrard and J. de Cuyper 1975) in order to see how the various heterogenites were distributed among the flotation concentrates and tailings when the sulfidization process was used. They clearly indicated that the amorphous varieties did float preferentially at the beginning of the flotation; in the head concentrate only 3 percent of the cobalt was present as crystallized oxides, while the tailings contained a much larger proportion of these varieties. Throughout this investigation, it was also noted that among the varieties showing a good degree of crystallization, those richer in copper had a better flotability. Very interesting results were finally obtained by using combined additions of alkylhydroxamate and amyl xanthate; this method allowed us to considerably improve the floatability of the amorphous heterogenites and at the same time, to get an important increase of the copper recovery, due to a much more selective flotation of the copper from the slimes.

Nickel-Cobalt Oxide Ores

The nickel oxide ores always contain some cobalt. However, their mineral texture and composition are such that no commercial beneficiation of these ores are considered as being completely refractory to beneficiation by froth flotation.

Taking account of the fact that liberation of the valuable minerals would occur only in the sub micron size range, one might think of possible enrichment methods by using selective flocculation and dispersion. Some patents have already been taken in this direction for floating laterite nickel ores (Weston 1973).

Cobaltiferous Manganese-Iron Oxides

Cobalt in the form of asbolite (an impure mixture of manganese and iron hydrated oxides) occurs as nodules, very irregularly distributed throughout the laterite at the upper part of some nickel oxide ore deposits. Their separation only needs scrubbing and common sizing methods.

The deep-sea manganese nodules should also be mentioned here. They consist of mixtures of crystalline and amorphous oxides, mainly manganese and iron. Cobalt is present as a minor element and seems to be more concentrated in the iron-rich amorphous oxides than in the manganese-rich crystalline oxides (Sorem and Fewkes 1979). Physical concentration methods do not appear to be useful for this type of material.

CONCLUSIONS

With the exception of the cobalt arsenides and sulfo-arsenides, which can be separated by physical concentration methods extracting cobalt concentrates assaying up to 15 percent Co from rich cobalt ores (i.e., containing 1 to 2 percent Co), cobalt is present in most ores with contents ranging from 0.1 to 0.6 percent and the cobalt concentrates produced are not richer than a few percent. In these low grade concentrates, cobalt is generally bound to other metals such as copper in carrollite and heterogenite, nickel in pentlandite, and iron in pyrite and pyrrhotite. This indicates that the main problems will then be shifted to the extractive metallurgical stage.

However, physical beneficiation, particularly flotation, still remains today the first stage of treatment for most cobalt ores. The only exceptions to this rule are found with the lateritic type ores and the deep-sea nodules.

While several improvements are still made by acting only on the degree of grinding and on the flotation flow-sheet (like in the Outokumpu mills), there is also room for improvement by working on the chemistry of cobalt minerals flotation. The successful results already obtained in the

Gecamines plants in the selective separation of carrollite and chalcocite are an illustration of this approach. Also new collectors are now in the development stage; along this line, one should specially mention the chelating agents studied by the CNR Institute for Mineral Processing in Rome, Italy, and the hydroxamates studied in our laboratory at the Catholic University of Louvain in Louvain-LaNeuve, which made us able to double the cobalt recovery in the flotation of some copper-cobalt oxide ores from the Zairian deposits, simultaneously improving the copper recovery and the cobalt content of the concentrates. These lines of research are now sufficiently promising to justify further advanced studies.

