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Process for Recovering Chromium and Other Metals From Superalloy Scrap

By J. J. deBarbadillo, J. K. Pargeter,
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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

CONTENTS--Continued

CONTENTS--Continued

ILLUSTRATIONS

TABLES

TABLES--Continued

PROCESS FOR RECOVERING CHROMIUM AND OTHER METALS FROM SUPERALLOY SCRAP[1]

by

J. J. deBarbadillo,[2] J. K. Pargeter,[3] and H. V. Makar[4]

ABSTRACT

This Bureau of Mines report describes a process for recovering chromium and other metals from superalloy scrap. Laboratory-scale experiments were conducted to test a complex flowsheet utilizing a wide range of extractive metallurgical operations. The novel basis for the process is the formation of a sulfide matte in which chromium is concentrated in a discrete chromium sulfide phase. Mineral processing and hydrometallurgical procedures are used to separate chromium sulfide from the other matte constituents.

The products of the process are a chromium-nickel alloy suitable for reuse in the superalloy industry, electrolytic nickel, electrolytic cobalt, and iron-molybdenum residue. Recovery of the principal elements contained in the scrap is chromium--93 percent, nickel--99 percent, cobalt--96 percent, and molybdenum--92 percent.

INTRODUCTION

From their inception, the industries associated with superalloy manufacture and use have been very conscious of metal recycling and have continually striven to increase product yield and to reuse scrap generated in alloy production and component manufacturing. The principal incentive has been the scarcity and thus the inherently high cost of metals required to give these alloys their unique properties. Occasional shortages in the supply of metals have also stimulated efforts to conserve raw materials. In recent times the supply of some critical metals has been influenced by international political events, in addition to the traditional marketing and technological factors.

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[1] This report was compiled and prepared by The International Nickel Co., Inc., Inco Research and Development Center, Suffern, N.Y., under Bureau of Mines contract number J0188056.

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In addition, as high-grade domestic ore deposits have been exhausted, the United States has become almost totally dependent on imports for its supply of such critical metals as nickel (Ni), cobalt (Co), chromium (Cr), columbium (Cb), and tantalum (Ta).

These concerns have stimulated renewed interest in metals conservation with the goal of further reducing the quantity of critical metals that are either discarded or downgraded. The present Bureau of Mines directed study is based on the desire of the Federal Emergency Management Agency (formerly Federal Preparedness Agency) to improve recovery of metals, especially chromium, in the superalloy industry. This report describes the results of experiments to test a novel process for recovering metals from superalloy scrap. Evaluation of a second novel recovery process was conducted by Kusik (20).[5]

Current Recycling Methods

The quantities of chromium-bearing scrap and waste generated in the United States and disposition of these materials have recently been discussed in detail by Curwick (7) and Kusik (19). The Curwick study showed that the raw materials charged for superalloy melting may contain 37 to 60 percent scrap, depending on the alloy. The study showed that, of the 291 million pounds of superalloy scrap generated in 1976, 62 percent was directly recycled by the alloy producers, 26 percent was downgraded for use in iron and steel, 6 percent was exported, and 6 percent was lost through service wastage or discarded in landfill. For the most part, it can be assumed that the scrap that is now directly recycled or exported is efficiently used. The material that is now considered waste is usually severely contaminated; consequently, much of it would require specialized and costly, though technologically feasible, methods for recovery. However, the material that is now downgraded provides the basis for significant improvement in recycling efficiency. The reasons for downgrading are numerous: Alloy is too complex for remelting into any other alloy; product quality specifications limit quantity of scrap remelted; scrap from dismantled fabricated components contains unwanted metals; there is contamination from tramp elements in coatings and brazes; scrap contains too much oxide or sulfide for induction melting, etc. Clean solid scrap that is downgraded is usually charged directly into alloy-melting furnaces. Less desirable forms of scrap, including turnings, grindings, and ladle skulls, are frequently melted by a refiner into a secondary alloy pig, which is then charged to an alloy-melting furnace. In either case, the more readily oxidizable elements are deliberately or inadvertently combined with the slag and lost. Valuable elements frequently lost in this manner include tantalum, columbium, titanium (Ti), tungsten (W), molybdenum (Mo), aluminum (Al), and chromium. Cobalt is not oxidized but is often lost through dilution in steels where it is a relatively ineffective alloying element.

Treatment of Superalloy Scrap To Recover Individual Elements

Scrap that is directly recycled by the superalloy producers is usually carefully sorted according to form and grade. Scrap that is downgraded is

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[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

often mixed and contaminated so that a simple recycling process dealing with any quantity of material would have to accept a feed with a variable composition and would produce a product with composition unlike that of any alloy now produced. The market for such a secondary product is likely to be quite restricted. Consequently, most of the procedures that have been proposed in the past for dealing with these materials have involved at least partial separation of the elements. A variety of processes have been tested or proposed to recover some of the elements in separated form. No process has been identified that economically recovers all of the elements contained in the feed. Most approaches depend on chemical methods for separating the elements, although an initial melting operation has often been used to homogenize the feed, obtain a partial separation of elements, and produce a more readily leachable granular product.

In the least selective processes, such as those currently used by many secondary alloy producers, the charge is melted and the metal bath is severely oxidized until a relatively pure alloy containing Ni, Co, Fe, and sometimes Cr remains. This material is then cast into pigs or shot and sold as a master alloy. As a refinement of this procedure Goto (12) oxidized the bath until all Cr and Fe were removed and then added S to form a matte. The matte was then treated using mineral-processing techniques employed widely in the primary nickel industry to separate nickel and copper sulfides (4).

A more selective separation was obtained by Aue (2) in which only very reactive elements such as aluminum and titanium were oxidized. The bath was then saturated with carbon and granulated to promote rapid dissolution in the subsequent chlorine leach. This carburizing treatment facilitated separation of Ni, Co, and Fe from Cr, Mo, W, Cb, and Ta, because the latter elements were bound as unleachable carbides. The transition metal carbides can be separated with some difficulty using a caustic fusion and water-leaching procedure. Variation of the caustic fusion process has also been used by Okano (21) and Petrova (22) to extract Mo and W directly from raw particulate superalloy scrap.

Although pyrometallurgical refining provides metallurgical advantages in separation of elements from superalloys, the operations are both capital and fuel intensive. Consequently, some investigators have relied on direct leaching [Brooks (5), Kruglikov (17) and Van der Meulen (23)] or have used melting only as a preliminary homogenization and granulation step [Baggott (3) and Kawakami (16)]. Following complete leaching in either chloride or sulfate solutions, the above procedures depend on a complex series of selective precipitation, solid or liquid ion exchange, or selective electrolysis steps to produce pure metal products. There are many problems associated with the hydrometallurgical approach, especially in the efficiency of solid liquid separations; however, there currently are no alternatives if complete elemental separation is desired.

One other procedure that provides partial elemental separations is high-temperature chlorination to produce gaseous metal chlorides that can be selectively condensed (15). This process separates Ni and Co from Fe, Cr, and the refractory metals, but aqueous chemical methods must be used for final separations and purification.

Technical Approach for This Process

The approaches described above have emphasized recovery of either Ni and Co or Mo and W, sometimes at the expense of recovery of other metals. Chromium, especially, has been viewed with ambivalence, perhaps because it is so readily available as ferrochromium. However, with growing concern for the long-range stability of chromium supplies and the relatively high prices of the pure chromium needed for superalloy melting, greater attention to recovery of this element while simultaneously achieving high recovery of the other valuable elements is justified. In the hybrid schemes that use selective oxidation of melted scrap followed by leaching, chromium can be either oxidized to the slag or retined in the metal depending on the degree of oxidation. Both approaches have drawbacks. It is difficult to oxidize all of the chromium with oxidizing substantial quantities of other metals, including nickel, and the resulting complex oxide slag is very difficult to treat. On the other hand, if chromium is present in the metal, it dissolves during the leach and causes great difficulty in solid-liquid separation of hydrolysis products. Other metals such as molybdenum and tungsten may also be present, thereby resulting in an extremely complex hydrometallurgical system.

The process described in this report uses an entirely new approach which avoids the problems mentioned above. A simplified flowsheet for the process is shown in figure 1. The process is based on the following principles.

As in other processes, a blended scrap charge is melted and partially oxidized, resulting in Ti, Al, zirconium (Zr), and hafnium (Hf), but little Cr, being segregated to the slag. The bath is then sulfidized to form a partial matte (mixture of molten metallic sulfides). When solidified, the matte essentially contains three components: nickel sulfide (Ni_3S_2), chromium sulfide (Cr_2S_3), and a nickel-rich metal phase. The sulfur content of the matte is critical. At the optimum sulfur level, virtually all of the chromium is contained in the chromium sulfide, and the best separation is possible. The subsequent separation of the metal and sulfides can be achieved by conventional magnetic separation and froth flotation or other mineral-processing techniques. The essentially chromium-free, nickel-rich components are then given a hydrochloric acid-chlorine leach ($HCl-Cl_2$) which leaves elemental sulfur as a recoverable residue. Iron and molybdenum are removed by hydrolysis. Solvent extraction and electrowinning are then employed to produce pure electrolytic nickel and cobalt. The chromium sulfide contains some dissolved nickel, which can be removed by leaching. However, since a chromium metal product containing nickel would probably be acceptable for the superalloy industry, further separation was not extensively investigated. The preferred process involves roasting to a low-sulfur oxide product in a fluidized-bed converter, followed by aluminothermic reduction. The latter process produces a chromium-nickel metal ingot.

The basic process described above was tested in a series of laboratory experiments. In some cases, modifications of the basic scheme were defined, and limited testing was conducted. Where appropriate, these alternatives are discussed in the text. Based on the results of the experimental work, a proposed pilot plant was designed. The plant was sized to treat 100 pounds of

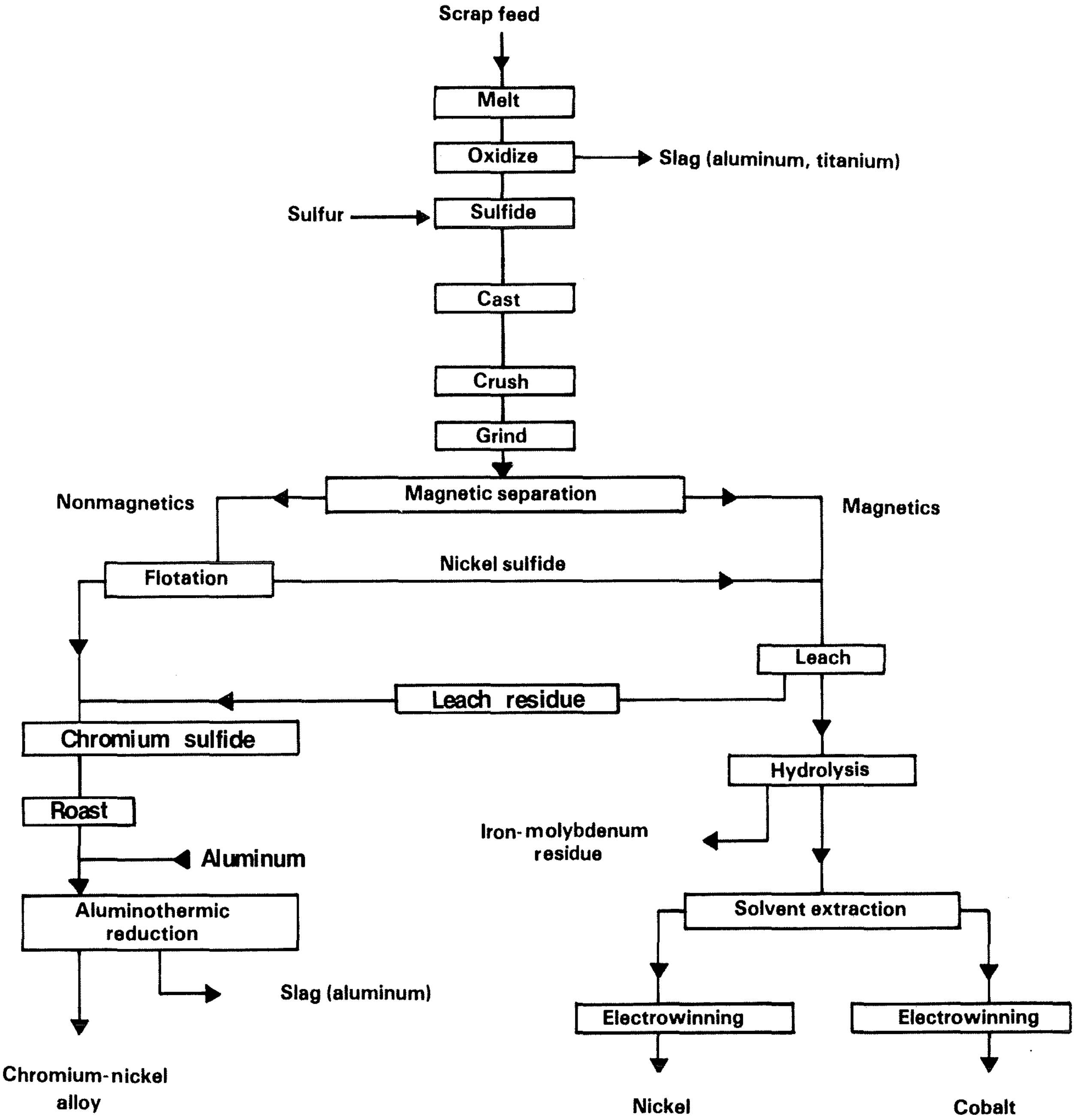

FIGURE 1. - Simplified process flowsheet.

scrap feed per hour. This plant is described in detail in the final contract report.

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The Federal Emergency Management Agency (formerly Federal Preparedness Agency) sponsored this research through the Bureau of Mines, U.S. Department of the Interior.

As is true with any large project, a number of people contributed in a significant way. The following Inco personnel had a substantial role throughout the project and were responsible for portions of the experimental work and preparation of the final report: J. Babjak, F. J. Hennion, C. Lam, B. Sandiford, and J. A. Thomas. G. Agar and V. Ettel were involved in the planning, oversight, and evaluation of the work. In addition, portions of the experimental program were conducted by U. M. Ahmad, J. Ambrose, R. A. Bradford. W. B. Kipkie, and G. Styles.

For their many insights, critiques, guidance of this program and assistance in manuscript reviews, we would like to express our appreciation to the following Bureau of mines personnel: Andrew Prokopovitsh, John L. Morning, Frank A. Peters, Frank Naughton, and Fred Ambrose.

A separate task of the contract under which this work was funded was a survey of the generation and use of scrap in the superalloy industry (7). Information derived from this survey was essential to identification of the composition, character, and value of feedstock for the process.

EXPERIMENTAL WORK

The basic flowsheet for the process shown in figure 1 incorporates operations from all phases of extractive metallurgy. The experimental program was subdivided for the sake of expediency into separate tasks with different investigators handling each task. In view of the overall complexity of the process, the tasks will be discussed individually in this presentation.

Superalloy Scrap

Since the purpose of this process was to recover metals from scrap, some introductory discussion of the raw materials selection is warranted.

Composition of Superalloy Scrap

Curwick (7) defines the quantity of scrap generated in the United States by the superalloy producers and users. The separation process under consideration appears to be applicable to four distinct classes of alloys identified in the Curwick study: investment cast nickel- and cobalt-base alloys, nickel- and cobalt-base hard-facing alloys, wrought nickel- and cobalt-base alloys, and wrought nickel-iron-base alloys. The average composition, composition ranges, and quantity of material potentially available for a recovery process are listed in table 1. This information was used to compute a weighted average nominal composition for a hypothetical scrap feed for experimental work.

TABLE 1. - Composition and quantity of superalloy scrap,[1] by alloy class (7)

Alloy class	Nominal composition, weight-percent									
	Cr	Ni	Co	Fe	Mo	W	Ta	Cb	Al	Ti
Aim..................	14.5	60.0	10.0	5.0	4.5	2.0	1.5	1.0	1.0	1.0
INVESTMENT CAST NICKEL- AND COBALT-BASE ALLOYS (12.1 MILLION POUNDS)										
Nominal..............	13.3	63.6	7.4	1.1	4.0	2.0	1.0	1.0	4.0	1.5
Range:										
High...............	30	75	70	20	10	10	5	7	7	4
Low................	5	0	0	0	0	0	0	0	0	0
WROUGHT NICKEL- AND COBALT-BASE ALLOYS (61.8 MILLION POUNDS)										
Nominal..............	18.2	62.5	4.8	7.0	4.0	0.5	<1.0	1.0	2.0	2.0
Range:										
High...............	25	80	80	20	25	5	5	7	5	4
Low................	15	0	0	0	0	0	0	0	0	0
WROUGHT NICKEL-IRON-BASE ALLOYS (31.7 MILLION POUNDS)										
Nominal..............	15.0	34.1	3.5	42.1	2.0	0.5	<0.1	0.2	0.2	1.5
Range:										
High...............	30	45	20	55	10	5	2	2	3	3
Low................	12	10	0	20	0	0	0	0	0	0
HARD-FACING CAST NICKEL- AND COBALT-BASE ALLOYS (6.0 MILLION POUNDS)										
Nominal nickel-base..	16.0	59.5	NAp	5.0	8.0	4.0	NAp	NAp	NAp	NAp
Nominal cobalt-base..	29.0	5.0	52.8	3.0	2.0	6.0	NAp	NAp	NAp	NAp

NAp Not applicable.

[1] Scrap downgraded, lost, or exported.

Form of Superalloy Scrap

A wide range of scrap forms are available as discussed by Cruwick (7). A detailed discussion of the procedures used by scrap dealers in identifying, sorting, and handling superalloy scrap is given by Cremisio (6). Dressel (11) provided information on additional forms of scrap. The scrap available for a separation process would range from very high quality "vacuum-grade" material consisting of identified, clean, solid scrap to low-quality "refinery-grade" material such as contaminated mixed alloy grindings. The prices paid for these materials depend on the degree to which they can be directly reused by the superalloy industry and on the recovery of the contained alloying elements. It is probable that a commercial plant would use a scrap feed that is a combination of mixed solid scrap, turnings, grindings, ladle skulls, slag cleanings, and grit from a variety of different alloys.

Raw Materials Used

As discussed below, small laboratory induction furnaces were used for alloy melting and refining. To avoid the melting difficulties and composition uncertainties posed by use of the lower grade scrap materials, it was decided to use only clean identified solid material. The first series of small heats in which the base composition was varied over a wide range was made from commercially pure primary metals. In the second phase of the program larger heats were made with the "aim" composition listed in table 1. For these heats, scrap from five selected widely used superalloys was obtained from a commercial scrap dealer. These scrap alloy compositions and forms are listed in table 2.

TABLE 2. - Composition of scrap used in experimental program

Commercial designation of alloy	Nominal composition, weight-percent[1]									Form
	Cr	Ni	Co	Fe	Mo	Ta	Cb	Al	Ti	
Inconel alloy 600....	15.5	76.5	NAp	8.0	NAp	NAP	NAp	NAp	NAp	Sheet punchings.
Waspaloy............	19.5	58.4	13.5	NAP	4.3	NAp	NAp	1.3	3.0	Engine frame part.
Inconel alloy 713C...	12.3	74.6	NAp	NAp	4.2	NAp	2.0	6.1	.8	Reject engine blade.
B-1900..............	8.0	65.0	10.0	NAp	6.0	4.0	NAp	6.0	1.0	Scrapped engine blade.
Inconel alloy 718....	19.0	53.0	NAp	18.5	3.0	NAp	5.1	.5	.9	Sheet punchings.

NAp Not applicable.

[1] Alloy manufacturer's aim composition; these alloys also contain minor quantities of C, Mn, Si, B, and Zr.

Melting and Casting[6]

This phase of the program incorporates the basic steps of scrap melting and homogenization, oxidation of the reactive elements, slag removal, sulfidation, casting, and slow cooling. The test work was carried out in three stages: (1) Melting and oxidation studies on 12-kilogram heats made from pure elemental raw materials and the "aim" composition, (2) sulfidation studies using similar procedures but with a range of base compositions, and (3) combined processing using 40-kilogram heats and scrap feed and the "aim" composition. Each of these stages will be discussed in turn.

Oxidation Tests

Oxidation of a molten bath is a convenient tool for refining superalloys provided that the oxidation reactions are selective and controllable and that efficient separation of the oxidation products and metal can be made. Important physical and thermodynamic criteria for selective oxidation include the stability and density of the oxides and the chemical activity of elements in the bath and the slag. There is not sufficient published data to enable prediction of the effect of oxidation on complex superalloys; hence, experimental work was required.

Testing Procedure

A 50-kilowatt coreless induction furnace with a high-density alumina crucible was used for melting heats of approximately 12 kilograms. Commercially pure raw materials were used to prepare alloys having the "aim" composition

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[6] The experimental work was planned and conducted by F. J. Hennion, Research Engineer, Resource Recovery, Inco Research and Development Center, Suffern, N.Y.

listed in table 1. The charge, exclusive of reactive metals, was melted under an argon cover and brought to about 2,850° F. The reactive metals (1.0 percent Al, 1.0 perent Ti, 0.25 percent Mn, 0.25 percent Si) were then plunged into the molten charge.[7] After a chemical analysis sample was taken, the bath was oxidized. Three different methods of oxidation were investigated: (1) Blowing a mixture of 75 percent oxygen and 25 percent argon at 30 cubic feet per minute through a lance onto the bath surface, (2) adding granular nickel oxide, and (3) adding ground chromite ore fines. Additions of lime and fluorspar were made to increase slag fluidity. The bath temperature was maintained at about 2,800° F, and samples were taken at various times for analysis. Ultimately the metal and slag were tapped into separate molds and preserved for later use.

Preferred Deoxidant

The first series of test heats showed that granular nickel oxide was the most suitable oxidant; consequently, all of the remaining work was done using that procedure. The oxygen-lancing technique resulted in excessive heating of the bath surface, and the oxygen flow was difficult to control and quantify for the small heats. However, the procedure would be effective for commercial-scale operations. Granular nickel oxide was easy to handle and reacted within a few minutes. Also, this material resembles oxidized nickel alloy waste, which would be a desirable oxidant for a commercial metals recovery plant. Ground chromite ore was tried in one heat to determine whether oxidized chromium, which would be present in a waste alloy oxidant, would be reduced under the test conditions. The experiment showed that chromium was reduced; however, the reaction rate was slow. Chromite ore was otherwise unsuitable as a deoxidant because all of the contained iron and silicon were reduced into the metal phase.

Quantity of Oxygen Required

A number of tests were conducted in which oxide was added gradually and intermediate samples were taken to define the quantity of oxygen required. Oxidation results for Al, Ti, and Ta from several tests are shown in figure 2. Aluminum and titanium were oxidized first. When the concentration of these elements was reduced to about 0.5 percent each, tantalum was oxidized. When the oxygen addition exceeded 1.5 percent, a significant amount of chromium was oxidized. The silicon and manganese contents of the bath did not change during oxidation in these tests. Recovery and distribution of elements between metal and slag are discussed below.