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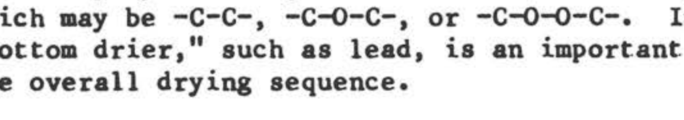
Appendix D

CHEMICAL PRINCIPLES IN PAINT DRYING

The efficacy of cobalt in paint driers is in its ability to catalyze the free radical polymerizations that originate from active hydrogens. These active hydrogens are associated with double bonds in the typical 18 carbon fatty acid chains of the triglycerides found in soybean, linseed, tung, and other oils commonly used in paints. The presence of only one double bond--as in oleic acid common to edible oils, such as soybean and cornoils--is insufficient for acceptable drying rates. The mixtures of one, two, and three double bonds in oleic, linoleic, and linolenic acids, found in soybean and linseed oils and their blends, are the bases for paint drying. For example, two or more double bonds at either 9, 12-carbon unconjugated positions, as in linseed oil, or at 9, 11-carbon conjugated positions, as in tung oil, serve as the foundation for the two sets of chemical mechanisms important in the drying of paints.

DRYING REACTION SEQUENCE

The slower reaction sequence is with the unconjugated position. In this slow first step there is an absorption of up to 14 percent by weight of atmospheric oxygen. This reaction is catalysed by radiant energy, such is visible and ultraviolet light to form a hydroperoxide at the labile hydrogen on C_{11} position between the C_9 and C_{12} points of unsaturation. Following this slow induction period, soluble cobalt by virtue of its cobaltous to cobaltic reduction potential, catalyzes a rapid scission of the pendant hydroperoxide to form free radicals on the C_{11} carbon position in the fatty acid chain. An example of an isolated radical (R·) is shown below:



$$\left[\begin{array}{l} CH_3(CH_2)_4\text{-}CH{=}CH\text{-}\dot{C}H\ \text{-}CH\ {=}CH(CH_2)_7\text{-}COOCH_2 \\ CH_3(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH(CH_2)_7\text{-}COOCH \\ CH_3(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH(CH_2)_7\text{-}COOCH_2 \end{array}\right]$$

(isolated trans-trans glyceryletrilenoleate free radical)

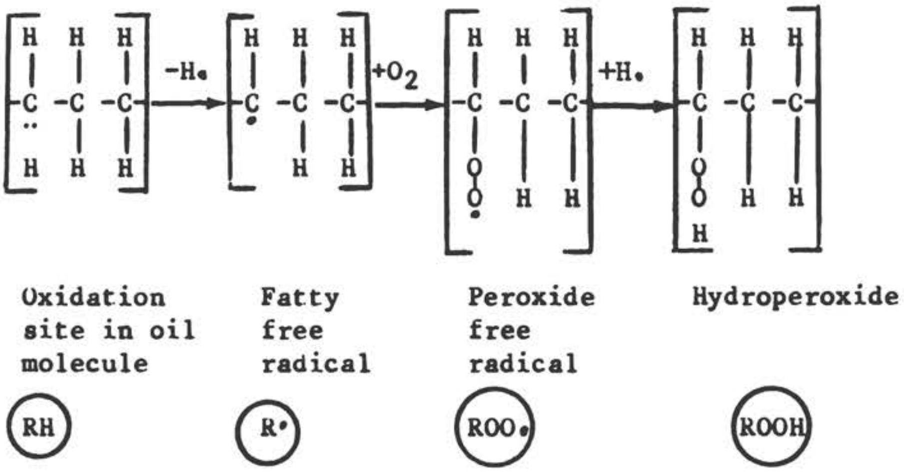
These free radicals then follow several competing chemical mechanisms to produce polymers at geometric rates, involving polymeric chemical bonds, which may be -C-C-, -C-O-C-, or -C-O-O-C-. In this slower mechanism, a "bottom drier," such as lead, is an important supplement to the cobalt in the overall drying sequence.

The faster reaction sequence is with the conjugated unsaturation, as found in tung oil, which contains much eleostearic acid with conjugated double bonds at the 9, 11, and 13 carbon positions. Here, there is little or no induction period and only about 3 percent by weight of oxygen absorption, that occurs perhaps on other fatty acids usually naturally present with the eleostearic acid. Rapid polymerization occurs mainly with -C-C- polymer bonds. Less cobalt is needed (e.g., at 0.01 percent) and with less need for an adjunct drier, such as lead, to form a simpler family of free radicals for faster polymerization.

The same catalyzed free radical mechanisms which promote rapid drying of paints are also the mechanisms for their slow degradation during years of service. Degradation occurs through scission, i.e., polymer chain breaking, at residual unsaturation in the fatty acid chain. An increase in weight due to oxygen absorption occurs early in the degradation process, followed by a slower, continuing weight loss of the paint film during years of exposure. These weight changes may be correlated with patterns of "time of wetness" exposure to moisture (including atmospheric) and solar radiation. The perfect chemical situation of having just enought useful unsaturation at an ideal concentration for fast drying is only partly realized by combining the drying oil fatty acids into alkyds. This mixture attains molecular weight increases from about 900 for soybean or linseed oils to perhaps 5000 for a practical alkyd. This blending process achieves the first weight change (the increase) before paint film application. Because cobalt and other metal driers also catalyze film degradation, the paint formulation always includes a compromise between drying speed and durability.

Some of the complexities of free radical oxidation of vegetable oil and of metal initiation of autoxidation are illustrated by the sample reaction in Figure D-1. The generalized kinetic chemical behavior that these reactions imply are shown schematically in Figure D-2 illustrating the diversity of free radical polymerizations and degradations shown below. The balancing of various amounts of cobalt, lead, and other metals in the paint formulations given in Chapter 5 is a result of having to deal empirically with a vast variety of these reactions.

Free radical oxidation of vegetable oil:



Metal initiation of autoxidation sequences

(1) Activate O_2:

$$Co^{+3} + O_2 \longrightarrow CoOO^{+3}$$

$$CoOO^{+3} + RH \longrightarrow CoOOH^{+3} + R\cdot$$

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

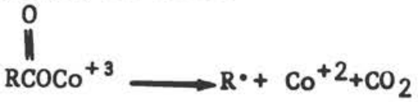
(2) Direct attack on hydrocarbon:

$$Co^{+3} + RH \longrightarrow Co^{+2} + R\cdot + H^+$$

(3) Direct attack on olefin:

$$Co^{+3} + RCH = CH_2 \longrightarrow R\dot{C}H\text{-}\dot{C}H_2 + Co^{+2}$$

(4) Induced decomposition of acid:



$$R\overset{\overset{O}{\|}}{C}OCo^{+3} \longrightarrow R\cdot + Co^{+2} + CO_2$$

Figure D-1 Oxidation process in paint drying.