The quantity of oxygen required obviously depends upon the initial concentration of reactive elements in the bath. In these tests, the apparent oxygen efficiency based on the amount theoretically required to oxidize aluminum and titanium was 125 percent. It is presumed that the additional oxygen was supplied by the atmosphere, the original metal charge, and the

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[7] Very reactive elements such as Hf, Zr, Ca, and Mg are also often present in superalloys. As it was judged that a composite scrap charge would probably contain less than 0.20 percent combined of these elements, they were not considered in the oxidation studies.

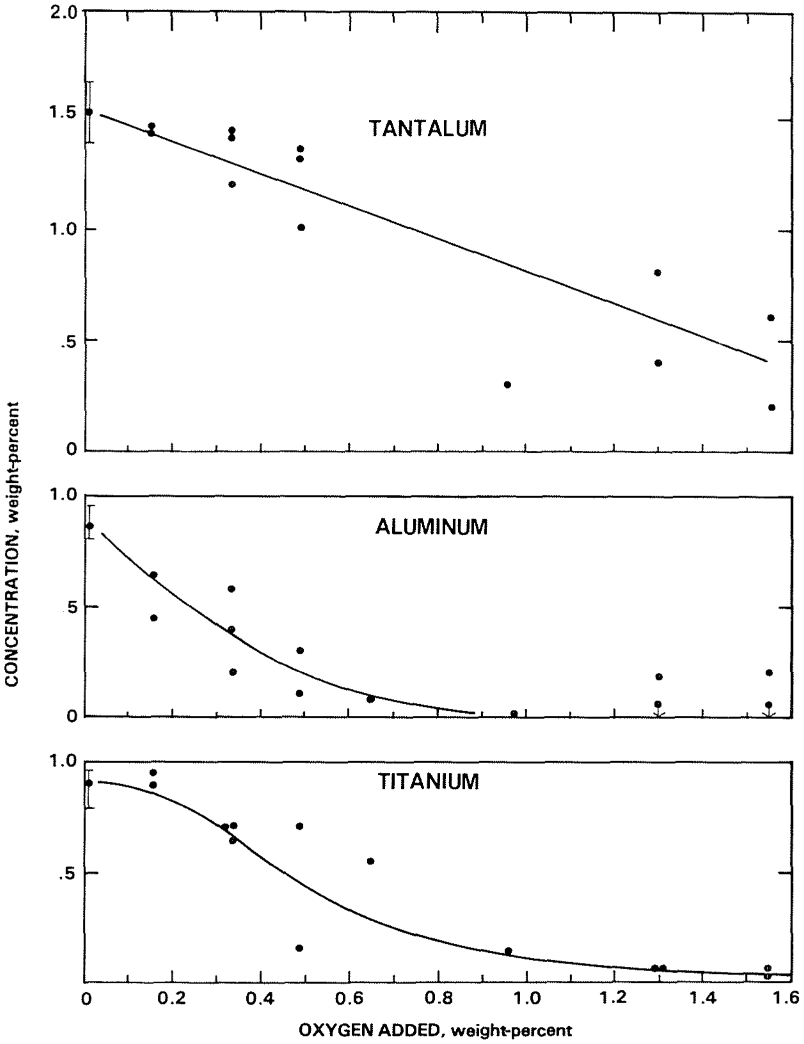

FIGURE 2. - Effect of quantity of oxygen added on composition.

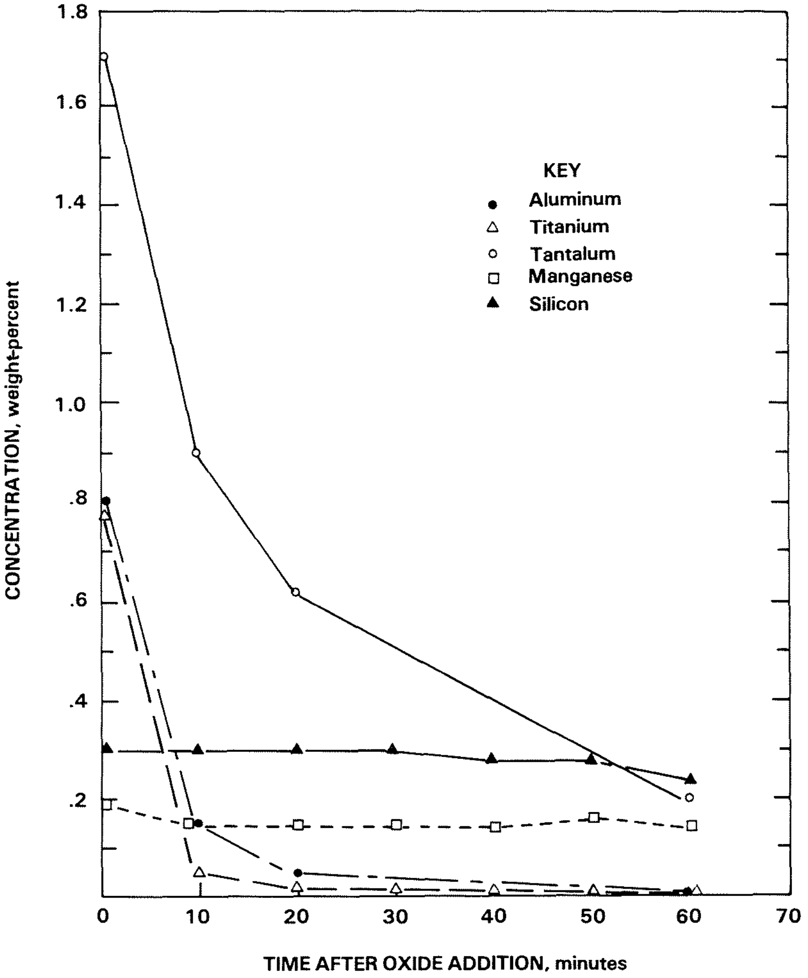

FIGURE 3. - Effect of holding time on composition of heat C.

crucible. From the small tests, it was concluded that an addition of oxygen as reducible oxide slightly exceeding the amount predicted from the stoichiometric ratio to convert all Al to Al_2O_3 and Ti to TiO_2 was satisfactory for the larger scale heats.

Rate of Deoxidation

A few tests were conducted in which the bath was held for a period of time following addition of the oxide. Figure 3 shows the concentration of Al, Ti, Ta, Mn, and Si as a function of holding time for heat C (composition shown in table 3). The aluminum and titanium contents of the bath were reduced to a residual level within about 15 minutes. However, the tantalum content decreased gradually over a 60-minute period. Although tantalum is probably oxidized at the same time as the other elements, the solid oxide Ta_2O_5 has a density nearly that of the liquid and hence is very slowly incorporated into the slag through induction stirring of the bath. The partitioning of tantalum to the slag is likely to be even slower in commercial-scale melts.

Character and Composition of Slag

The oxides of most of the reactive elements are solid at the temperatures used in this work. Consequently it was necessary to add fluidizing agents to form a liquid slag which could be separated with a minimum loss of metal. Lime (CaO) and fluorspar (CaF_2) were found to be suitable fluxes. The amount of flux needed varies with the initial alumininum and titanium content, with an addition of about 10 percent of the expected weight of slag being satisfactory.

Typical slag compositions are listed in table 3. The principal elemental constituents are, as expected, Ti, Al, Ta, and calcium (Ca). One sample had a high nickel content which may have been due to entrapment of metal or unreacted nickel oxide. The high tungsten contents are also believed to be due to entrapment, because very little tungsten was oxidized. The slag taken from heat C, which had the largest oxygen addition, contained 6 percent chromium. The slags produced were rather hard but porous and amenable to grinding for physical recovery of entrapped metal if necessary.

TABLE 3. - Oxidation[1] test results

Sample	Ni	Cr	Fe	Co	Mo	W	Cb	Ta	Al	Ti	Si	Mn	C	O	Ca	Mg
HEAT A, 0.49 PERCENT OXYGEN ADDED																
Bath, weight-percent:																
Before oxidation...........	58.0	14.8	5.6	10.0	4.6	1.8	1.4	1.4	0.85	0.90	0.32	0.23	0.06	0.010	NA	NA
After oxidation............	60.6	14.5	5.7	10.1	4.5	1.8	1.4	1.4	0.10	0.10	0.45	0.22	0.06	0.014	NA	NA
Recovery..percent of charge..	100	100	100	100	100	100	100	80	12	11	100	NAp	NAp	NAp	NAp	NAp
Slag.........weight-percent..	1.4	0.6	2.3	<0.05	0.2	6.1	0.2	8.5	14.6	24.5	0.6	0.1	NA	NA	17.3	0.8
HEAT B, 0.96 PERCENT OXYGEN ADDED																
Bath, weight-percent:																
Before oxidation...........	58.9	14.7	4.7	10.0	4.7	2.0	1.4	1.4	0.84	0.81	0.37	0.16	0.06	0.003	NA	NA
After oxidation............	61.7	14.7	4.8	10.1	4.5	1.9	1.3	0.3	0.01	0.11	0.37	0.15	0.06	0.008	NA	NA
Recovery--percent of charge..	100	100	100	100	100	100	100	18	1	13	100	100	NAp	NAp	NAp	NAp
Slag.........weight-percent..	7.8	1.9	0.1	<0.05	<0.1	9.6	0.4	14.3	9.4	>30	0.8	0.3	NA	NA	10.3	0.8
HEAT C, 1.56 PERCENT OXYGEN ADDED																
Bath, weight-percent:																
Before oxidation...........	59.5	14.5	4.5	9.9	4.5	1.8	1.4	1.7	0.82	0.79	0.3	0.19	0.06	0.0004	NA	NA
After oxidation............	63.8	13.5	4.7	10.1	4.4	1.7	1.1	0.2	<0.05	0.01	0.23	0.13	0.06	0.016	NA	NA
Recovery..percent of charge..	100	98	100	100	100	100	90	12	<7	1	77	68	NAp	NAp	NAp	NAp
Slag.........weight-percent..	0.5	6.3	0.1	<0.01	<0.01	2.7	0.7	16.4	11.2	24.1	1.3	0.8	NA	NA	2.6	0.5

NA Not available.

NAp Not applicable.

[1] Oxygen added as nickel oxide granules.

Recovery of Metals

The partitioning of the metals between slag and melt is estimated for three heats in table 3. Considerable difficulty was experienced in establishing a precise material balance because of the uncertainty in actual slag weight and homogeneity. However, it appears that virtually all Al and Ti can be removed with negligible loss of Ni, Cr, Fe, Co, Mo, and W and only a small loss of Cb. Tantalum is distributed in both the metal and the slag with the relative recovery being dependent on quantity of oxygen added and the holding time.

Sulfidation Tests

The addition of sulfur to a molten bath to form either a partial or a full matte is a process widely used in the pyrometallurgical refining of nickel ores. The addition procedures, thermochemistry, and phase relationships of the solidified matte have been studied intensively (4). However, the matte technology had never before been applied to such complex feeds. Consequently, the existing information and experience on nickel mattes could only serve as a starting point in dealing with superalloy mattes.

Testing Procedure

The initial sulfidation tests were conducted in a 50-kilowatt coreless induction furnace lined with a monolithic high-density graphite crucible. Graphite was used in these tests because it acted as a susceptor to aid in heating and was inert to sulfidation. The charge of approximately 10 kilograms consisted of pure nickel sulfide master alloy (26 percent sulfur) to provide a low-melting heel and either solid or molten oxidized and deslagged simulated superalloy scrap. When the bath was fully molten and homogenized, it was brought to about 2,400° F and sulfur additions were made. To insure high recovery, pure sulfur flour was compacted into small cylinders in a mechanical press. These cylinders were manually held under the bath surface with a graphite rod. Almost 100 percent recovery of sulfur was realized in the small tests using this technique. When the desired sulfur content was achieved, the bath was heated to about 2,750° F, the slag was skimmed, and the matte was poured directly into molds preheated with a gas torch. A variety of refractory molds were used in an effort to minimize the cooling rate of the ingot. Ultimately, a dry silica sand mold backed and covered with high-porosity insulating brick was used. The entire mold was supported by a sand bed and encased in a 1-foot-thick blanket of loose vermiculite. The ingot cooling rate was determined using an embedded thermocouple. All chemical analyses and microstructural studies were performed on samples taken from the solid matte block.

Microstructure of Superalloy Matte

The microstructure of a typical slow-cooled matte sample is shown in figure 4. The composition of the various phases, determined using an electron microprobe analyzer, is shown in table 4. Four distinct phases are visible in this photograph: (A) Light brown nickel sulfide (Ni_3S_2), (B) dark gray chromium sulfide (Cr_2S_3),[8] which often has a dendritic structure, which is usually continuous, (C) white or very pale yellow metallic phase, and (D) gray heavy metal sulfide (often MoS_2), which is usually in the form of flakes. As discussed below, the composition of each of the four primary phases varies with the base metal feed composition and sulfur content of the matte. The heavy-metal phase is particularly variable and may actually be representative of a series of stoichiometric heavy-metal phases with similar physical characteristics. Heavy-metal carbides and oxides were also observed in selected samples. The grain size distribution is fairly restricted in the sample shown in figure 4; however, within a given matte casting, a wide range of grain sizes as well as occluded grains and highly irregular grain boundaries was observed. The effect of grain shape on phase separation is discussed in a subsequent section.

TABLE 4. - Composition of phases in superalloy matte[1]

Phase	Composition, weight-percent[2]								
	Ni	Cr	Co	Fe	Mo	Cb	Ta	W	S
Matte[3].................	53.4	10.1	6.4	3.4	2.9	0.8	0.2	1.1	24.5
Metallic phase.........	75.0	.1	14.0	8.7	1.0	<.01	<.01	<.01	.8
Nickel sulfide.........	65.0	.1	3.5	.1	.4	<.01	<.01	<.01	25.5
Chromium sulfide.......	8.0	40.0	4.5	1.4	1.4	<.01	<.01	<.01	46.6
Heavy metal sulfide....	5.2	3.0	2.4	.8	16.0	25.0	<.01	<.01	36.0

[1] Sample microstructure shown in figure 4.

[2] Phase composition determined by electron microprobe analysis.

[3] Matte composition determined by wet chemical analysis.

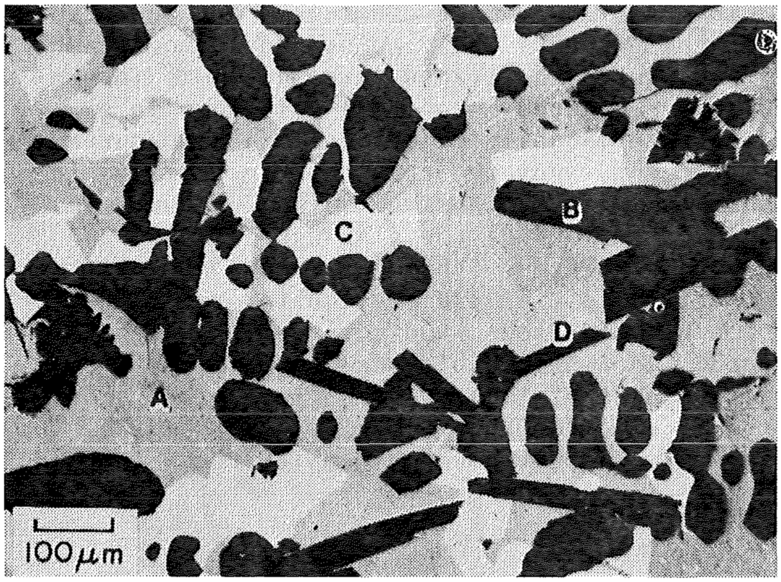

FIGURE 4. - Microstructure of superalloy matte.

Effect of Sulfur Content on Element Distribution

The sulfur content of the matte has by far the greatest effect on the distribution of elements among the various phases. Sulfur affects not only the quantity of the phases but also the concentration of elements, melting point and grindability of the matte, flotation characteristics, volume of leach residue, plant emissions, and many other factors.

A series of heats with similar base composition but having sulfur contents

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[8] This identification is tentative. Other sulfides such as Cr_3S_4 have been reported in the literature, but the microprobe results support the Cr_2S_3 stoichiometric ratio.

ranging from 13 to 32 percent were prepared. Although the proportion of the phases changed, their morphology was basically the same at all sulfur contents. At the lower end of the range the metallic phase was continuous, and the matte samples were difficult to crush. Very little metallic phase was present in the 30-percent sulfur samples, and nickel sulfide was continuous. These alloys were extremely brittle.

The composition of the three primary phases is shown as a function of sulfur content in figures 5-7. The chromium content of the metallic phase decreases progressively as sulfur is added to the matte until at 20 percent sulfur it is less than 1 percent. Nickel and chromium sulfides are both always present as distinct phases in the matte. Note that, although nickel sulfide contains virtually no chromium, a significant quantity of nickel is always present in chromium sulfide. At 15 percent sulfur, about 50 percent of the matte is sulfide. With further increases in sulfur content, the distribution of elements between the phases changes. Heavy metal sulfides are formed, hence the concentration of these elements in the metallic phase progressively declines. At the same time there is a significant increase in the Fe, Co, and Mo content of the chromium sulfide. Figure 8 shows the cumulative weight-percent distribution of the phases estimated from the microprobe results and corroborated by visual observation of microstructure.

The primary goal of the sulfidation procedure is to effectively separate chromium from the other metals. Based on the preceding data, it was estimated that at 15 percent sulfur, the chromium sulfide contains 93 percent of the chromium in the matte. At 20 percent sulfur, 98 percent of the chromium is in this phase. Consequently, the best Cr-Ni separation is obtained at 20 percent or more S. The effect of S on separation of Cr from Co and Mo is more complex, since the concentration of these elements increases with sulfur content. Because of this, the optimum sulfur content appears to be about 17 percent for the feed composition used for these tests. It should be noted, however, that this point was not recognized until late in the program; consequently, most of the matte heats prepared for use in the separation and leaching studies contained about 23 percent sulfur.

Effect of Base Composition

The separation of chromium from the other superalloy constituents for the scrap composite aim composition was very good. However, since heat-to-heat variation in the composition of the scrap feed was likely, an examination of the effect of selected elements on separation was made. As expected, varying chromium and nickel contents did not have much effect on the phase compositions and hence had little effect on the degree of separation.

The element that had the most significant effect was iron. Base alloys containing 10, 15, 20, and 55 percent iron were studied. When more than 10 percent iron was present, additional sulfide phases were formed which produced an extremely complex distribution of elements. In addition to Ni_3S_2 and Cr_2S_3, a number of iron-nickel and iron-chromium sulfides of undetermined stoichiometric ratio were observed. This, along with the very high melting point of iron-rich matte, suggested that the average iron content of the composite scrap feed be limited to 10 percent.

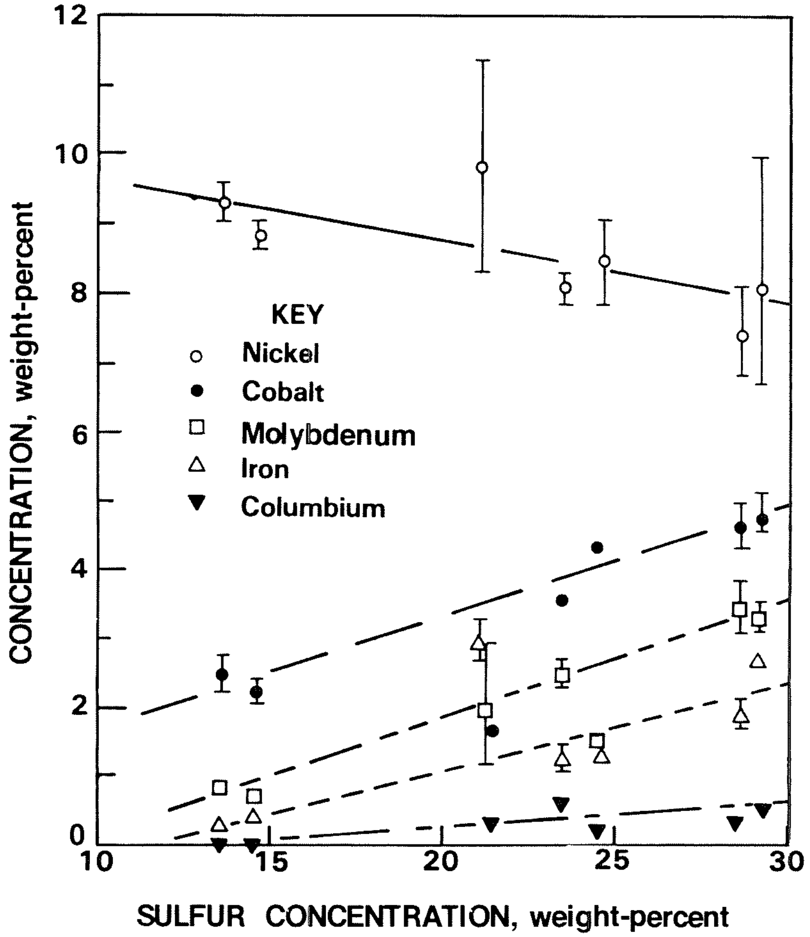

FIGURE 5. - Effect of matte sulfur content on composition of chromium sulfide.

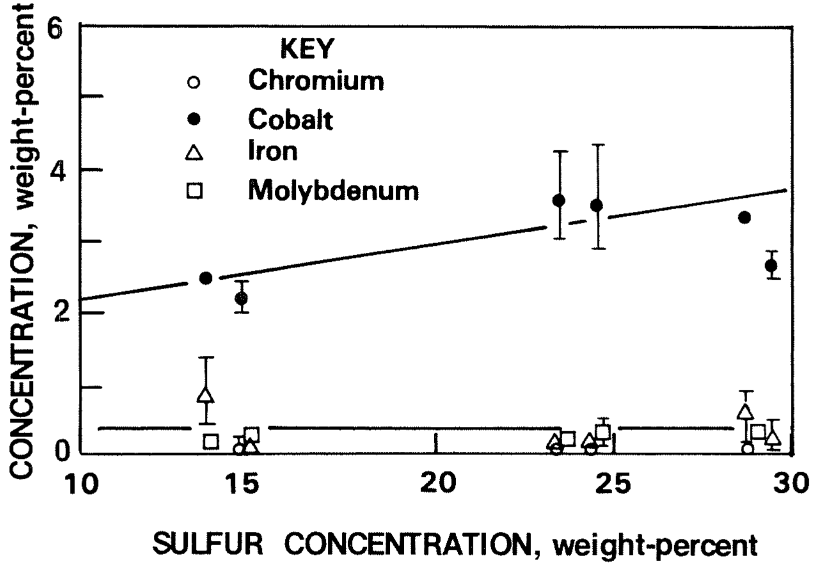

FIGURE 6. - Effect of matte sulfur content on composition of nickel sulfide.