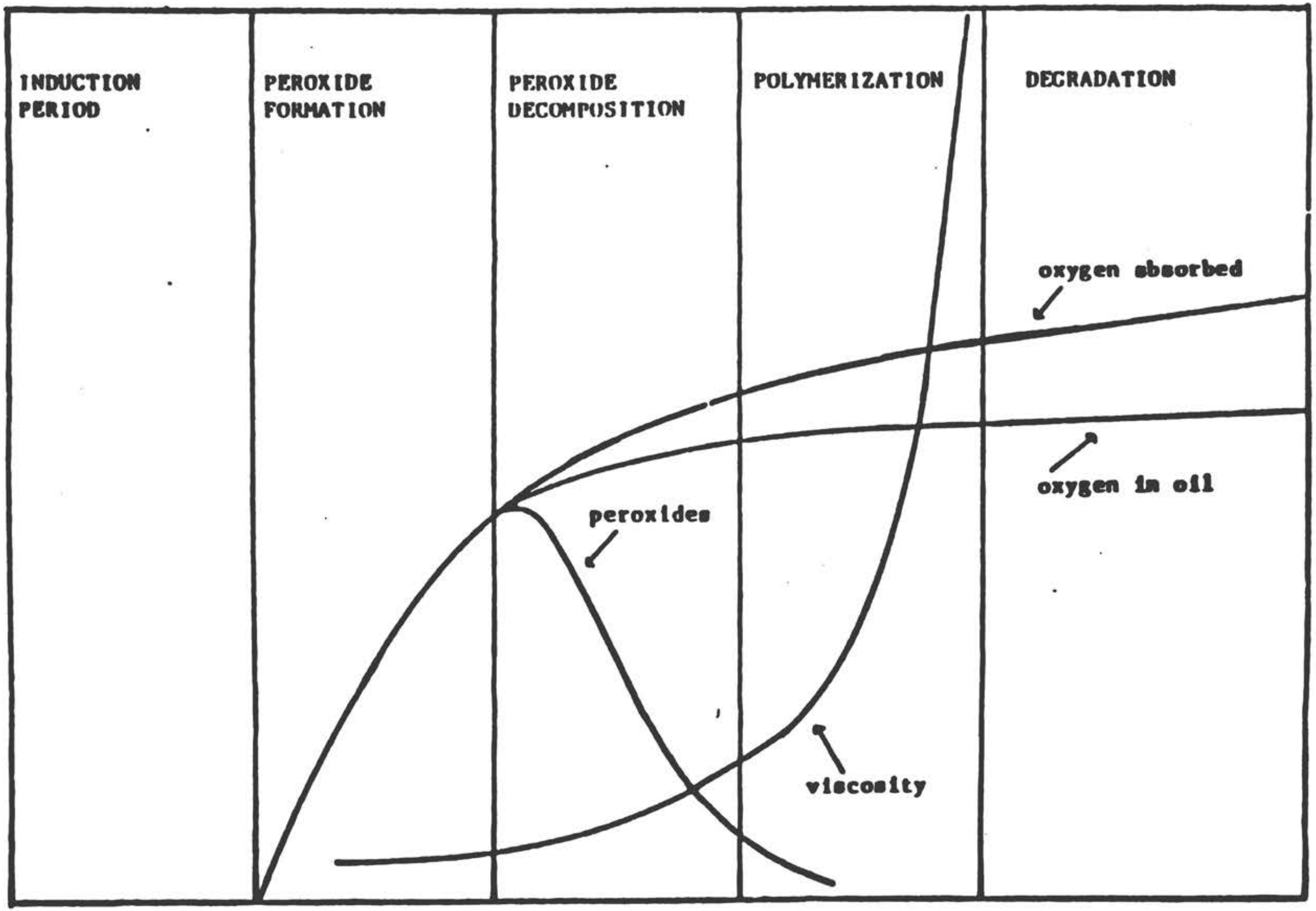


Figure D-2 Schematic kinetics of paint drying reactions.

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16. Abstracts

Cobalt is an important and perhaps indispensable element used in a variety of critical industrial and military applications - superalloys, cemented carbides, tool steels, magnets, chemicals, paints and driers, and catalysts. The United States depends entirely on foreign sources of supply for primary cobalt making this country very vulnerable to supply disruptions. Currently some 70 percent of the Western World's supplies of cobalt come from Central Africa.

Since the United States is entering a period of increasing materials scarcity and growing dependence on imported materials, several studies have been undertaken recently to develop contingency plans for the utilization of critical materials that could reduce the adverse effects of supply disruption. This study discusses for cobalt: substitution; conservation through improved processing, design and recycling; stockpiling; resource exploration and development; and diversification of supply.

17. Key Words and Document Analysis. 17a. Descriptors

Cobalt conservation
Superalloys
Cemented carbides
National Defense Stockpile
Permanent magnets
Cobalt chemicals
Enamel ground coat
Tool steels
Catalysts
Rare earth cobalt magnets
Extra fine cobalt powder
Powder metallurgy
Rapid solidification technology
Hardfacing alloys
Cutting tools
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Scrap reclamation
Paints and driers
Materials recycling
Cobalt bearing ores

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