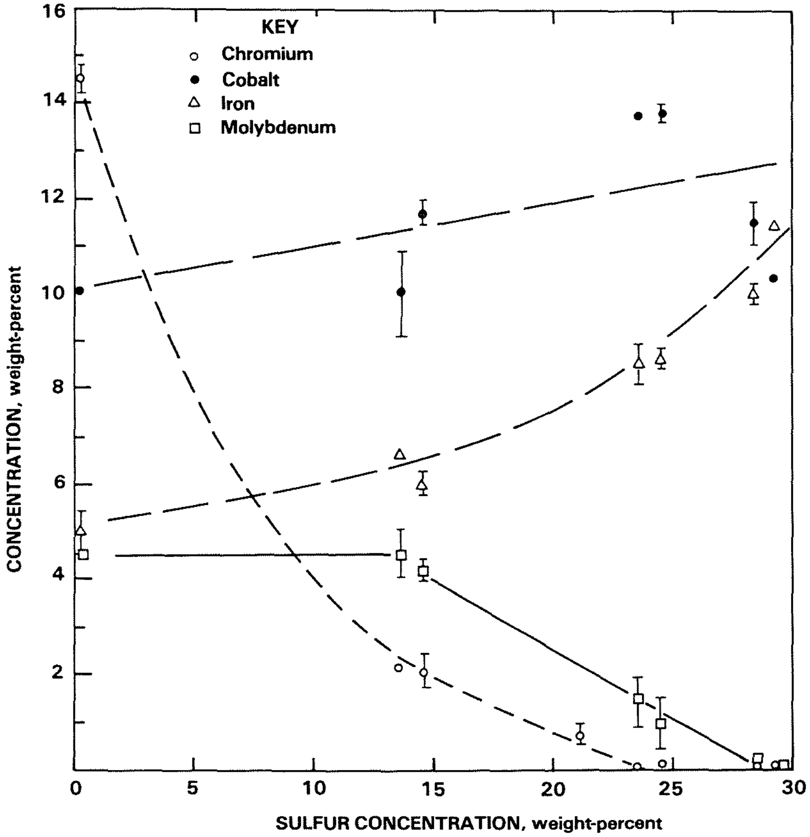

FIGURE 7. - Effect of matte sulfur content on composition of metallic phase.

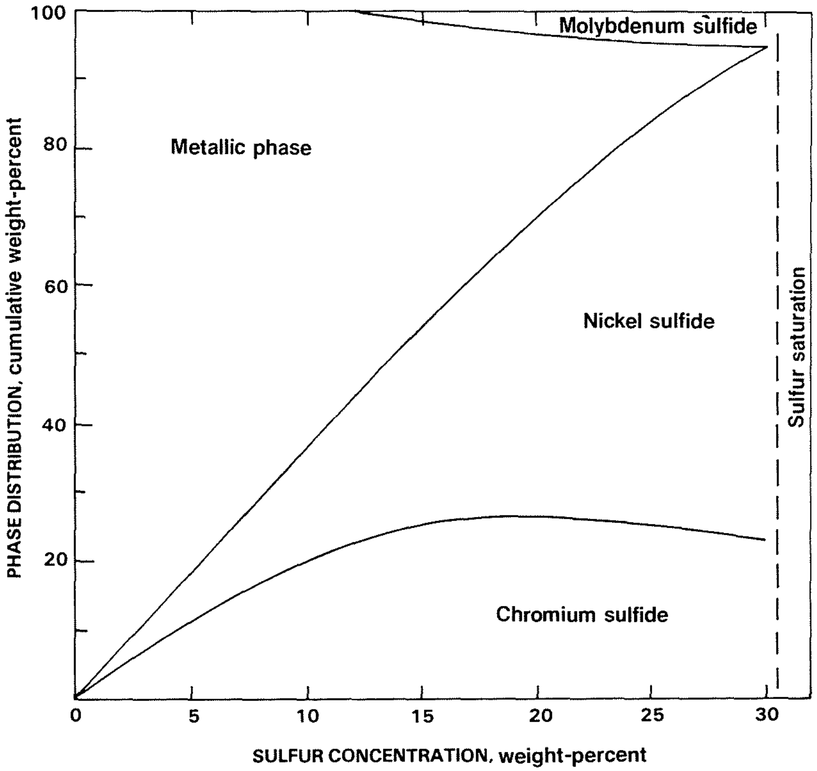

FIGURE 8. - Effect of matte sulfur content on phase distribution.

The effect of up to 15 percent cobalt and 10 percent molybdenum in the feed was also examined. No new sulfide phases were introduced in either case, and the overall chromium separation efficiency appeared to be unchanged, although the relative distribution of elements within the chromium sulfide phase was somewhat different. Consequently, it appears that iron is the only major constituent of superalloy scrap that should be restricted. It was not possible in this program to determine whether the optimum sulfur level for chromium separation is significantly affected by base composition.

Effect of Cooling Rate on Element Distribution

In the various experiments, matte cooling rate was varied over a wide range. The slowest cooling rate was obtained for a small sample that was program-cooled in a muffle furnace (0.2° F/min). Samples cast in the sand and refractory brick molds described above cooled at rates of 0.4° to 15° F/min depending on their size, degree of mold preheating, matte superheat, etc. Microprobe examination showed no variation in the composition of any of the major phases that could be associated with cooling rate. However, in a test to be described later, a sample of molten matte was granulated in a water stream. This produced a cooling rate of about 20,000° F/min. Microprobe examination of the granulated material showed a small but distinct decrease in the degree of chromium-nickel separation. This finding has implications for an alternative flowsheet using direct leaching of the matte, which is discussed in a subsequent section.

Effect of Cooling Rate on Grain Size

The first matte samples were cast into poorly insulated unheated molds. The resulting grain size appeared to be satisfactory to facilitate phase liberation without excessive grinding. With further testing, liberation was quite difficult and an excessive quantity of fines was generated which adversely affected chromium-nickel separation during froth flotation. Following this observation, a number of improvements in casting procedure were made, which reduced the cooling rate by two orders of magnitude. The average grain size was determined for a number of these heats by a linear intercept method. The relationship between grain size and cooling rate fits a straight line for a log-log plot over five orders of magnitude, including the water-granulated sample (fig. 9). Note that the plot shows average grain diameter for a composite of the four phases (Ni_3S_2, Cr_2S_3, MoS_2, and the metallic phase). The average diameter for each of the individual phases would be slightly different, but the relationship with cooling rate would be the same.

Effect of Composition on Melting Point of Matte

The melting point of the composite superalloy scrap is between 2,400° and 2,600° F. When sulfur is added, the melting point is depressed significantly. Since nickel is the principal constituent of the matte, the nickel-sulfur phase diagram (1) provides a good first approximation of the melting point characteristics. The eutectic between the metallic and β-nickel sulfide phase (Ni_3S_2) lies at about 22 percent sulfur and 635° C (1,175° F). The liquidus temperature rises steeply on both sides of the eutectic. Since there are

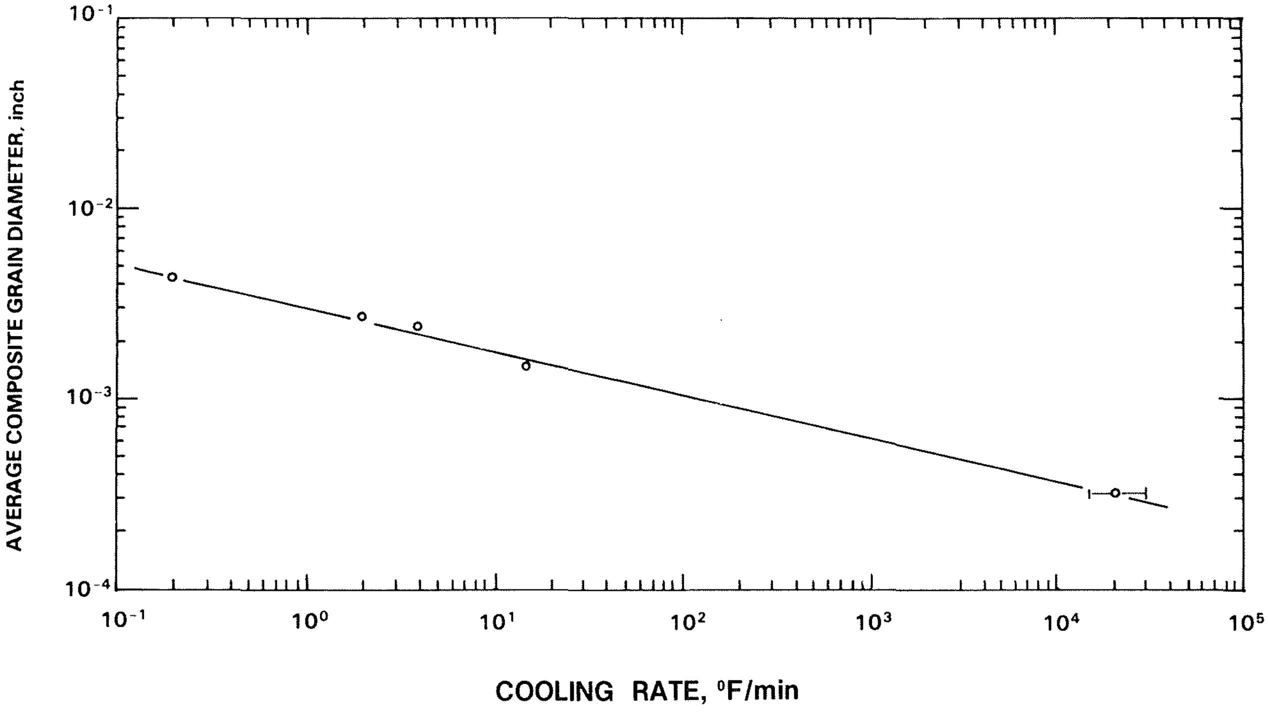

FIGURE 9. - Variation of average grain diameter with cooling rate.

obvious operating advantages in working with a matte of near eutectic composition, cooling curves of the various heats were examined to determine the critical temperatures. The results indicate that the ternary eutectic for the "aim" superalloy composition lies at about 950° F and 24 percent sulfur. The liquidus temperature for a matte having 17 percent sulfur is about 2,000° F. Although no difficulty was experienced in this program in working well above this temperature during sulfiding and casting, there would be an advantage in the form of energy saving to produce a lower-melting-point matte. The effect of the major elements in the scrap charge on the melting point of the matte, within the range that provides satisfactory chromium separation, is much less significant than total sulfur content. However, very high liquidus and eutectic temperatures (2,200° and 1,270° F) were observed for a 30 percent Fe-25 percent Ni-17 percent Cr matte.

Integrated Oxidation-Sulfidation Tests

The work discussed in the foregoing sections was performed on 12-kilogram heats using a pure metal charge in most cases. The next step in demonstrating the process was to scale-up and integrate the melting-oxidation-sulfidation-casting operations. This step was also necessary to produce sufficient matte for test work on other parts of the recovery flowsheet. Actual superalloy scrap was used as the metal feed for the first time in these experiments.

Testing Procedure

Six heats were made in this portion of the program, each having somewhat different procedures to test various aspects of the process. Only a generalized description of the procedure will be provided here.

Melting

In every case a blended charge of 27 kilograms of alloy scrap with the "aim" composition was air-melted with a 300-kilowatt coreless induction furnace in a high-density alumina crucible. The molten charge was brought to 2,950° F and sampled for chemical analysis. Nickel oxide granules were then fed into the bath to oxidize the reactive metals. The oxygen addition of 2.5 percent was selected on the basis of the previous tests and the aluminum and titanium content of the scrap. Lime and fluorspar were added as fluxes along with the nickel oxide. After holding the bath for 20 minutes with furnace power on a low setting, the slag and metal were sampled and the slag was removed.

Sulfidation

Sulfidation was done either in a separate graphite-lined 50-kilowatt furnace (four heats) or in the original melting furnace (two heats). Transfer to the adjacent furnace was done in a preheated refractory-lined ladle. When the two-furnace method was used, 8.5 kilograms of nickel sulfide master alloy was premelted and heated to 1,000° F. The metal charge was tapped into the vessel, and sulfidation was completed by adding pure sulfur briquets in the manner described on page 13. When the sulfidation was done in the original melting furnace, only sulfur briquets were used. The "aim" sulfur content was 20 to 23 percent. In each case, the bath temperature was allowed to fall gradually to the desired tap temperature of 2,250° F.

Casting

Slow-cooled castings were produced from five of the heats. The apparatus and procedure for slow cooling was described earlier. The cooling rate for the 42-kilogram ingots was about 0.4° F/min.

Granulation

Matte samples from three heats were water-granulated. In these tests approximately 10 kilograms of matte was tapped into a small refractory-lined ladle, transported to the granulation station, and poured into a preheated refractory-lined tundish. This tundish was mounted 1 foot above a cylindrical water tank, 6 feet in depth by 3 feet in diameter. The system was designed so that the molten matte stream from a 1/2-inch-diameter zirconia nozzle intersected a high-pressure water stream. The water flow was about 5 gallons per minute. The solidified matte granules were collected on a screen at the bottom of the tank.

Gas and Dust Monitoring

The melting furnaces were served by hoods mounted on flexible exhaust vents driven by a blower mounted on the foundry roof. The vent was punctured about 20 feet from the furnace and fitted with a bypass pipe. A portion of the effluent was drawn into the bypass using a small fan-driven sampling device. Dust was collected on the filter pads, and gas was collected in a large syringe. The pads were weighed and analyzed by wet-chemical analysis. The gas samples were analyzed in a gas chromatograph. The gas velocity in the stack was measured with a velometer.

General Observations

For the most part, the melting behavior of the large-scale integrated heats was similar to that of the small heats. No difficulty was experienced in melting the solid scrap. It was observed that the meltdown proceeded faster when lower-melting-point scrap such as B-1900 and alloy 713C was charged first. Oxidation during air melting was negligible so that little slag was present before the oxide was added.

Oxidation using nickel oxide was very quiet and efficient. The light reactive metal oxides separated and floated readily to form the slag, as observed in the small heats. However, tantalum partitioning to the slag was considerably less than before, despite the long reaction period (table 5). Recovery in the oxidized bath averaged 97 percent for Cr, 95 percent for Mo and W, 90 percent for Cb, and 50 percent for Ta. Recoveries of Ni, Co, and Fe were nearly 100 percent.

Scale-up of the sulfidation procedure also presented no new difficulties. Recovery of sulfur was greater than 95 percent. The matte was essentially slag-free, indicating that all metals should have been fully recovered in this operation. However, in a few cases, the matte compositions show variations of major elements before and after sulfidation. This is attributed to difficulty in standardizing chemical analyses and chemical inhomogeneities in the solidified matte. The carbon content of the heats made using the two-furnace practice was 0.6 to 2.2 percent, which resulted in the formation of heavy metal carbides in the matte. The carbon content was 0.2 percent or less when the single furnace practice was used and no carbides were present in the ingot.

TABLE 5. - Results of integrated oxidation-sulfidation tests

Sample	Composition, weight-percent[1]																	
	Ni	Cr	Co	Fe	Mo	W	Cb	Ta	Al	Ti	Mn	Si	Zr	B	O	C	S	Ca
HEAT D, 2 FURNACES, INGOT CAST																		
Molten charge[2]	64.4	16.5	5.0	5.9	3.3	NAp	1.4	0.67	2.40	1.16	0.15	0.08	0.040	0.003	0.003	0.06	0.004	NAp
Oxidized charge[3]	67.9	16.2	5.2	6.0	2.9	NAp	1.2	.36	<.05	.14	.05	.13	.01	.007	.013	.058	.004	NAp
Matte[4]	55.3	8.5	2.8	3.8	2.2	NAp	.4	<.2	NAp	NAp	.3	<.05	NAp	NAp	1.7	1.4	23.4	NAp
Slag[5]	2.3	2.6	<.05	.13	.2	NAp	.6	5.3	14.8	>50	.03	<.05	.2	NAp	NA	NAp	NAp	4.3
HEAT E, 2 FURNACES, INGOT CAST																		
Molten charge[2]	63.5	16.5	4.7	6.3	3.3	NAp	1.5	0.58	2.1	1.20	0.08	0.09	0.04	0.007	0.004	0.06	0.004	NAp
Oxidized charge[3]	68.6	15.2	4.7	6.3	2.9	NAp	1.3	.48	.05	.20	.08	.13	.01	.004	.012	.05	.098	NAp
Matte[4]	58.6	8.5	2.4	4.2	2.1	NAp	.4	.35	.13	.19	.03	<.05	<.01	.001	1.0	.62	21.5	NAp
Slag[5]	8.5	6.7	.03	.25	.2	NAp	1.1	7.1	10.5	46	.11	.15	.2	NAp	NA	NAp	NAp	6.3
HEAT F, 2 FURNACES, INGOT CAST																		
Molten charge[2]	63.2	16.3	5.0	6.2	3.4	NAp	1.5	0.9	2.2	1.10	0.05	0.15	0.04	0.006	0.003	0.06	0.004	NAp
Oxidized charge[3]	68.5	15.2	5.0	6.2	3.0	NAp	1.2	.34	<.05	.14	.05	.34	.01	.003	.01	.06	.006	NAp
Matte[4]	56.1	8.3	2.3	4.3	2.2	NAp	.4	.17	<.1	.21	.04	<.05	<.01	<.001	1.1	2.2	22.6	NAp
Slag[5]	3.0	3.8	<.01	.13	.3	NAp	.9	6.8	13.2	>50	.11	.6	.1	NAp	NA	NAp	NAp	4.5
HEAT G, 2 FURNACES, INGOT CAST, GRANULATED																		
Molten charge[2]	63.4	16.3	5.0	5.9	3.3	NAp	1.4	1.2	2.0	1.10	0.08	0.19	0.05	NAp	0.03	0.07	0.003	NAp
Oxidized charge[3]	68.7	14.9	4.9	5.9	3.0	NAp	1.2	.8	.06	.15	.08	.20	<.01	NAp	.04	.07	.005	NAp
Matte[4]	55.5	8.0	3.1	5.2	2.4	NAp	.4	.4	.005	.21	.07	.16	.05	NAp	2.0	.004	22.5	NAp
Slag[5]	8.4	7.3	.14	.52	.2	NAp	.7	6.5	10.0	45	.05	<.01	.3	NAp	NA	NAp	NAp	3.9
HEAT H, SINGLE FURNACE, INGOT CAST, GRANULATED																		
Molten charge[2]	63.9	15.8	4.8	6.0	3.2	0.96	1.4	0.8	2.2	0.92	0.1	0.11	0.03	NAp	0.016	0.09	0.005	NAp
Oxidized charge[3]	68.4	14.9	4.8	6.0	2.8	.90	1.3	.4	.04	.24	.1	.1	<.01	NAp	.013	.06	.004	NAp
Matte[4]	56.6	5.6	3.7	6.3	2.6	.88	.5	.4	.005	.20	<.01	<.01	<.01	NAp	1.0	.21	22.0	NAp
Slag[5]	6.2	8.3	.10	.15	.3	1.6	.5	5.4	12.4	24	.03	<.01	.2	NAp	NA	NAp	NAp	NAp
HEAT I, SINGLE FURNACE, GRANULATED																		
Molten charge[2]	63.0	15.9	5.0	5.7	2.9	1.6	1.3	0.88	2.2	1.20	0.08	0.12	0.05	NAp	0.008	0.068	0.006	NAp
Oxidized charge[3]	67.3	15.0	4.8	6.9	2.7	1.4	1.1	.33	.05	.19	.10	.16	.02	NAp	.01	.13	.008	NAp
Matte[4]	55.6	7.0	3.9	8.0	2.5	1.3	.5	.30	.10	<.10	<.05	<.05	<.01	NAp	2.1	.20	19.3	NAp
Slag[5]	6.4	5.4	.12	.24	.4	3.8	.6	3.0	14.4	12.9	.05	<.05	.5	NAp	NA	NAp	NAp	4.2

NA Not available.

NAp Not applicable.

[1] Nickel by difference.

[2] Small chill casting poured after scrap charge was molten.

[3] Small chill casting poured after oxidation reactions were judged complete.

[4] Blended sample taken from solid matte block.

[5] Blended sample taken from solid slag.

Material Balance

Material balances were prepared for several heats based on the known or inferred weights of the charge and products. The balance for heat D, which was typical of the two-furnace ingot-casting procedure, is shown in table 6. Base metal losses to the slag were about 1 percent of the charge weight. Accounting for other known losses, the amount of material that could not be accounted for was 2 kilograms (4.5 percent of charged weight). This was in the form of spills, splatters, spoon and stirrer rod skulls, ladle skulls, and mold fins. Many of these waste products would be recovered in a commercial operation by recycling back to the melting furnace or incorporation with the crushed matte casting.

TABLE 6. - Material balance for heat D

Component	Weight, kilograms	
	In	Out
MELTING AND OXIDATION		
Scrap charge:		
Inconel alloy 718	6.0	NAp
Inconel alloy 600	6.0	NAp
Waspalloy	6.0	NAp
Inconel alloy 713C	4.6	NAp
B-1900	4.6	NAp
Total	27.2	NAp
Flux (CaO + CaF_2)	0.2	NAp
Dust	NAp	<0.1
Slag	NAp	2.5
Nickel oxide	3.6	NAp
Chemical analysis samples	NAp	.4
Charge to ladle	NAp	[e]28.1
MATTE FORMATION		
Charge to furnace	[e]28.1	NAp
Nickel sulfide heel	8.5	NAp
Sulfur	7.9	NAp
Dust	NAp	<0.1
Slag	NAp	<0.1
Chemical analysis samples	NAp	0.2
Charge to ingot mold	NAp	[e]44.3
YIELD		
Material added	[e]44.3	NAp
Matte castings and slag	NAp	42.3
Losses not accounted for	NAp	2.0

[e]Estimated.

NAp Not applicable.

Granulation

Although water granulation is often used for fragmenting nickel-copper mattes, its applicability to the superalloy matte was uncertain because of the possibility that chromium might react with water. The granulation proved quite successful, however, and a clean convoluted product was obtained with a particle size range of 0.1 to 0.5 inch. No evidence of hydrogen evolution was observed during granulation, and the final oxygen content of the matte was only slightly higher than that of the slow-cooled matte. The fragmented product was very friable, and the particles could be crushed with the fingers. The microstructure was similar to that of the slow-cooled matte, although the grains were much finer. The phase composition and grain size of the material were discussed earlier. All in all, water granulation appeared to be a highly desirable means of producing a feed for direct matte leaching. (See discussion in the section on leaching.)

Refractory Wear Tests

As noted, the initial 40-kilogram heats were melted and oxidized in an alumina-lined furnace and transferred to a graphite-lined furnace for sulfidation. This practice was used because these materials were known to be very resistant to attack under the specific conditions. For both capital and operating cost reasons, a two-furnace practice would be undesirable in a commercial plant. Consequently, a series of immersion tests were performed using coupons cut from commercial-grade refractories. The samples were exposed in one test to slag and metal at 2,950° F and in another test to matte at 2,250° F. In both cases the tests were run for 30 minutes with the furnace power at a low setting.

The results of tests are expressed in qualitative terms in table 7. As expected, the oxide refractories showed the greatest resistance in the oxidizing environment, while the carbon-containing refractories were more resistant in the sulfiding environment. Only high-density alumina was resistant to attack in both environments.

TABLE 7. - Observed resistance of common refractories to erosion[1]

Refractory	Oxidation at 2,950° F	Sulfidation[1] at 2,250° F
Alumina.................	None.......	Slight.
Zirconia................	...do......	Severe.
Magnesia................	...do......	Do.
Chrome-magnesite.........	Moderate...	Do.
Silicon carbide..........	Severe.....	None.
Clay-graphite............	...do......	Do.
Graphite.................	...do......	Do.

[1] 30-min immersion.

Based on this information, a single-furnace test was conducted using an alumina crucible in a 300-kilowatt induction furnace. Only the surface slag was removed after oxidation, leaving a thin skull of slag on the refractory. The sulfidation was then carried out in the normal fashion with no refractory attack observed. The carbon content of the matte made with this procedure was only 0.2 percent, compared with 2.2 percent using the two-furnace procedure. Consequently, it was concluded that a one-furnace approach would be feasible for a commercial operation.

Furnace Emissions

The furnaces used for oxidation and sulfidation were open to the air with exhaust hoods located about 2 feet above the bath to permit access for sampling and charging. There was visible dusting during both operations. The exhaust system appeared to capture virtually all of this dust. Samples of dust taken from the stack bypass were analyzed for the major constituents. The results are shown in table 8. The dust from the oxidation test appeared to be a mixture of slag, oxidized superalloy, and perhaps some fine nickel oxide. The dust from the sulfidation test was a mixture of oxidized superalloy, slag, and elemental sulfur. The presence of the latter was verified by the bright yellow color of the residue. The volume of dust was extremely small, as would be expected for the charging and melting procedures employed. Pneumatic addition of any particulates, such as superalloy grindings, mill scale, or sulfur, would produce dust loadings of about 0.5 percent of the bath weight, and oxygen lancing could result in losses of as much as 1 percent. In a commercial facility this dust would be recycled back into the melt charge.

TABLE 8. - Composition of dust samples[1]

	Oxidation	Sulfidation
Quantity....................grams..	[2]7.0	[3]4.5
Composition, weight-percent:		
Aluminum........................	3.3	0.97
Calcium.........................	9.8	2.6
Chromium........................	1.1	1.7
Cobalt..........................	0.16	0.5
Columbium.......................	0.38	0.56
Iron............................	1.1	2.8
Molybdenum......................	0.57	1.8
Nickel..........................	4.9	1.2
Sulfur..........................	0.8	8.9
Tantalum........................	<0.1	<0.1
Titanium........................	1.6	0.35

[1] Samples taken during heat E (table 5).

[2] Cumulative for 13-min period. Dust loading was 3.9×10^{-4} g/ft^3 exhaust air, or 0.03 pct of bath weight.

[3] Cumulative for 22-min period. Dust loading was 1.5×10^{-4} g/ft^3 exhaust air, or 0.01 pct of bath weight.

Furnace gases were sampled as described previously (under Testing Procedure). Gas drawn from the ventilation system of the oxidizing furnace was indistinguishable from foundry air. The gas from the sulfiding furnace contained some sulfur dioxide (SO_2), but the quantity was less than 1 percent.

Discussion

The experimental work demonstrated the technical feasibility of the process of generating a solid matte with more than 95 percent of the chromium in one phase which, in principle, can be separated from the other phases by physical or chemical means. At 100 percent separation efficiency, a chromium concentrate having 40 percent chromium and a nickel concentrate having less than 1 percent chromium could be produced. The actual separation procedures and efficiencies are discussed in the next section.

In the laboratory-scale work, recovery of the valuable constituents of the scrap was excellent. Table 9 shows nominal distribution of elements based on a 100 percent scrap charge, the "aim" composition, and nickel oxide and elemental sulfur as the oxidant and sulfidant, respectively. In a commercial operation, skulls and dusts would be recycled so that the only elemental losses would be in the slag. The most valuable constituent of the slag would be tantalum when it was present in the scrap feed. The possibility of selling the slag to a refiner for recovery of tantalum should be explored.

Although it would be desirable to apply the matte separation process to any chromium-bearing feed, it is now apparent that composition restrictions must be applied at least to the composite charge. A composite analysis falling within the following ranges (in weight-percent) should produce a good separation of chromium without severe processing difficulties:

	Ni	Cr	Co	Fe	Mo
High....	95	20	20	15	10
Low.....	50	5	0	0	0

It is possible that the limits for Co and Mo may be higher and therefore Ni lower, but the full range was not covered in this program. It should be obvious that only the composite analysis need fall within the indicated range; any combination of alloys including iron-base superalloys could be used to make up the melting charge.

TABLE 9. - Distribution of elements in feed and products for integrated oxidation-sulfidation tests[1]

Material	Relative quantity	Ni	Cr	Co	Fe	Mo	W	Cb	Ta	S	Others	Source or disposition
INPUT												
Scrap feed......kilograms..	100	62.5	16.1	5.0	5.8	3.3	1.0	1.4	0.7	NAp	4.2	Feed.
Nickel oxide.......do......	13	9.8	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	3.2	Do.
Flux..............do......	1	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	1	Consumable.
Sulfur............do......	27.5	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	27.5	NAp	Recycle.
PRODUCTS AND RECOVERY												
Matte...........kilograms..	125.6	68.1	14.9	4.8	5.5	3.1	0.9	1.0	0.3	26.0	1.0	Separation.
Recovery..........percent..	88.8	94.2	92.5	96.0	94.8	93.9	90.0	71.4	40.0	94.5	11.9	
Skulls, spills, and prills. kilograms..	6.8	3.6	0.8	0.2	0.3	0.2	0.1	0.1	<0.05	1.4	0.1	Recycle.
Recovery..........percent..	4.8	5.0	5.0	4.0	5.2	6.1	10.0	7.1	<7.0	5.1	1.2	
Dust............kilograms..	0.1	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	0.1	NAp	Do.
Recovery..........percent..	<0.1	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	0.4	NAp	
Slag............kilograms..	9.0	0.6	0.4	NAp	NAp	NAp	NAp	0.3	0.4	NAp	7.3	Sell for Ta recovery.
Recovery..........percent..	6.4	0.8	2.5	NAp	NAp	NAp	NAp	21.4	53.3	NAp	86.9	

NAp Not applicable.

[1] 100 kg feed assumed.

The scrap feed used in these experiments was all clean, identified, "vacuum-grade" scrap. There is no reason why the process could not be applied successfully to treat other forms of scrap. For example, crushed and de-oiled turnings, skulls, spills, and mixed scrap of all types could be readily melted. Grindings could be treated provided a system for adding them without excessive dusting was used. The tolerance of the process contaminated scrap is unknown. However, certain contaminants such as lead (Pb), bismusth (Bi), tin (Sn), arsenic (As), silver (Ag), and others should be avoided as a matter of principle because of the serious detrimental effect they have on superalloy properties, unless it can be shown that they are effectively removed in the process. Nickel oxide was used as the oxidant in the experimental program because it provided reproducible and quantifiable oxygen additions. In practice, it should be possible to use an oxidized superalloy scrap or waste to supply oxygen. This could take the form of furnace flue dust, mill scale, or even dried pickle sludge. Recovery of elemental oxides reducible by aluminum and titanium should be good.

All experiments were conducted in coreless induction furnaces. This type of furnace is the most convenient for small batch treatments and provides considerable flexibility in control and feeding. The induction furnace would also be suitable for melting in a commercial-scale plant with a single 10,000-pound-capacity furnace being adequate for treating 5,000 tons per year of scrap. Development work for a commercial plant using this melting system would be straightforward. It is possible that other melting furnaces could be used that would reduce energy consumption and possibly increase throughput or reduce the number of plant personnel by operating on a continuous basis. Systems based on submerged arc or plasma heating would be worthy of consideration, but investigation of them was beyond the scope of the present program.

Most of the raw materials were charged by hand in the laboratory work. However, mechanical methods should be used for larger scale systems. Solid scrap would be charged from a tote box or hopper. Particulates such as grindings and oxides could be successfully gravity-fed from an overhead hopper. In this program, sulfur was added as nickel-sulfide master alloy or as briquets. Since sulfur is most readily available as a powder, a method that feeds this material directly would be convenient. Limited experimentation showed that direct addition of powder to the bath surface generated flaring and dusting and resulted in low sulfur recovery. A pneumatic system that injects sulfur powder into the downswirl of a stirred bath should provide adequate recovery, although dusting would be greater than in the laboratory heats.

Although some difficulty was experienced in achieving a sufficiently coarse grain size, this should prove no problem for a commercial-scale plant where ingots of several tons would be cast and allowed to solidify for several days in an insulated holding pit. As an alternative, when direct leaching was employed, the matte could be water-granulated directly in the casting pit.

Separation of Sulfides[9]

In this phase of the operation, superalloy matte was crushed and ground to liberate the phases. Magnetic separation was employed to separate the ferromagnetic nickel-rich metallic phase. The nonmagnetic nickel and chromium sulfides were subsequently separated by froth flotation.

Experimental Procedure

Raw Materials

Samples of broken matte from several heats were used for the initial exploratory testwork. However, the material used for all of the tests reported here was obtained from a single 40-kilogram heat. The composition of this material was 58.7 percent Ni, 8.92 percent Cr, 22.1 percent S, and balance primarily Fe, Co, and Mo. Note that this is a sample analysis; the heat analysis, which is representative of the composition of the entire matte block, differs slightly (table 5, heat D).

Crushing, Grinding, and Magnetic Separation

The matte sample was crushed in stages in a 5- by 6-inch jaw crusher to minus 1 and split into 1 kilogram parcels for storage in a freezer to prevent surface oxidation which could have affected the flotation results. Each sample was crushed to minus 6 mesh just before use.

A 7- by 14-inch laboratory rodmill was used for all of the grinding tests. Samples were wet-ground for various times (10 to 40 minutes per kilogram) using a 50-percent-solids pulp. Magnetic separation was performed manually in a separated cell after completion of the grinding operation. A small laboratory flotation machine was used (without aeration) for these tests. A permanent bar magnet inserted in a plastic casing was employed. Magnetic material was recovered by dipping the encased magnet into the stirred pulp at regular intervals. The magnetic material was released by withdrawing the magnet from the casing. The field strength of the magnet was varied from 0.045 to 0.068 Tesla by inserting spacers between the magnet and the casing.

Flotation

Flotation was performed on a small laboratory flotation machine with a 3-liter capacity. The aeration was monitored and controlled with a rotameter. The chemicals and reagents used for the flotation studies are commercially available and are identified by their respective trade or generic names.

The basic flowsheet adopted for the test work is shown in figure 10. This flowsheet is based on the matte separation practice used commercially by Inco at the Copper Cliff Ontario Smelter for treating nickel-copper matte (4).

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[9] The experimental work was planned and directed by C. Lan, research engineer, Mineral Processing, Inco Metals Co., J. Roy Gordon Research Laboratory, Mississauga, Ontario, Canada.

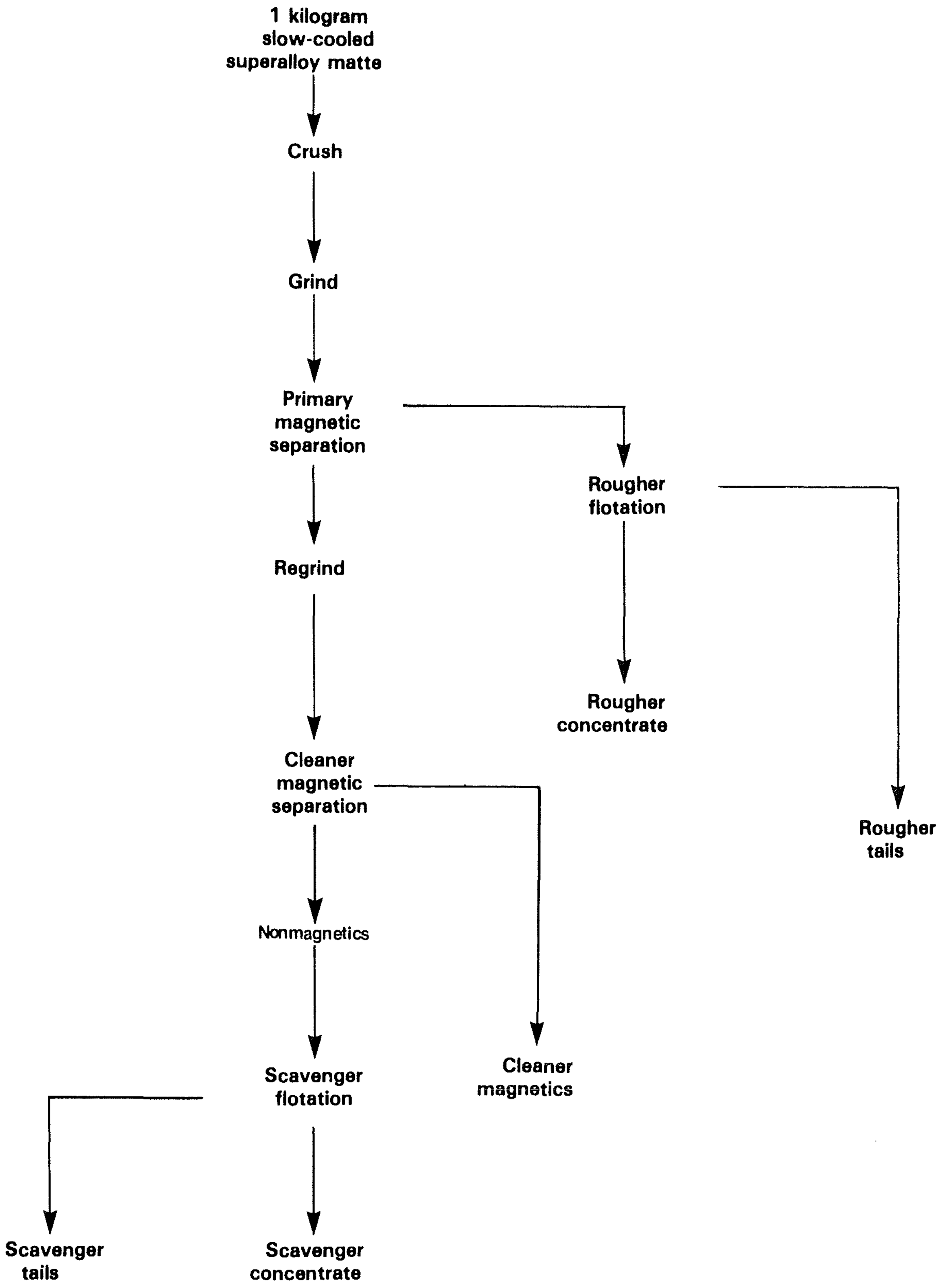


FIGURE 10. - Base flowsheet for separation tests.

The flowsheet employs a two-stage sequence of grinding, magnetic separation, and flotation. The test conditions were varied in accordance with the overall goals of minimizing chromium sulfide content of the metallic concentrate and maximizing nickel-chromium separation during flotation. Details of variables studies for these tests are described in the following sections. Complete separation of the metallic and nickel sulfide phases was not considered important because they are recombined for leaching.

Determination of Optimum Grinding Time

The grinding time for phase liberation was studied from two aspects: (1) Effect on nickel and chromium recovery in the metallic fraction in the primary and cleaner magnetic separation, and (2) effect on nickel and chromium separation in rougher and cleaner flotation.

Effect on Magnetic Separation

The effect of time during the primary grind on nickel and chromium recovery in the metallic fraction is shown in figure 11. The objective was to have the lowest chromium content in the fraction "cleaner magnetics," which is the feed for the leaching circuit. The results show that increased primary grinding reduces chromium in the intermediate "primary magnetics" product. However, increased primary grinding time has a much smaller effect on the reground "cleaner magnetics" product. As might be expected, the total weight of "cleaner magnetics" was not greatly affected by primary grinding time.

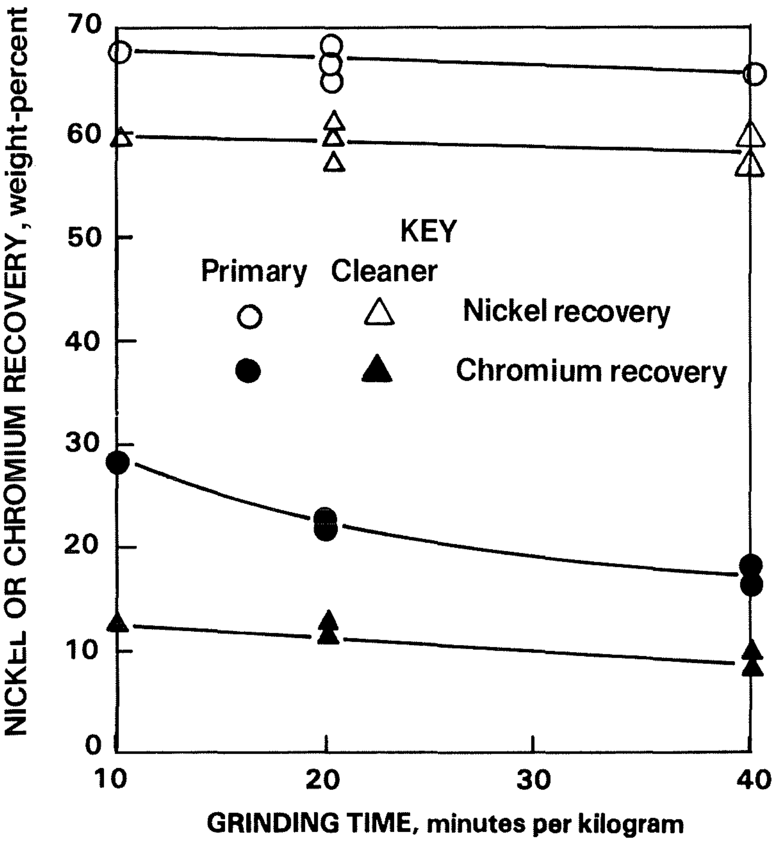


FIGURE 11. - Effect of primary grind time on efficiency of magnetic separation.

Effect on Flotation Separation

Tests showed that the natural hydrogen ion concentration (pH) of the pulp was 8.5. The initial flotation tests were conducted at this natural pH, using potassium amyl xanthate (KAX) as collector and methyl isobutyl carbonyl (MIBC) as frother. The indicator for effect of grinding time in this case is the separation of nickel and chromium, nickel being recovered in the froth and chromium in the tails. The results presented in figure 12 show a small increase in nickel-chromium separation in the rougher flotation circuit but almost no effect on separation in the scavenger circuit. Analysis of the results of the test indicated that nickel sulfide-chromium sulfide liberation was improved with longer grinding but at the expense of the formation of a higher proportion of hard-to-float nickel sulfide slimes (particles smaller than 10 micrometers).

Based on the above results, grinding times of 20 and 8 minutes per kilogram were selected for the primary and secondary grinding steps.

Magnetic Separation Conditions

An additional series of tests was run on the cleaner magnetic separation circuit to improve separation of metallics from the sulfides. These tests were run using various magnetic field strengths and impeller speeds for agitation of the ground matte pulp. The results in figure 13 show chromium and sulfur recoveries as a function of impeller speed and magnetic field strength, based on the composition of the cleaner magnetic separation feed. The effect of speed of agitation was negligible within the range tested (22 to 25 revolutions per minute). The effect of magnetic field strength was the inverse of what was expected; for example, there was more nonmagnetic phase in the magnetic fraction at higher field strength. Microscopic examination indicated that this effect was due to the presence of fine particles of metallic phase (<5 micrometers diameter) disseminated within the sulfide grains. Further grinding to free these particles was judged to be impractical.

Flotation Separation of Nickel and Chromium Sulfides

As noted previously, maximum separation of nickel and chromium was sought in the flotation operation. The degree of separation can be expressed in terms of separation efficiency defined as the difference in nickel and chromium recoveries. Complete separation of the elements by flotation giving an efficiency of 1.0 is impossible in this situation because the chromium sulfide phase contains some dissolved nickel. An efficiency of about 0.9 is the theoretical maximum.

It was established early in the test program that the nickel sulfide flotation rate was quite slow at the natural pH of 8.5 using KAX as collector. Also, the nickel recovery was low so that a chromium concentrate containing a high proportion of free nickel sulfide was produced. The following program was designed to improve separation efficiency.

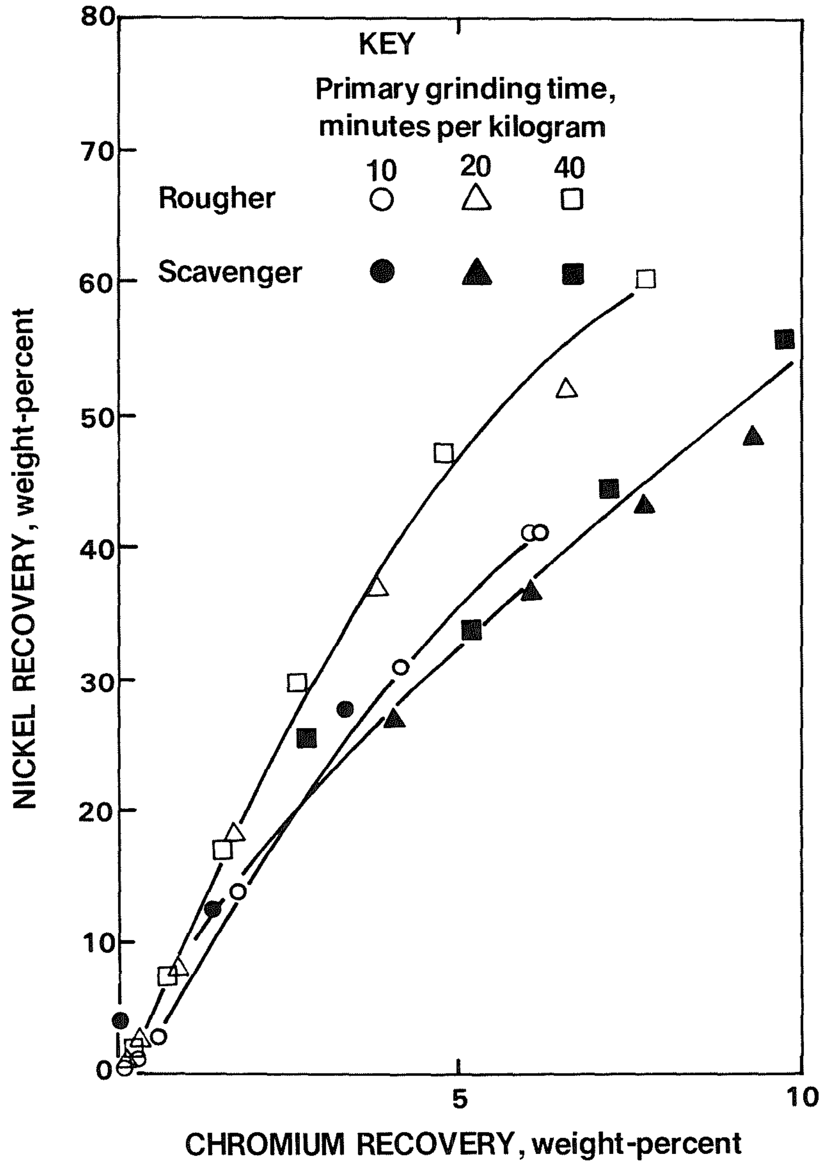


FIGURE 12. - Effect of primary grind time on efficiency of flotation separation.

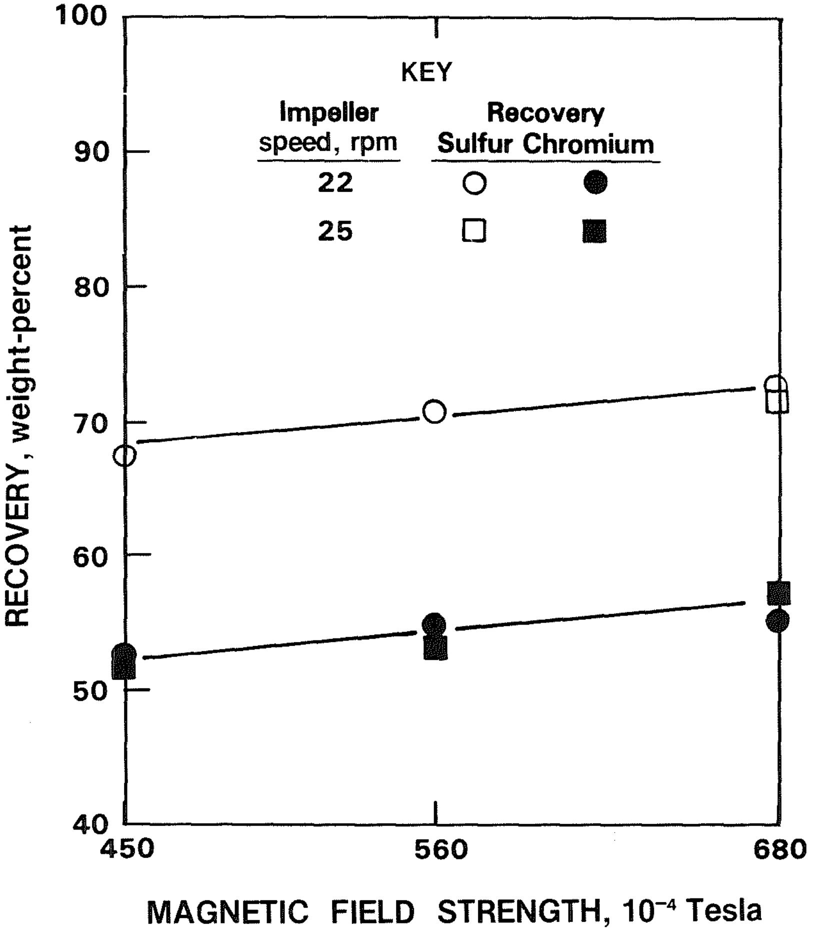


FIGURE 13. - Effect of magnetic field strength and impellor speed on magnetic separation.

Effect of pH

The flotation conditions used in this study are listed in table 10. The test results are shown in figure 14. The flotation rate of nickel sulfide exceeded that of chromium sulfide over the entire range of pH studied. The best separations were achieved at the natural pH of 8.5 and at pH 10. Based on this information, all subsequent flotation tests were done at natural pH.

TABLE 10. - Conditions used for flotation pH tests[1]

Item	Test 1	Test 2	Test 3	Test 4	Test 5
Nominal cell pH...........	5	8.5	10	11	12.6
pH regulator..............	H_2SO_4	None	NA_2CO_3	NaOH	CaO
Collector.................	A208	KAX	KAX	KAX	KAX

[1] MIBC used as frother for all tests.

Effect of Collector

The six collectors listed in table 11 were evaluated at natural pH using the rougher flotation feed. The results of these tests are shown in figure 15. Z200 provided the highest separation efficiency, 0.47 versus 0.42 for KAX and DPG. However, owing to its low aqueous solubility, a relatively large quantity of Z200 was required. Larger additions of KAX were also examined, but significantly higher separation efficiencies were not obtained. Both Z200 and DPG were very selective in producing a low-chromium, high-nickel concentrate. However, the overall nickel recovery and flotation rate obtained with these collectory was not as good as that provided by KAX. KAX was ultimately specified as the collector, since it provided the best overall flotation behavior.

TABLE 11. - Flotation collectors tested

Designation	Generic name	Quantity added, gram per kilogram feed	Separation efficiency, dimensionless[1]
KAX.........	Potassium amyl xanthate........	0.12	0.42
Pennac SDED.	Alkyl dithiocarbamate..........	.25	.18
LIX 65N.....	Hydrobenzophenone oxime........	1.0	<.1
Z200........	Isopropyl ethyl dithiocarbamate	1.0	.47
DPG.........	Diphenyl guanadine.............	1.0	.42
A208........	Alkyl dithiophosphate..........	.08	.22

[1] Based on a theoretical maximum of 0.9 as defined on page 32.

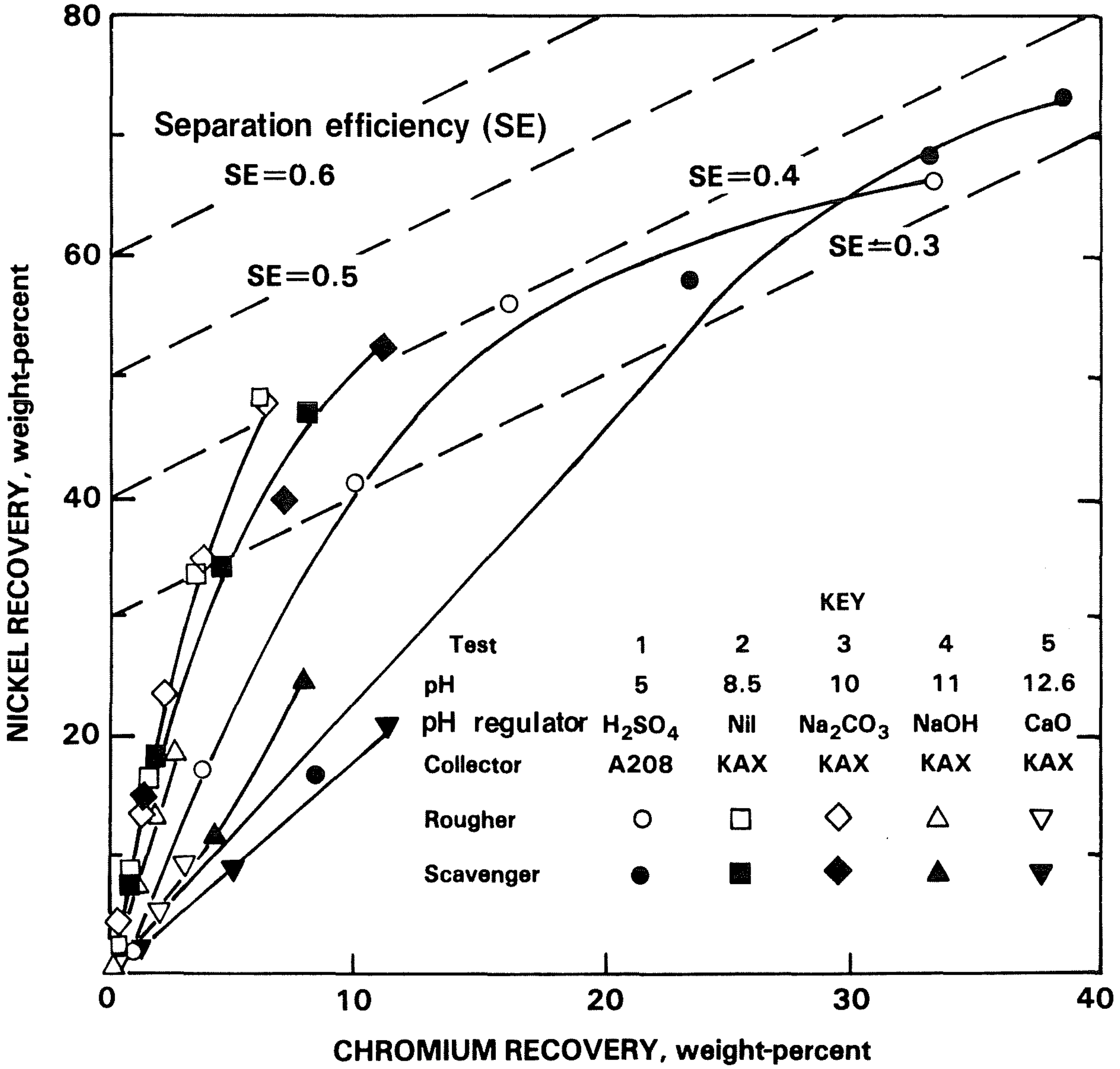


FIGURE 14. - Effect of pH on flotation separation of nickel and chromium sulfide.

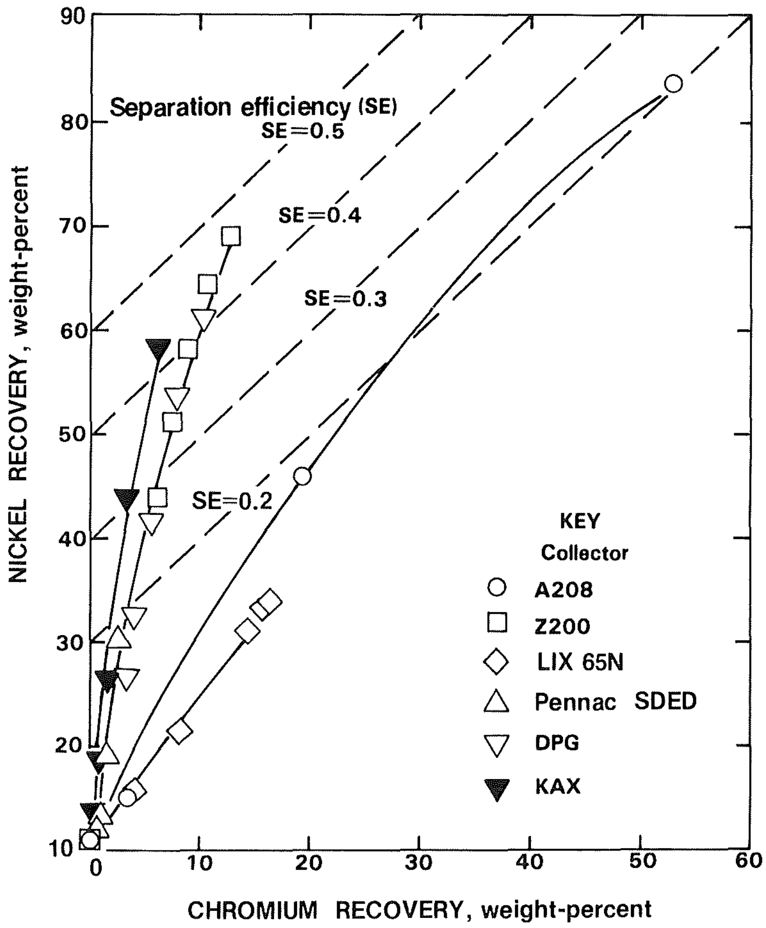


FIGURE 15. - Effect of flotation collector on separation.

Preflotation Activation

Activation with cupric sulfate (0.25 and 1.0 gram per kilogram of feed) using KAX as collector was studied for the rougher flotation feed. This procedure greatly accelerated the flotation rate of both nickel sulfide and chromium sulfide (figs. 16-17). Unfortunately, there was no significant improvement in separation efficiency. The relatively high nickel content of the chromium sulfide may account for the lack of selectivity of cupric sulfate activation.

Best Conditions

An open circuit material balance is shown in figure 18 for the best separation obtained in this work. The specific test conditions are enumerated in the figure. Combination of the rougher and scavenger flotation tails gives a chromium sulfide concentrate of 34 percent of the original matte weight; 81.4 and 21.0 percent, respectively, of the contained chromium and nickel are recovered. This concentrate is composed of about 50 volume-percent each of chromium sulfide and nickel sulfide.

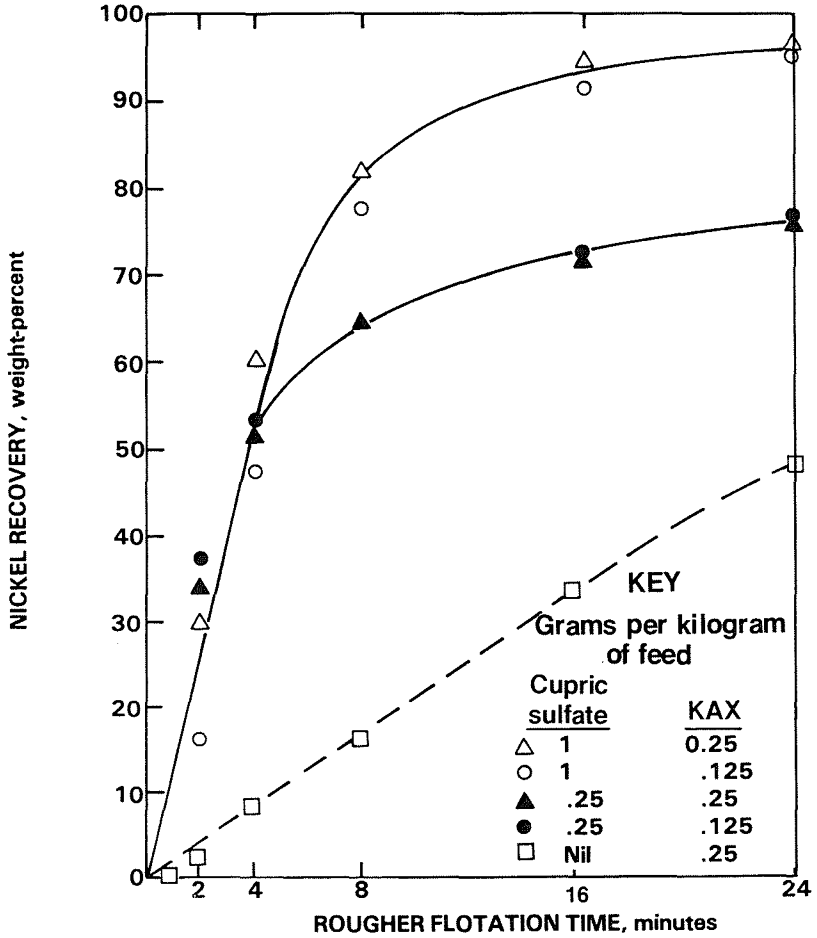


FIGURE 16. - Effect of activation on flotation rate of nickel sulfide.

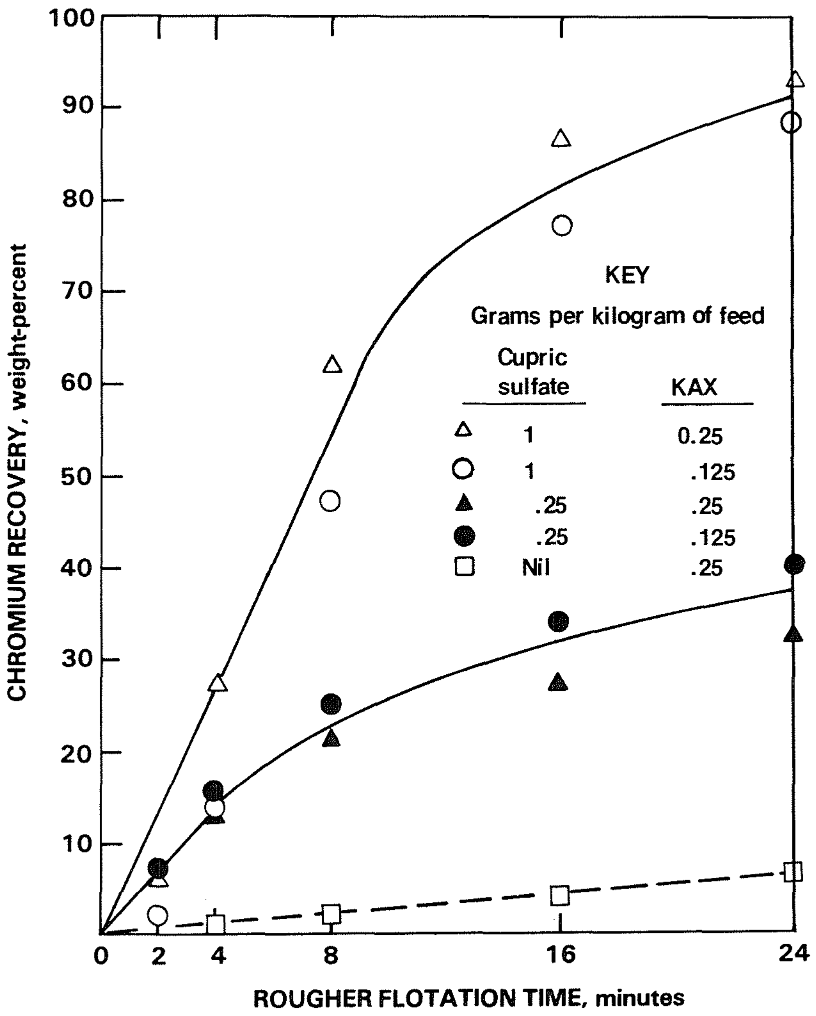
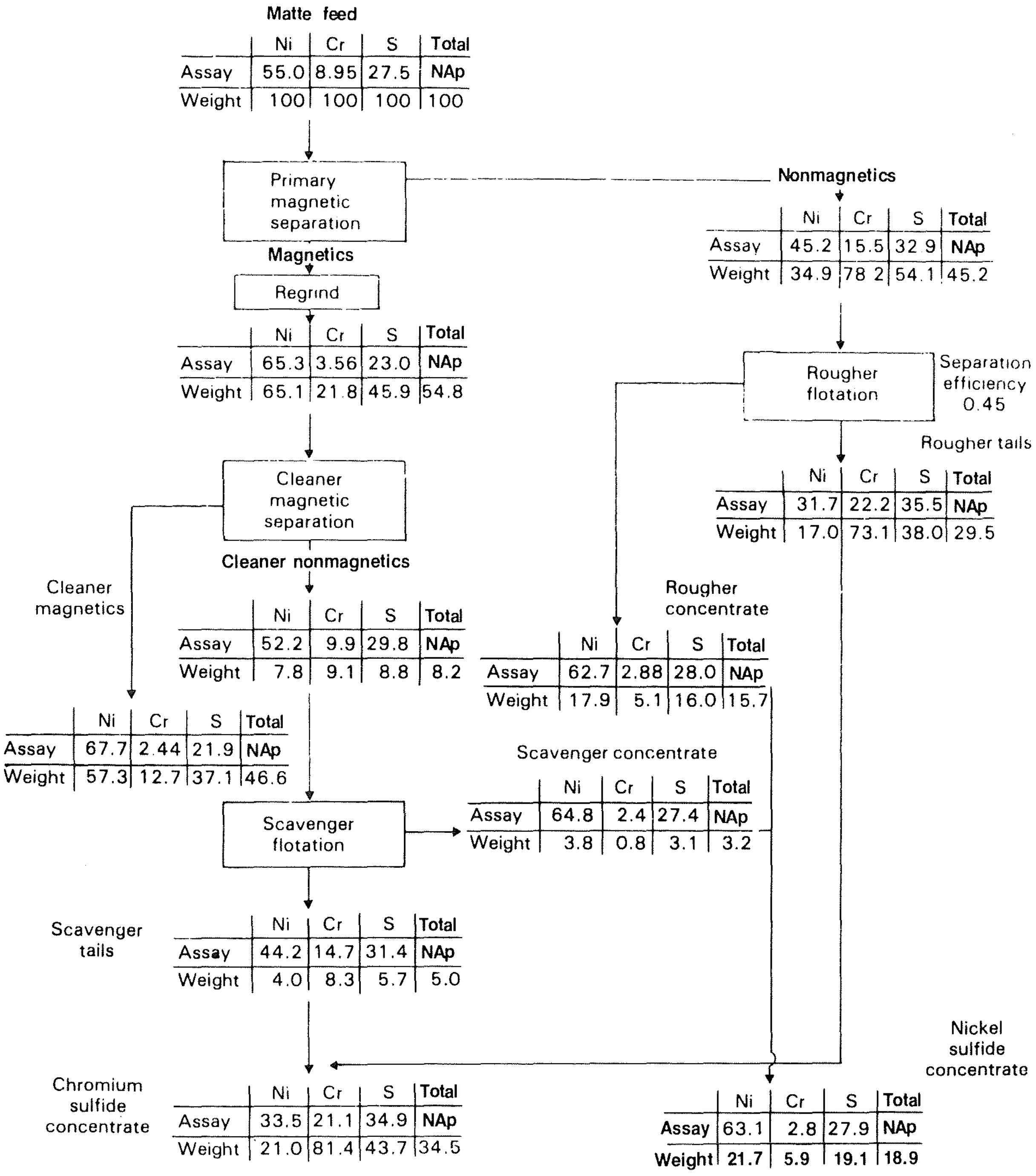


FIGURE 17. - Effect of activation on flotation rate of chromium sulfide.



Matte feed

	Ni	Cr	S	Total
Assay	55.0	8.95	27.5	NAp
Weight	100	100	100	100

Magnetics (after regrind)

	Ni	Cr	S	Total
Assay	65.3	3.56	23.0	NAp
Weight	65.1	21.8	45.9	54.8

Nonmagnetics

	Ni	Cr	S	Total
Assay	45.2	15.5	32.9	NAp
Weight	34.9	78.2	54.1	45.2

Rougher tails

	Ni	Cr	S	Total
Assay	31.7	22.2	35.5	NAp
Weight	17.0	73.1	38.0	29.5

Cleaner magnetics

	Ni	Cr	S	Total
Assay	67.7	2.44	21.9	NAp
Weight	57.3	12.7	37.1	46.6

Cleaner nonmagnetics

	Ni	Cr	S	Total
Assay	52.2	9.9	29.8	NAp
Weight	7.8	9.1	8.8	8.2

Rougher concentrate

	Ni	Cr	S	Total
Assay	62.7	2.88	28.0	NAp
Weight	17.9	5.1	16.0	15.7

Scavenger concentrate

	Ni	Cr	S	Total
Assay	64.8	2.4	27.4	NAp
Weight	3.8	0.8	3.1	3.2

Scavenger tails

	Ni	Cr	S	Total
Assay	44.2	14.7	31.4	NAp
Weight	4.0	8.3	5.7	5.0

Chromium sulfide concentrate

	Ni	Cr	S	Total
Assay	33.5	21.1	34.9	NAp
Weight	21.0	81.4	43.7	34.5

Nickel sulfide concentrate

	Ni	Cr	S	Total
Assay	63.1	2.8	27.9	NAp
Weight	**21.7**	**5.9**	**19.1**	**18.9**

FIGURE 18. - Open circuit material balance for best conditions.

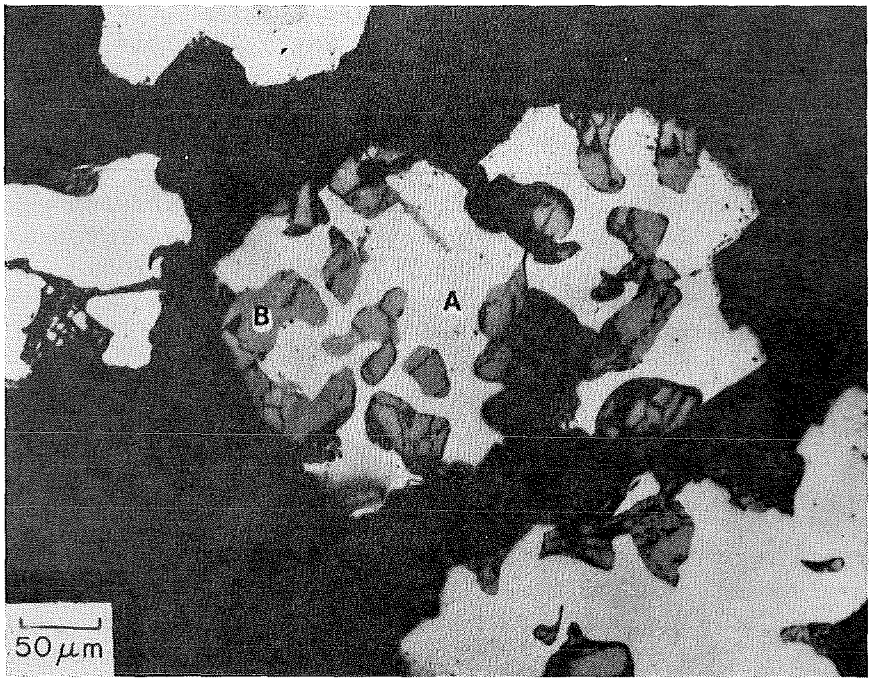


FIGURE 19. - Microstructure of metallic-phase particle from plus 212-μm screen fraction showing locked sulfide particles. *A*, Nickel sulfide; *B*, chromium sulfide.

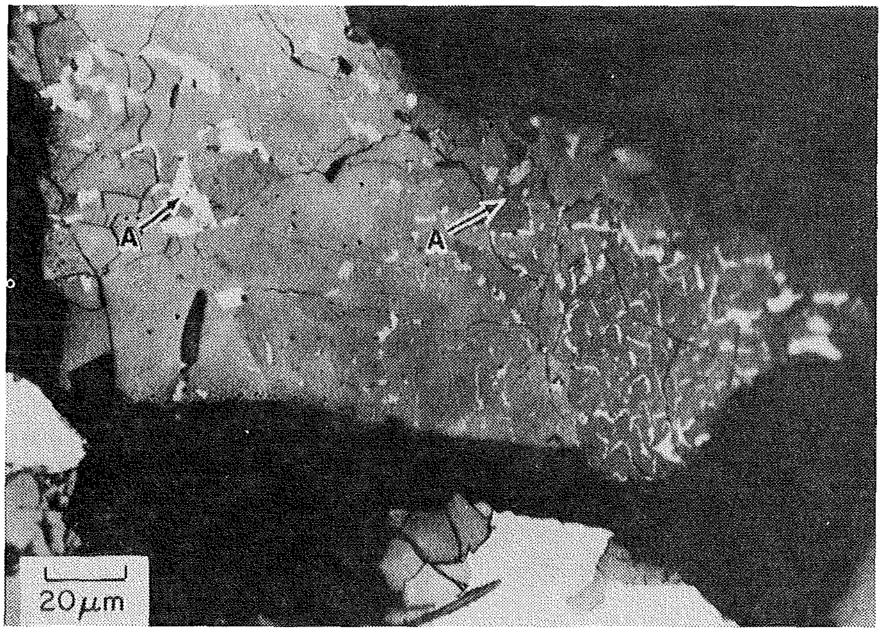


FIGURE 20. - Microstructure of nickel sulfide particle from plus 106-μm screen fraction showing fine precipitate of metallic phase (*A*).

Mineralogical Studies

During the program, several mineralogical studies were made of the ground matte using optical microscopy and electron beam microprobe analysis. These studies showed that phase liberation was not as good as had been expected on the basis of the original matte grain size and shape. Figure 19 shows a representative metallic phase grain from the plus 212 micrometer screen fraction. The grain contains numerous locked sulfide particles. These particles could not be liberated through additional grinding without creating an excess of sulfide phase fines. It was also noticed that extended grinding resulted in deformation of the ductile metallic phase to the extent that some sulfides were actually enveloped by the metallic phase.

Figure 20 shows a small liberated nickel sulfide particle which contains a significant amount of metallic phase. This precipitate probably results from solid state rejection of nickel from solution during cooling, as would be expected from the nickel-sulfur phase diagram (fig. 10). The magnetic nickel phase would be weakly attracted by a magnetic field, thus reducing the efficiency of the magnetic separation step.

Discussion

It is evident from the preceding sections that the mineral separation section of the flowsheet is not as efficient as anticipated. Two major contributing factors were (1) relatively poor liberation of primary sulfide particles from the metallic phase during grinding and (2) solid state precipitation of metallic phase particles within the nickel sulfide grains. Both of these problems would be alleviated but not necessarily eliminated by the slower cooling rate that would be achieved with large ingots in a commercial-scale plant.

Problems were also encountered in the flotation separation that are unrelated to prior processing history. Because of their extreme brittleness, the sulfides are prone to formation of fines during grinding. In the case of nickel sulfide, the fines are difficult to float without the use of activators. Unfortunately, chromium sulfide, perhaps because of its dissolved nickel, was also activated by copper sulfate. Consequently nickel-chromium separation was not as good as desired. It should be pointed out, however, that there is no body of experience to draw on for flotation of chromium sulfide. It is possible that further experimental work may define reagents and processing systems that will permit a closer approach to the theoretical maximum nickel-chromium separation efficiency of 0.9.

It was noted in an earlier section that phases containing the heavy metals may also be present in the matte. The phase occurring in the greatest quantity was a molybdenum-tungsten sulfide. The amount of this phase increases with the sulfur content of the matte. In the magnetic separation circuit discussed above, Mo_2S reports to the nonmagnetic sulfide fraction; limited testing using KAX as collector showed that Mo_2S floats more rapidly than Ni_3S_2 and consequently is almost entirely contained in the nickel concentrate. This distribution is desirable from the standpoint of maximum recovery of molybdenum in the leaching circuit as discussed below.

The best chromium concentrate produced in the laboratory work contained approximately equal amounts of nickel and chromium sulfides. If further test work does not significantly improve the flotation separation efficiency, alternative means for further concentrating the chromium sulfide must be used. One method is to use a partial leach to selectively dissolve nickel sulfide. This procedure is discussed in the leaching section of this report.

Fluidized-Bed Roasting of Chromium Sulfide[10]

The chromium concentrate produced either directly as flotation tails or indirectly as a leach residue is composed primarily of chromium sulfide with chromium comprising about 80 percent of the metal content. Nickel and molybdenum sulfides would be present in the flotation tails along with heavy metal oxides. The leach residue would also contain a substantial quantity of elemental sulfur which would be removed in a commercial operation by flotation.

The next step in the production of metallic chromium is removal of combined sulfur by roasting in a highly oxidizing environment. Fluidized-bed roasting was selected for this operation because it provides excellent contact between the product and the reacting gas and hence good operating efficiency. The process is applied on a commercial scale to the roasting of nickel sulfides; hence experience with this system may be applicable to the present problem.

Chemical Reactions

The reactions that would be expected in a reactor treating a slurried feed of chromium sulfide are listed in table 12. The heat of reaction of the Cr_2S_3 phase has apparently never been determined. Consequently this quantity was estimated from information available on related chromium sulfide compounds (9, 18, 24). For roasting a pure chromium sulfide the overall reaction is clearly exothermic. The actual chromium sulfide phase in the concentrate has Ni and small quantities of Co, Fe, and Mo atoms substituted for Cr atoms. The basic oxidation reaction does not change, but the heat evolved in the reaction is approximately 10 percent lower than that of the pure chromium sulfide.

TABLE 12. - Chemical reactions in roasting of chromium sulfide

Reaction	$\Delta H_{298^\circ K}$, cal/mole
(1) $Cr_2S_3 = 2Cr + 3S$............	[1]110,000
(2) $2Cr + 3/_2O_2 = Cr_2O_3$.........	[2]-270,000
(3) $S + O_2 = SO_2$................	[2]-71,000
$\Delta H_4 = \Delta H_1 + \Delta H_2 + 3\Delta H_3$ (4) $Cr_2S_3 + 9/2O_2 = Cr_2O_3 + 3SO_2$	-373,000

[1] Estimated from data on CrS (9), Cr_3S_4 (24), and recommended estimating techniques (18).

[2] Reference 18.

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[10] The work on roasting and reduction to chromium metal was planned and conducted by F. J. Hennion, research engineer, Resource Recovery, Inco Research and Development Center, Suffern, N.Y.

The heat balance for a fluidized-bed roaster using this feed can be estimated provided certain assumptions are made. The heat balance shown in table 13 was derived using the assumptions listed in the table. The heat losses are obviously a function of the size and efficiency of the roaster and may be as low as 1 percent of the heat of reaction in a large commercial-scale roaster (4). Based on experience in operating this type of system, a roaster handling more than a few kilograms per hour should be self-sustaining. The analysis presented in table 13 assumes an oxidation efficiency of 90 percent. If this estimate is correct, the exit gas will contain approximately 11 mole-percent SO_2 which must be removed by wet scrubbing before venting to the atmosphere.

TABLE 13. - Heat balance for fluidized-bed roasting of chromium concentrate

Reaction	ΔH, cal
HEAT INPUT	
(1) Heat of reaction....................	-185,640
HEAT OUTPUT	
(2) Sensible heat, solids...............	15,112
(3) Sensible heat, gas..................	107,328
$\Delta H_4 = \Delta H_1 + \Delta H_2 + 3\Delta H_3$	
(4) Net.................................	-63,200

Assumptions:

1. Analysis is based on 100 g of feed (dry basis).
2. Feed is a slurry of chromium sulfide (M_2S_3) containing 15 wt-pct water.
3. M represents a metal atom with a ratio 4Cr:1Ni.
4. ΔH for M_2S_3 and M_2O_3 are 10 pct lower than the ΔH for the pure chromium compounds.
5. Feed enters the reactor at 20° C and exits at 1,073° C.
6. Gas enters the reactor at 20° C and exits at 1,073° C.
7. The oxidizing gas is air, and the oxidizing efficiency is 90 pct.
8. Exit gas composition is mole-pct: N_2-78, SO_2-13, H_2O-13, H_2O-7, O_2-2.
9. Heat capacity of gas mixture calculated from data in reference 18 as 8.2 cal/deg-mole.
10. Heat capacity of solids calculated from data in reference 18 as 27.6 cal/deg-mole.

Experimental Procedure

Although the roasting process should be thermally autogenous on a pilot- or commercial-scale reactor, this is not the case for a reactor suitable for handling the small quantities of material available in the laboratory program. Consequently, reactor design and experimental objectives had to take this limitation into account.

Reactor Design

The configuration of the apparatus used for fluidized-bed roasting evolved over the period of the testing program, as operating problems were identified. Only the final, most efficient design will be discussed. The schematic diagram of the apparatus is shown in figure 21. External heating was provided by a gas torch in the annular heating chamber. The reactor was fed by a motor-driven screw feeder which introduced a slurry of ground matte or flotation concentrate containing 5 to 10 percent water. The feed rate was approximately 20 grams per minute. Cold reaction gas was fed at a rate of 150 cubic feet per minute into the bottom of the reactor through a ceramic honeycomb. The fluidizing gas was oxygen-enriched air. The bed height was approximately 12 inches with a product discharge into an open container. The gaseous products were passed through a cyclone to remove dust and then vented to the foundry offgas treatment system.

Raw Materials

Considerable difficulty was experienced in obtaining a feed for the roaster which was truly representative of that expected for the unified flowsheet. This was largely the result of the difficulty in separating nickel sulfide fines in froth flotation as discussed earlier. A portion of the feed was minus 200-mesh blended product of a number of flotation tests containing approximately 35 percent Ni, 20 percent Cr, and 35 percent S. A few tests were also conducted using high-sulfur matte ground to minus 40 mesh and concentrated by magnetic separation. This material contained 45 percent Ni, 15 percent Cr, and 33 percent S.

Results

Because of the small size of the reactor, it was difficult to operate in a continuous mode. Use of the screw feeder greatly improved particle circulation within the reactor; however, it was not possible to fully eliminate channeling. As a consequence, the sulfur content of the bed was inhomogeneous during the initial stages of a run. This inhomogeneity precluded accurate sampling to develop information on kinetics of desulfurization. Consequently, the variables discussed in the subsequent sections were evaluated on the basis of the final bed composition.

Effect of Water Content

It was found that a reaction temperature of 1,800° to 2,200° F was needed to achieve desulfurization. This temperature is higher than the melting point of the sulfide; consequently rapid fusion of the charge occurred when dry concentrate was fed into the reactor. This problem was solved by blending the feed with 5 to 10 percent water. The actual mechanism by which water solves this problem is not known, but it is presumed that water promotes more rapid surface oxidation, which in turn prevents formation of agglomerated particles too large to fluidize.

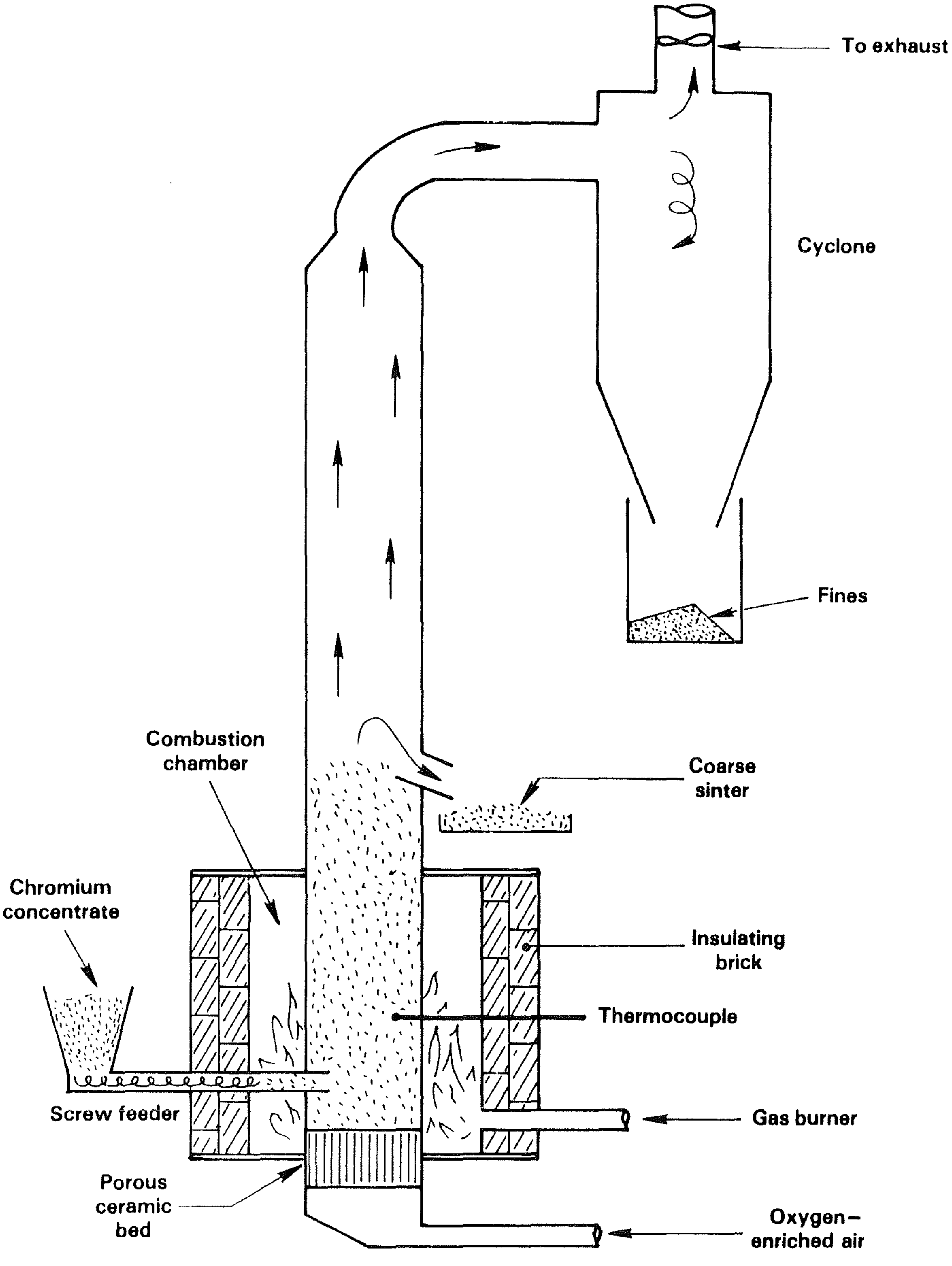

FIGURE 21. - Schematic diagram of fluidized-bed reactor.

Effect of Initial Particle Size

Limited testing showed that feed particle size was very important. The minus 325-mesh flotation concentrate was desulfurized within 15 minutes at 2,000° F, while minus 40-mesh ground matte required 4 hours. The feed for a commercial plant would, of course, resemble the flotation concentrate.

Minimum Final Sulfur Content

Although rapid desulfurization to 2 percent sulfur could be achieved, further reduction as required for a product for the superalloy industry took considerably longer owing to instability of the system. The lowest sulfur level achieved by direct roasting was 0.23 percent. When this material was water-agglomerated and reroasted, a product containing 0.022 percent sulfur and 21 percent oxygen was obtained.

Discussion

The roasting studies described above demonstrated the feasibility of achieving low sulfur levels in a chromium flotation concentrate despite the difficulties associated with operating the small system. With a more stable bed, it should be possible to achieve the 0.005-percent sulfur levels desired for the product. The chilling effect of the inlet gas contributed to the excessive roasting times experienced in the laboratory experiments. A gas preheating system (designed to utilize the sensible heat of the exhaust gas) would be desirable to improve the efficiency of the reaction system. Although other roasting methods could be applied, based on past experience in roasting nickel sulfides it appears that the fluidized-bed system would be the most efficient and provide the most desirable product for aluminothermic reduction.

Aluminothermic Reduction to Chromium Metal

Two methods are used commercially to produce pure chromium metal: Aluminothermic reduction and electrowinning. Both processes are capable of generating a product of purity sufficient for use in the superalloy industry. The reason for selecting the former process is that the fluidized-bed roaster product contains nickel and possibly some heavy metals along with chromium. Production of chromium by electrowinning requires an electrolyte of relatively high purity, and hence a complex hydrometallurgical purification circuit would be needed. However, aluminothermic reduction can be used directly on a mixed metal feed. Since a chromium product destined for use in superalloys could tolerate a significant quantity of nickel, aluminothermic reduction was a logical choice. The basic reduction process is well known; however, it has not generally been applied to a derivative of a sulfide intermediate. Consequently, efficiency of desulfurization was a factor in the experimental demonstration as well as overall chromium recovery.

Chemical Reactions

Aluminothermic reduction depends upon the heat of reaction of the products being greater than the heat of reaction of the reactants. These reactions must be highly exothermic so that the reaction products are not only molten but sufficiently fluid to facilitate separation of metal and slag. The reactions for this system are listed in table 14.

TABLE 14. - Chemical reactions in aluminothermic reduction of chromium oxide (18)

Reaction	$\Delta H_{298^\circ K}$, cal/mole
(1) $Cr_2O_3 = 2Cr + 3/2O_2$.........	270,000
(2) $2Al + 3/2O_2 = Al_2O_3$.........	-400,000
$\Delta H_3 = \Delta H_1 + \Delta H_2$......	
(4) $Cr_2O_3 + 2Al = Al_2O_3 + 2Cr$...	-130,000

The charge for a metallothermic reduction system is generally cold. Since fluxes are also added to promote a fluid slag, the reaction mmust be sufficiently exothermic to melt the entire charge. A heat balance for a hypothetical reaction is shown in table 15, along with the assumptions used. The heat evolved is sufficient for melting the reaction products from a chromium concentrate charge having a 4Cr:1Ni ratio. Although there is a surge of dust during the brief reaction period, there are no gas-producing reactions; thus only dust removal is required for treating the exhaust gas from this type of reactor.

Experimental Procedure

Metallothermic reductions are conducted on a batch basis. As noted above the process can be carried out on rather small charges provided the reaction is sufficiently exothermic. Consequently, most of the problems of scale encountered with fluidized-bed roasting did not apply to the reduction tests.

Raw Materials

The feed for these tests consisted of roasted chromium concentrate or pure metal oxides blended to provide a composition similar to that expected for an integrated flowsheet. This material was mixed with aluminum powder (reductant) and lime and fluorspar (fluxes).

Testing Procedure

The reaction vessel consisted of a clay-graphite crucible backed with foundry sand and contained in a steel shell. The oxide charge weight ranged from 0.52 to 1.0 kilograms. The quantities of aluminum reductant and flux were also varied. Emphasis was placed on defining a reductant and flux combination that would provide maximum chromium recovery in the metal and maximum sulfur recovery in the slag. The procedure, which was used for all of the tests, was to preheat the crucible with a gas torch to about 1,200° F. A plastic bag containing the charge was dropped into the crucible and ignited with the torch. The metal and slag were allowed to solidify in the reaction vessel.

TABLE 15. - Heat balance for aluminothermic reduction of roasted chromium concentrate[1]

Reaction	ΔH, cal
HEAT INPUT	
(1) Heat of reaction.....................	-106,760
(2) Heat of formation of $CaO.Al_2O_3$........	-2,516
HEAT OUTPUT	
(3) Heat of fusion, metal.................	6,120
(4) Sensible heat, metal..................	16,940
(5) Heat of fusion, slag..................	17,000
(5) Sensible heat, slag...................	49,408
$\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$	
(6) Net..................................	-19,808

Assumptions:

1. Analysis is based on 100 g of dry chromium concentrate.
2. Feed is roasted chromium concentrate (M_2O_3), lime (CaO), and metallic aluminum powder.
3. M represents a metal atom with a ratio of 4Cr:1Ni.
4. Slag is $CaO.Al_2O_3$.
5. ΔH for M_2O_3 is 10 pct lower than ΔH for Cr_2O_3.
6. ΔH for $CaO.Al_2O_3$ is -3,700 cal/mole (18).
7. Reactants are charged at 20° C.
8. Products reach a maximum temperature of 1,750° C at which point both metal and slag are fully molten.
9. Reduction is 100 pct efficient.
10. Heat of fusion of alloy estimated from reference 18 is 4,500 cal/mole.
11. Heat of fusion of slag estimated from data on related compounds from reference 18 is 25,000 cal/mole.
12. Specific heat of alloy calculated from data in reference 18 as 7.2 cal/deg-mole.
13. Specific heat of slag calculated from data in reference 18 as 42.0 cal/deg-mole.

Results

General Observations

Seven aluminothermic reduction tests were performed. In general the reactions were relatively mild and controlled, each lasting about 20 seconds. Complete melting and separation of the metal and slag were achieved in every case. The slag could be easily separated from the metal on removal from the crucible as there was no interpenetration during solidification. No crucible reaction were observed. The results of selected tests are shown in table 16. Based on these results, it appears that virtually all of the Cr, Ni, Co, Fe, and Mo contained in the charge report to the metal ingot. Columbium and tantalum, when present in the feed, were distributed in both metal and slag phases. Recovery of aluminum in the metal was very low.

TABLE 16. - Results of selected aluminothermic reduction tests[1]

Sample	Weight, grams	Composition, weight-percent											
		Ni	Cr	Co	Fe	Mo	Cb	Ta	Al	Ca	S	O	C
HEAT J: 540 GRAMS ROASTED CHROMIUM CONCENTRATE, 176 GRAMS ALUMINUM, 20 GRAMS SODIUM NITRATE, 48 GRAMS LIME, 32 GRAMS FLUORSPAR													
Feed..	540	42	18.9	2.9	3.6	1.8	0.9	0.3	NAp	NAp	0.49	(2)	NAp
Metal.	227	57.0	23.9	4.2	3.7	1.5	1.2	<.1	0.4	NAp	.46	0.10	0.11
Slag..	NA	.30	7.6	.01	.24	.2	2.0	1.8	26.0	9.5	.11	(2)	NAp
HEAT K: 528 GRAMS ROASTED MATTE, 169 GRAMS ALUMINUM, 20 GRAMS SODIUM NITRATE, 48 GRAMS LIME, 32 GRAMS FLUORSPAR													
Feed..	528	46	10.5	0.1	11.0	1.6	3.0	NAp	NAp	NAp	0.073	(2)	NAp
Metal.	240	67.7	14.1	.1	13.8	1.1	2.4	NAp	0.32	NAp	.068	0.022	0.14
Slag..	325	5.4	4.7	.1	1.0	.5	3.7	NAp	29.5	7.6	.02	(2)	NAp
HEAT L: 1,000 GRAMS SYNTHETIC CONCENTRATE, 370 GRAMS ALUMINUM, 250 GRAMS FLUORSPAR													
Feed..	1,000	18.4	39	NAp	4.8	6.1	NAp	4.1	NAp	NAp	0.15	(2)	NAp
Metal.	625	26.2	52.4	NAp	7.5	8.5	NAp	2.0	0.07	NAp	.033	NAp	0.4
Slag..	975	.68	1.5	NAp	.12	.69	NAp	1.7	23.8	13.8	.15	(2)	NAp

NA Not available.
NAp Not applicable.

[1] Sum of analyses may not equal 100 pct because of lack of appropriate analytical standards. Spectrographic survey analysis indicated that the discrepancy was not due to presence of elements not reported in this table.

[2] Balance of composition is oxygen.

Desulfurization

The sulfur content of the metal ingot should be less than 0.010 percent, and preferably less than 0.005 percent, if it is to be acceptable for use in superalloys. The partitioning of sulfur during an aluminothermic reaction depends largely on the character of the slag formed from the reaction products. An acid slag will not hold much sulfur and, as a result, the sulfur content of the metal product will be about the same as that of the charge, as illustrated by heats J and K in table 16. The basicity of the slag can be increased by using lime, magnesia, fluorspar, or other additives. The effectiveness of this approach is shown by the results of heat L, in which the sulfur content was lowered from 0.15 percent to 0.033 percent. Although the target sulfur level of 0.005 percent was not achieved, the initial sulfur level in the charge was quite high. A roaster product having a sulfur level of 0.02 percent, which was achieved in previous trials, should provide a final product with the desired sulfur content.

Material Balance

A material balance was prepared for heat L. The information is shown in table 17. For this test only 20 grams, or 1 percent of the charge weight, could not be accounted for. It is assumed that this material was lost as dust. The individual element recoveries do not agree quite so well, primarily because of the slag analyses, which appear low. The metal recoveries in this test were Cr--85 percent, Ni--90 percent, Fe--98 percent, Mo--90 percent, and

Ta--32 percent. Distribution of sulfur was 13 percent in the metal and 87 percent in the slag.

TABLE 17. - Material balance for heat L[1]

Material	Calculated weight of contained elements, grams											Measured weight, grams[2]
	Ni	Cr	Fe	Mo	Ta	Al	Ca	S	O	F	C	
					REACTANTS							
Sintered chromium concentrate......	184	390	48	61	41	NAp	NAp	1.5	27.5	NAp	NAp	1,000
Aluminum..........	NAp	NAp	NAp	NAp	NAp	370	NAp	NAp	NAp	NAp	NAp	370
Flux..............	NAp	NAp	NAp	NAp	NAp	NAp	169	NAp	NAp	81	NAp	250
					PRODUCTS							
Chromium alloy....	163	328	46	53	13	0.4	NAp	0.2	NAp	NAp	2.5	625
Slag..............	7	15	1	7	17	232	135	1.4	[e]500	[e]60	NAp	975

[e] Estimated.

NAp Not applicable.

[1] Composition listed in table 16.

[2] Sum of calculated weights may not equal measured weight because of analytical difficulties indicated in footnote 1 of table 16 and owing to rounding of numerical data.

Discussion

The restricted testing program that was possible with the limited amount of feedstock available demonstrated that the aluminothermic reduction operation was feasible and appropriate for producing a useful melting ingot. Further optimization of the operation in process scale-up would provide higher recovery of the metals in the ingot through more efficient utilization of heat and slower freezing. Efficiency of desulfurization would also be improved.

As noted above, recovery of columbium and particularly tantalum in the ingot was poor. Since the concentration of these elements is likely to vary considerably in the initial feedstock, it is difficult to predict typical levels in aluminothermic reduction slags. However, it is assumed that when the tantalum content of the slag is sufficiently high, recovery through additional slag treatment would be possible. Investigation of tantalum recovery from slag was considered to be beyond the scope of this ivestigation.

Leaching[11]

This portion of the flowsheet involves leaching of the nickel-rich metallic concentrate from magnetic separation and the nickel-sulfide flotation product. The basic chlorine leach system has been used for leaching nickel mattes (13) and metallic superalloy scrap (5). This system was adopted for its rapid leaching kinetics and selectivity and the compatibility of chloride

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[11] The experimental work was planned and conducted by J. A. Thomas, Group Leader, Hydrometallurgy, J. Roy Gordon Research Laboratory, Mississauga, Ontario, Canada.

solutions with cobalt solvent extraction systems. The leaching circuit also involves separation of the raffinate from the leach residue, hydrolysis to remove Fe, Mo, and Cr, and filtering of the residue. The resulting purified nickel-cobalt liquor proceeds to solvent extraction.

Raw Materials

A variety of materials were used in the leaching studies. Most of the batch tests and all of the continuous leaching tests were performed on material obtained from the 40-kilogram heats made from superalloy scrap. The actual samples used for leaching were a composite of the cleaner magnetics fraction produced in the separation testwork. The head feed analysis reported below for the leaching studies represents the blended fractions and thus does not correspond to the composition of the product of optimum test conditions.

A limited number of batch leaching tests were performed on other feed material. These included a sample of cleaner magnetics containing tungsten, various samples of ground, unseparated matte, and a sample of chromium concentrate.

Batch Leaching Tests

The initial testwork was carried out on direct leaching of magnetic concentrate in 1-liter batches. The analysis of a typical sample head feed is shown in table 18. The test program was performed in baffled beakers with vigorous agitation. The first few tests were performed at 80° to 95° C with chlorine as the oxidant and various mixtures of HCl, water, and nickel chloride as the lixivant. The results showed that the leaching rate was very slow; leaching times of 10 hours were required for 98-percent extraction of nickel.

TABLE 18. - Batch leaching of magnetic fraction

Test	Ni	Co	Fe	Cr	Mo	S
Head feed................weight-percent..	62.4	8.2	4.3	5.3	2.2	16.8
Extraction 1[1].....percent of feed weight..	98.7	94.2	95.2	62.6	80.7	64.0
Extraction 2[2]..............do............	98.9	94.1	96.3	16.8	68.6	19.0
Extraction 3[3]..............do............	99.7	98.8	99.2	3.0	84.0	10.7

[1] 10-hr leach, chlorine + HCl, 60 g/l Ni.

[2] 1-hr leach, chlorine + HCl wigh Cu^{+2}, 80 g/l Ni, 60 g/l Cu, final redox potential >+900 mV.

[3] 1-hr leach, chlorine + HCl with Cu^{+2}, 80 g/l Ni, 60 g/l Cu, redox potential controlled to +560 mV.

Effect of Copper Activation

Based on prior experience in chlorine leaching of nickel mattes (14), the effect of copper was investigated as a means of increasing the leaching rate. Copper was added as cupric chloride to make a synthetic spent electrolyte solution containing 80 grams per liter of nickel and 60 grams per liter of copper. Copper is believed to act as a chlorine carrier through the operation of the cuprous-cupric ion couple. The effects of copper on leaching of superalloy-derived matte were dramatic: the leaching rate was increased by an order of magnitude. In addition, it was observed that oxidation of sulfur to sulfate and leaching of chromium were significantly reduced and chlorine efficiency was improved. This is desirable, as sulfate must ultimately be removed from the system, while the dissolved chromium makes subsequent purification by hydrolysis more difficult. The effect of the copper addition is illustrated in table 18.

Effect of Redox Potential Control

It was observed that, as chlorine was added during the leach and the redox potential rose, chromium extraction and sulfur oxidation both increased. Additional tests showed that, if the leach was stopped at a potential of about +550 millivolts (platinum versus standard calomel electrode), almost complete extraction of nickel and cobalt were achieved with very little extraction of chromium. The results of a 1-hour batch leach with redox potential of +560 millivolts are shown in table 18. This observation of selective leaching of nickel and chromium sulfides has a number of implications for the overall recovery process, which are discussed in the discussion section for the leaching experiments.

Copper Removal

When copper is used for leaching, a means for copper removal and recycling must be provided. One method that was tried was direct cementation using the raw magnetics concentrate. This approach was not successful, and very little copper was precipitated. Previous experience has shown that cementation can be improved through the use of elemental sulfur, which promotes precipitation of copper sulfide as discrete particles rather than metallic copper films which coat the matte particles and impede the reaction. The addition of sulfur in the atomic ratio of four sulfur to one copper was examined in a batch test. In this test a solution containing 148 grams per liter of nickel and 4.8 grams per liter of copper was contacted with 180 grams per liter of magnetics feed and 1.9 grams per liter of elemental sulfur. After 30 minutes the solution contained 158 grams per liter of nickel and only 0.12 gram per liter of copper.

Countercurrent Leaching System

Based on the results of the preceding tests, a countercurrent leaching scheme was proposed to facilitate recirculation of copper within the leaching system. This scheme is illustrated in figure 22. In this system, the feed is initially contacted with the filtrate solution containing copper. Partial leaching is accompanied by copper cementation. The slurry is then pumped to a thickener, the overflow of which constitutes the pregnant liquor for nickel and cobalt recovery. The underflow, about 90 percent of the original leach feed, goes to the completion leach. In this step spent electrolyte returning from electrowinning is used with chlorine under controlled redox potential to extract as much nickel and cobalt as possible without leaching chromium. The copper sulfide dissolves during this step. The effluent is filtered to remove the residue, mainly sulfur and chromium sulfide, and returned to the cementation leach.

The proposed system was tested using a batch simulation which showed that it was workable. The system was then adopted for the scale-up of continuous leaching.

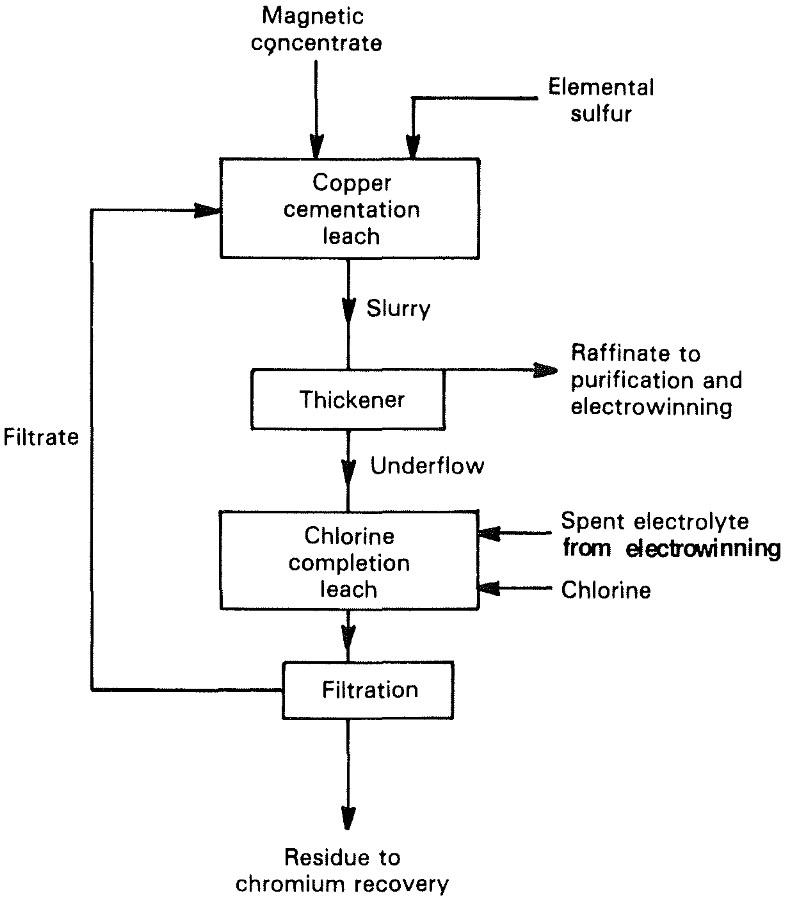

FIGURE 22. - Countercurrent leach flowsheet.

Raffinate Purification

As shown in table 18, the chlorine leach also extracts Fe and Mo, along with Ni, Co, and a small amount of Cr. The separation of nickel and cobalt cannot be performed until other elements are removed from solution. This can be accomplished by pH adjustment which precipitates Fe, Mo, and Cr as hydroxides. Nickel carbonate was a logical choice because contamination of the system was thereby avoided. The effectiveness of the hydrolysis procedure is demonstrated by the results shown in figure 23. The precipitate formed during hydrolysis was somewhat difficult to filter. Tests showed that, when high chromium extractions were acheived, the nickel losses to the filter cake became excessive. In the test cited above, the precipitate contained 17 percent Fe, 13 percent Cr, 10 percent Mo, and 10 percent Ni. About half of the latter was recovered by washing, giving a total nickel and cobalt recovery in this operation of 97.5 percent.

Continuous Leaching Tests

An apparatus was set up to conduct countercurrent leaching and hydrolysis on a continuous basis. A schematic diagram of this system is shown in figure 24. The vessels, which had a 1.5-liter operating volume, were maintained at 80° C using titanium steam coils. Titanium agitators and baffles were employed. Chlorine was added to the leach tanks under redox control with solenoid-actuated valves made of Teflon[12] controlling the chlorine flow.

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[12] Reference to specific brands is made for identification only and does not imply endorsement by the U.S. Bureau of Mines or by The International Nickel Co., its affiliates, or its subsidiaries.

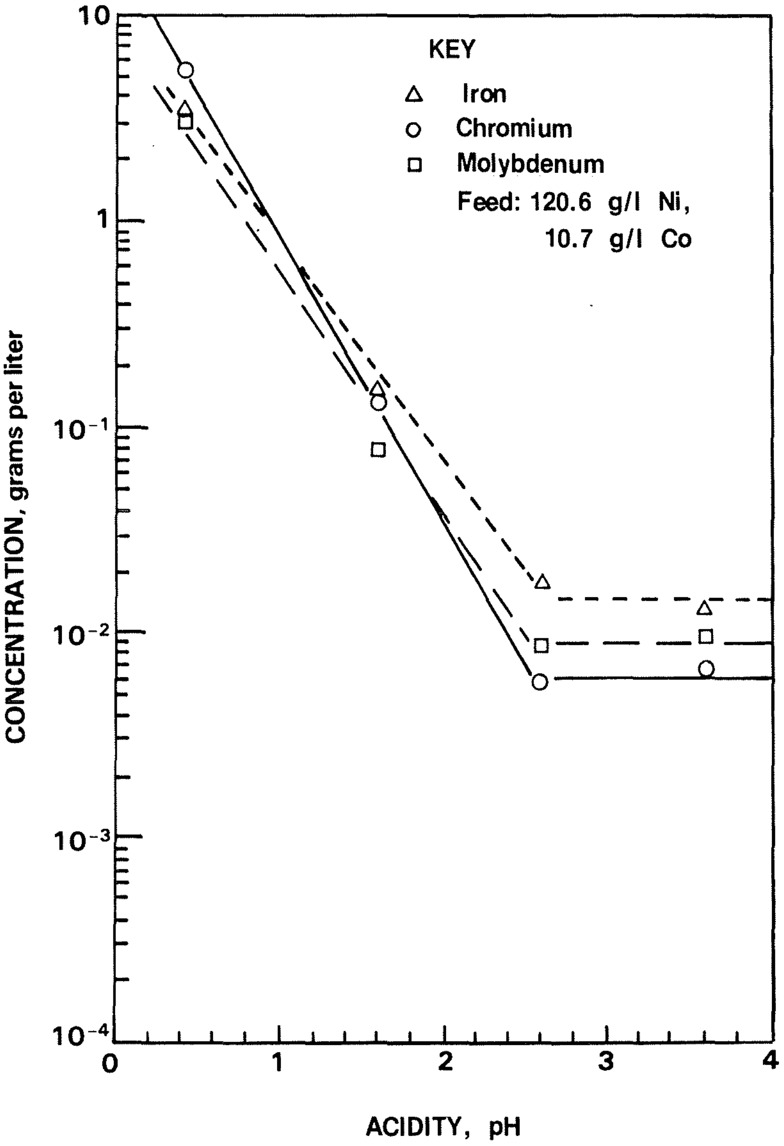

FIGURE 23. - Hydrolysis-effect of pH on concentration of Cr, Mo, and Fe.

The first leaching vessel was controlled at +400 millivolts and the second at +550 millivolts. A glass separatory funnel was used as a thickener.

Results of First Continuous Test

The results of the first eight-hour test are contained in table 19. Operating problems were encountered during the test; however, acceptable nickel and cobalt extractions were obtained (97.5 and 94.9 percent, respectively). Copper cementation was irregular owing to variable flow rates, and a buildup of particles in the cementation leach vessels made it difficult to maintain the desired copper level in the completion leach vessels. One encouraging sign was that chromium extraction and sulfate formation were both low, indicating the effectiveness of redox potential control. The hydrolysis system worked quite well with very low and stable levels of Fe, Cr, and Mo in the filtrate. The hydrolysis slurry was filtered at a rate of 1,500 liters per square meter per hour. Washing effectively removed the entrained nickel and cobalt. Under stable operating conditions at the end of the test, the nickel and cobalt losses to the filter cake were 0.3 and 2.1 percent, respectively.

TABLE 19. - Continuous leaching of magnetic fraction

	Ni	Co	Cu	Fe	Cr	S	Mo	W	Cb	Ta
EXTRACTION IN LEACH, PERCENT										
2.25 hours.....	76.1	84	NAp	93.8	8.2	NAp	NAp	NAp	NAp	NAp
3.15 hours.....	69.8	88.7	NAp	96.2	16.7	NAp	NAp	NAp	NAp	NAp
6.05 hours.....	91.0	88.8	NAp	95.0	5.1	NAp	NAp	NAp	NAp	NAp
7.0 hours......	95.7	94.9	NAp	97.7	8.6	NAp	94	<23	<7	<28
COMPOSITION OF LEACH LIQUOR, THICKENER OVERFLOW, GRAMS PER LITER										
2.25 hours.....	117	1.8	0.02	3.3	0.05	NAp	NAp	NAp	NAp	NAp
3.15 hours.....	120	2.0	.008	4.1	.13	[1]1.9	NAp	NAp	NAp	NAp
6.05 hours.....	139	2.7	.49	5.3	.007	[1]1.6	NAp	NAp	NAp	NAp
7.0 hours......	186	6.2	.18	10.3	.19	[1]1.7	1.0	<0.01	<0.02	<0.02
COMPOSITION OF LEACH LIQUOR AFTER HYDROLYSIS,[2] GRAMS PER LITER										
2.25 hours.....	117	1.8	0.02	0.001	>0.001	NAp	NAp	NAp	NAp	NAp
3.15 hours.....	120	2.0	.008	.4	.001	[1]1.9	NAp	NAp	NAp	NAp
6.05 hours.....	139	2.6	.49	>.001	.004	[1]1.6	NAp	NAp	NAp	NAp
7.0 hours......	185	6.1	.18	.001	.002	[1]1.7	0.002	<0.01	<0.02	<0.02
COMPOSITION, WEIGHT-PERCENT										
Feed...........	72.6	4.0	0.09	6.3	2.4	9.4	1.48	<0.03	0.22	0.05
Leach residue..	19.6	1.8	2.3	1.5	10.8	58.6	2.0	NAp	NAp	NAp
Hydrolysis cake..........	4.5	2.1	.7	42.1	1.5	NAp	3.6	NAp	NAp	NAp

NAp Not applicable.

[1] SO_4.

[2] After start of test.

The distribution of the heavy metals Mo, W, Cb, and Ta was assessed at the end of the run. The results indicate that the latter three elements were not dissolved in the chlorine leach and reported to the leach residue. Very high extraction of molybdenum was achieved, along with virtually complete precipitation during hydrolysis. Consequently, most of the molybdenum in the feed was captured in the hydrolysis filter cake.

Results of Second Continuous Test

Because of the difficult in pumping the coarse feed particles through the system, the feed for the second test was screened to minus 85 mesh. Although solids buildup was eliminated, uneven flow produced a large variation in the copper concentration of the final leach liquor (from 0.1 to 1.0 gram per liter). Subsequent batch tests showed that copper levels of <10 milligrams per liter could be achieved and thus should be realized in large-scale operation where the flow can be more readily controlled.

Cleaner Leach of Chromium Concentrate

Examination of the primary leach residue showed it to consist of a mixture of chromium and heavy metal sulfides and elemental sulfur. This indicated that under redox control, chromium sulfide was practically unleached. Physical separation of matte produced and chromium concentrate which contained a significant amount of unfloated nickel sulfide, along with nickel dissolved

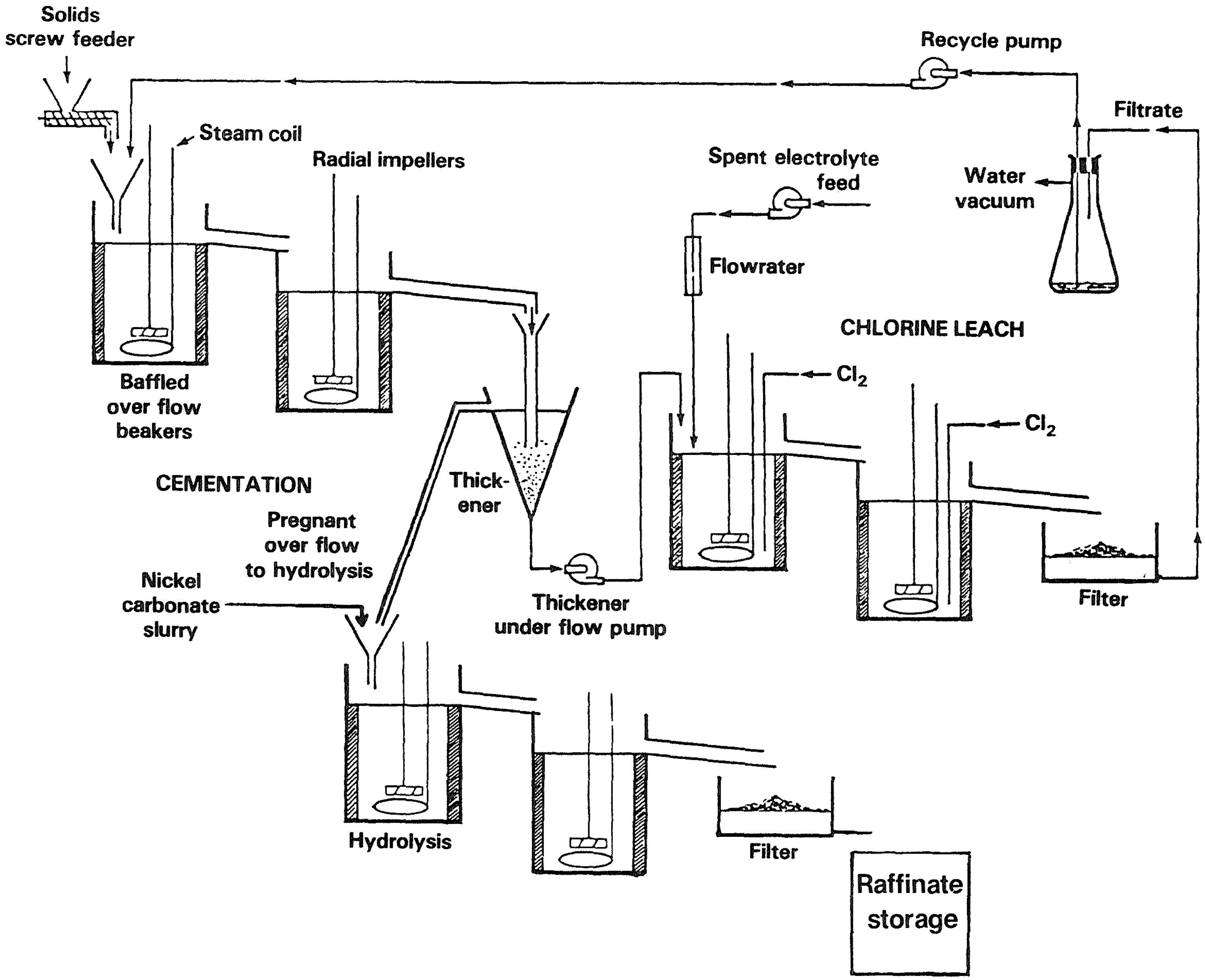

FIGURE 24. - Schematic diagram of equipment used for continuous leach tests.

in chromium sulfide. In an effort to further concentrate chromium, a sample of flotation tails was given a chlorine leach at a controlled redox potential of +550 millivolts in the presence of copper. In this small batch test, the concentrate was upgraded from a chromium-nickel ratio of 0.48:1 to 1.08:1. Chromium extraction was 9.3 percent (results listed in table 20). The test conditions were not optimized for this feed; however, the results indicates that it is feasible to leach nickel sulfide from the concentrate. It is assumed that nickel dissolved in the chromium sulfide will not leach, and hence the theoretical best chromium-nickel ratio that can be achieved is 4:1.

TABLE 20. - Leaching of chromium sulfide concentrate[1]

	Ni	Cr	Co	Fe	Mo
Head feed[2]............weight-percent..	38.3	18.4	2.1	2.8	2.3
Extraction....percent of feed weight..	60	9.3	24.3	15.5	33
Residue...............weight-percent..	20.0	21.7	1.9	1.7	2.1

[1] 3-hr leach at 80° to 90° C; redox potential +550 mV.
[2] Minus 48 mesh.

Direct Leaching of Superalloy Matte

The results of the preceding test suggested that it might be possible to directly leach the superalloy matte, recover most of the nickel and cobalt, and reject chromium to the leach residue, where it could be recovered without going through the inefficient magnetic and flotation steps. To test this idea, several batch tests using a range of leaching conditions were conducted on samples of freshly ground matte. The results of the best test are shown in table 21. The separation of nickel and chromium was extremely good with the residue chromium-nickel ratio approaching the theoretical 4:1. Only limited experimental work was done on the direct leaching approach, since its feasibility was not realized until the very end of the testing program. However, on the basis of the results, it offers the possibility of greatly simplifying the metal recovery process.

TABLE 21. - Direct leaching of ground superalloy matte[1]

Fraction	Ni	Cr	Co	Fe	Mo
Head feed[2]........weight-percent..	58.1	8.0	3.1	5.2	1.7
Filtrate[3]........................	96.8	3.9	72.0	74.5	48.3
Residue...........weight-percent..	4.96	20.8	2.42	3.71	2.38

[1] 20 hr leach at 100° C; redox potential +400 mV.
[2] Minus 48 mesh.
[3] Percent recovery from head feed.

Discussion

The results of the leaching experiments clearly established the technical feasibility of this portion of the recovery flowsheet. The observation that a nickel-chromium separation could be made through controlling the leaching conditions was not anticipated at the outset of the program. Consequently, it was not possible to fully explore the implications of this separation within the time limitations. In view of the limited amount of data available on the direct matte leach procedure as well as flotation separation, both schemes require more study to determine the more acceptable approach.

It was not possible in the laboratory work to do more than a cursory evaluation of the effect of matte composition on leaching. A number of questions would have to be resolved at a pilot plant stage or in further laboratory studies. In particular, the effect of iron content should be examined in detail. As noted earlier, when the iron level in the feed reaches 20 percent, iron-chromium sulfides are formed. The behavior of this sulfide in the leach is unknown. Iron is also the major constituent in the hydrolysis filter cake, and difficulties in handling this cake and attendant nickel and cobalt losses would be expected to increase with increasing iron content. Copper is also a frequent constituent of nickel alloy scrap. A high copper level in the feed could cause an excessive buildup of copper within the leaching circuit. Finally, the leaching behavior of the many trace elements known to affect the properties of superalloys must ultimately be determined.

The character of the two filter residues is critical to the success of the leaching scheme. The leach residue contains essentially all of the chromium plus heavy metals and elemental sulfur. Filtering of this residue was relatively easy. In a commercial operation, the sulfur would be removed by flotation, dried, and recycled to the melting step. The remaining portion of the primary leach residue would be blended with the flotation tailings or the residue from a chromium concentrate cleaner leach to form the feed for fluidized-bed roasting and chromium recovery.

The residue from the hydrolysis operation presents more difficulty in filtering and must be carefully washed to avoid nickel and cobalt losses. The components of the residue are primarily iron and molybdenum hydroxides. The results of the laboratory work indicates that between 30 and 70 percent of the molybdenum present in the scrap feed will report to the residue. Factors that affect molybdenum recovery at this stage would include sulfur content of the matte and the initial molybdenum level. Because of its intrinsic value, it is important that the hydrolysis residue be treated for molybdenum recovery. Treatment to separate the metals from the cake could be done using established technology and hence was not investigated in the program.

Cobalt Extraction[13]

Following hydrolysis, the leach liquor contains only Ni, Co, and possibly small quantities of Cu and sulfate. Since the objective of the recovery process was to produce metal products that would be widely useful for superalloys, electrowinning from solution to pure metals was selected. Although a number of procedures for extracting cobalt from nickel solutions are known, solid-liquid ion exchange and liquid-liquid solvent extraction appeared most suitable for this application. The feed for the initial batch tests was

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[13] The experimental work on cobalt extraction and electrowinning was planned and directed by J. Babjak, Group Leader, Electrochemistry, Inco Metals Co., J. Roy Gordon Research Laboratory, Mississauga, Ontario, Canada.

synthetic, while in later tests purified raffinate from continuous leach experiments was employed.

Ion Exchange Tests

Cobalt loading isotherms were developed for three strong base and two weak base resins. Amberlite IRA-400 (quaternary ammonium-gel type resin) gave the best distribution ratio for a synthetic raffinate containing 189 grams per liter of nickel and 9.9 grams per liter of cobalt. This system was then tested in a fixed-bed column containing 1.21 liter of resin. Loading characteristics were excellent, and the cobalt concentration of the effluent averaged 5 milligrams per liter. Unfortunately, despite the good extraction, very poor cobalt-nickel separation was obtained during elution with 0.01-normal hydrochloric acid. The eluate contained 78 grams per liter of cobalt and 47 grams per liter of nickel. Because of this poor separation, additional eluate treatment would be required with this system.

Solvent Extraction

Efficient extraction of cobalt from a chloride solution using tertiary amine triisooctylamine was reported by Brooks (5). Although it was known that phase separation was somewhat difficult with this type of system, it was felt that better separation of nickel and cobalt could be obtained.

The initial tests were conducted using a synthetic raffinate containing 168 grams per liter of Ni, 10 grams per liter of Co, and 243 grams per liter of Cl^{-2}. The solution was contacted at various phase ratios with a mixture of 25 volume-percent Andogen 381 (triisooctylamine) hydrochloride in Solvesso 150 at 22° C. The cobalt-loading isotherm constructed from these tests is shown in figure 25. As can be seen, three theoretical stages are necessary to reduce the concentration of cobalt from 10 grams per liter in the aqueous solution to the desired level of 10 milligrams per liter.

The loaded organic was stripped with 0.01-normal hydrochloric acid at various phase ratios to generate the cobalt-stripping isotherm shown in figure 26. Three theoretical stages were needed to produce a strip liquor containing 60 grams per liter of cobalt and a stripped organic containing approximately 0.2 grams per liter of cobalt.

As noted previously, difficulty was expected in separating the aqueous and organic phases in a mixer-settler system. The reciprocating-plate column has been developed to improve phase separation. A 4-centimeter-diameter column, similar to that described by Dim (10), having adjacent plates moving 180° out of phase was used for subsequent continuous extraction tests. The loaded organic phase was stripped continuously with 0.01-normal hydrochloric acid in two mixer-settlers.

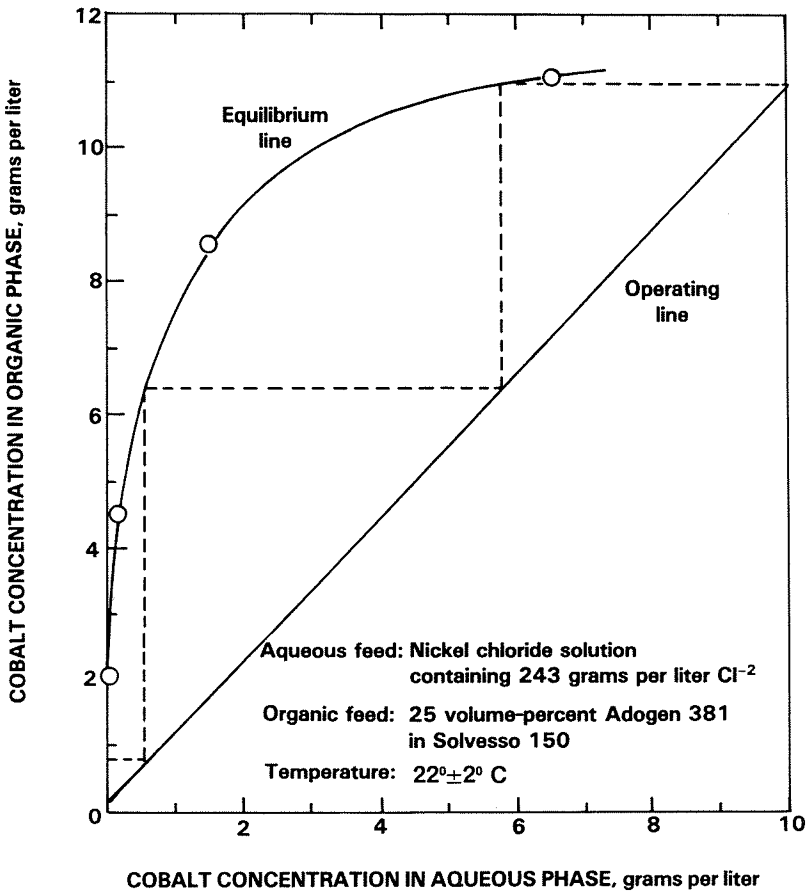


FIGURE 25. - Cobalt-loading isotherm.

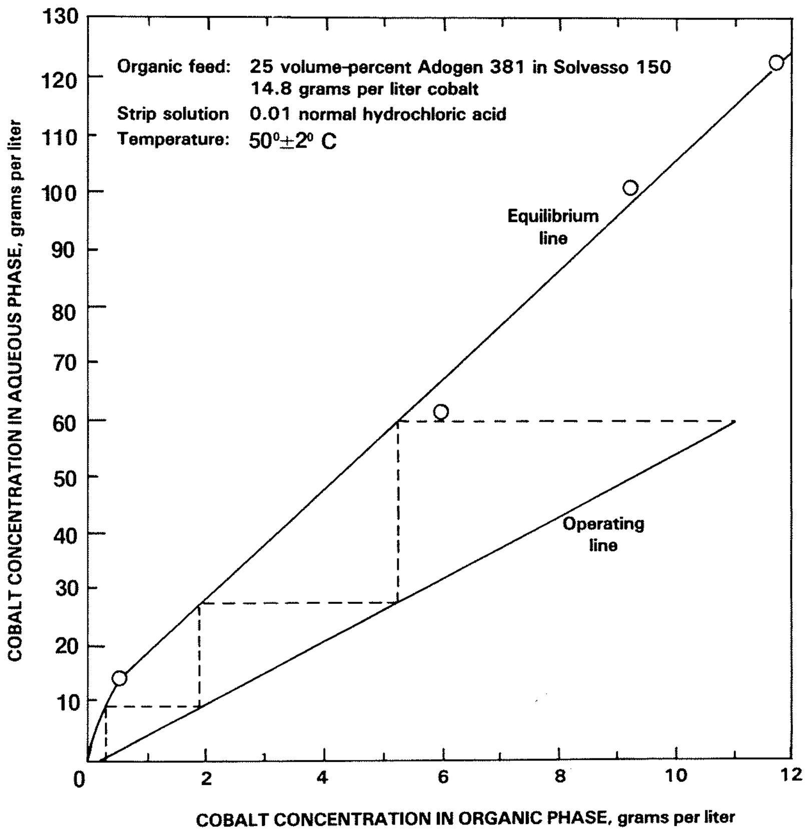


FIGURE 26. - Cobalt-stripping isotherm.

The results of these tests are contained in table 22. Entrainment of the aqueous phase in the loaded organic was very low in these tests, producing a composite strip liquor with a cobalt-nickel ratio of 650. Note that the operating efficiency of the column was better at the higher throughput because it facilitated operation under more favorable values of plate amplitude and frequency. Considerably higher throughput with no loss of efficiency would be produced in a circuit specifically designed for the job.

TABLE 22. - Extraction of cobalt in reciprocating plate column[1]

Fluid velocity, meters per hour		Cobalt, grams per liter				Plate frequency, cycles per second	Number of theoretical stages	HETS,[3] meter
Aqueous	Organic	Aqueous feed	Organic[2] feed	Loaded organic	Raffinate			
2.34	2.48	9.8	0.1	7.2	1.3	10.5	1	1
2.34	2.48	9.9	.1	7.1	1.0	11.7	1	1
2.34	2.48	10.0	.1	7.9	.85	10.8	1	1
4.30	4.77	9.7	.10	7.5	.30	11.7	1.4	.71
5.73	7.16	9.7	.14	7.2	.20	11.7	1.6	.63
10.7	10.7	9.7	.70	9.1	.30	13.3	1.8	.56

[1] Conditions:

Aqueous feed: Simulated superalloy scrap leach liquor containing ~10 g/ℓ Co, 186 g/ℓ Ni, and 270 g/ℓ total chloride.
Organic feed: 25 pct Andogen 381 hydrochloride in Solvesso 150.
Column: 0.04-m diam by 1-m plate section.
Amplitude of plates: 2 mm.
Temperature: 50° C.

[2] Stripped organic.

[3] Height equivalent of theoretical stage.

Discussion

The experimental program demonstrated the viability of a tertiary amine solvent extraction system using reciprocating plate column for extracting cobalt. The principal factors that affect this system are the efficiencies of the preceding raffinate purification steps, since iron and molybdenum are also extracted by the system chosen. The hydrolysis test results indicate that the levels of these elements should be low enough that major contamination of the cobalt circuit should not occur.

Copper is also extracted by the tertiary amine system, and some means of copper removal must be provided prior to electrowinning of cobalt. The raffinates from the continuous leaching tests contained an average 0.15 gram per liter of copper, but concentrations as high as 0.5 gram per liter were observed owing to flow surges and incomplete cementation. The copper content of the raffinate in a commercial facility should be more stable and average perhaps 0.1 grams per liter. This small quantity of copper could be extracted with one of several solid ion exchange resin systems. No experiments on copper removal were conducted in the present program because the technology was considered well developed.

Removal of sulfate in a continuous operation would be done prior to solvent extraction by adding barium carbonate in a settling tank. The resulting barium sulfate would be discarded. No experiments on sulfate removal were conducted.

Electrowinning

A number of methods can be used to produce nickel and cobalt metals from the purified chloride liquors. However, electrowinning seemed to be a logical choice, since it was most compatible with the leaching circuit; that is, spent electrolyte, cathode rinse water, and chlorine generated in the electrolytic cell can be fully recycled. Also, the metal product is quite suitable as a melt charge material for superalloy production.

Experimental Work

Very limited work was done on electrowinning because it involves well-known technology which is widely employed on a commercial basis. In the case of cobalt, the quantity of electrolyte derived from superalloy matte was so limited that a meaningful demonstration could not be conducted. Considerably more nickel electrolyte was produced during the preceding hydrometallurgical work; consequently, it was possible to conduct a nickel-electrowinning test. The principal objective was to determine whether any trace element impurities derived from the scrap feed would interfere with nickel deposition or contaminate the product.

A bench-scale test was conducted on electrolyte derived from previous studies. The composition of the feed is shown in table 23. Titanium inert anodes coated with a platinum-group metal oxide were used. Kenekaron anode bags were employed. Cathodes were AISI 316 stainless steel masked with epoxy to produce 1-inch-diameter round buttons. The circuit was operated for 103 hours at a current density of 250 amperes per square meter at 70° C. Current efficiency was calculated to be 93 percent.

TABLE 23. - Electrowinning of nickel

Sample	Ni	Co	Fe	Cu	Pb
Feed electrolyte..........grams per liter..	158	0.0006	0.002	0.002	NA
Spent electrolyte...............do.........	84	NA	NA	NA	NA
Nickel electrodeposit[1].....weight-percent..	([2])	0.024	0.003	0.003	0.0009

NA Not available.

[1] Less than 0.0003 pct each: Cd, Ba, As, B, Si, Al, Cr, W, Ag, Ta, Mo, Cb, V, Bi, Te, Mg, Sn, Sb, Mn, Ti, Ca, Zr, Zn, Na, Ge, In, Ga.

[2] Balance.

The appearance of the nickel deposit was very good, although a few pits were observed. The composition of the product is shown in table 23. The purity of the material compares favorably with that of commercial grades of electrolytic nickel, and the material would be acceptable for use in superalloys.

Discussion

The test described above was encouraging in that it demonstrates that good-quality nickel can be produced from superalloy scrap using the matte separation process. It should be emphasized, however, that the scrap material used in the melt stock was "vacuum grade" quality and thus represents the upper range of scrap metals purity that would be treated in a recovery process. Lower quality scrap feed will contain tramp elements which, if not removed at some point in the process, will cause difficulty in the electrowinning of both cobalt and nickel. An assessment of the individual or combined effects of trace elements is a difficult task which was well beyond the scope of this experimental program.

GENERAL DISCUSSION

The laboratory-scale testing program has shown the technical feasibility of the process flowsheet initially selected for recovery of metals from complex superalloy scrap. The basic concept of separating chromium from the other metals by forming a matte in which chromium sulfide is a distinct phase was substantiated, although the separation efficiency was not as good as anticipated. Also, considerable difficulty in separating the sulfide phases by physical methods was experienced. Leaching of the metallic and nickel sulfide phases was quite effective. It was found that, if the redox potential was controlled, the chromium sulfide phase remained inert during the leach, and chromium remained in the leach residue. The principal uncertainty for the process that could not be tested fully was the range of variation of feed composition that could be accommodated by the process.

Material Balance

All of the test work discussed in this report was conducted on a batch or limited-unit continuous basis. It was not possible to test a fully integrated system of the type that would be employed in a commercial plant. To provide information on quantities and compositions of process streams at each stage of the flowsheet, as well as probable compositions and quantities of products, a material balance for an integrated system was prepared for the hypothetical "aim" composition. The compositions and element distributions at each stage of the recovery process are shown in table 24. The streams are identified by number on the table and on the simplified flowsheet shown in figure 27. Following solvent extraction (H), approximately 7-1/2 percent of the nickel electrolyte is separated from the circuit. This is reacted with sodium carbonate to form a nickel carbonate residue and a sodium-rich effluent. The nickel carbonate is reverted to the hydrolysis stage to precipitate Fe and Mo impurities prior to solvent extraction. The nickel carbonate is thus used for maintaining purity in this part of the process. Note that with reverting of nickel electrolyte and nickel carbonate from solvent extraction back to the primary leach and hydrolysis stages, the quantity of solution and nickel at stages E, G, H, and I will increase almost twofold before stabilizing. Concurrently, the concentrations of Cr, Co, Mo, and Fe will decrease at stages E, G, and H. The final concentrations are approximated in table 24, key No. 8.

TABLE 24. - Material balance for integrated flowsheet

Key[1]	Stream	Ni	Cr	Co	Fe	Mo	W	Cb	Ta	Al	Ti	S	Other	Total, kilograms
1	Scrap:													
	Composition...weight-percent..	62.5	16.1	5.0	5.8	3.3	1.0	1.4	0.7	2.2	1.0	NAp	1.0	NAp
	Distribution.......kilograms..	62.5	16.1	5.0	5.8	3.3	1.0	1.4	0.7	2.2	1.0	NAp	1.0	100
2	Oxidant:													
	Composition...weight-percent..	40.0	10.3	3.0	3.6	2.1	0.6	0.9	(2)	(2)	(2)	NAp	39.4	NAp
	Distribution.......kilograms..	13.2	3.4	1.0	2.3	0.7	0.2	0.3	NAp	NAp	NAp	NAp	13.0	33
3	Flux:													
	Composition...weight-percent..	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	100	NAp
	Distribution.......kilograms..	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	1	1
4	Slag:													
	Composition...weight-percent..	3.5	2.3	NAp	NAp	NAp	NAp	1.7	2.3	NAp	NAp	NAp	91.2	NAp
	Distribution.......kilograms..	0.6	0.4	NAp	NAp	NAp	NAp	0.3	0.4	NAp	NAp	NAp	16.8	18.5
5	Oxidized bath:													
	Composition...weight-percent..	65.0	16.5	5.2	6.0	3.5	1.0	1.2	0.3	NAp	NAp	NAp	1.2	NAp
	Distribution.......kilograms..	75.1	19.1	6.0	7.0	4.0	1.2	1.4	0.3	NAp	NAp	NAp	1.4	115.5
6	Sulfur:[3]													
	Composition...weight-percent..	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	100	NAp	NAp
	Distribution.......kilograms..	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	34.3	NAp	34.3
7	Matte:[4]													
	Composition...weight-percent..	49.9	12.7	4.0	4.7	2.7	0.8	0.9	0.2	NAp	NAp	22.6	NAp	NAp
	Distribution.......kilograms..	75.1	19.1	6.0	7.0	4.0	1.2	1.4	0.3	NAp	NAp	34.0	2.3	150.4
8	Magnetics:													
	Composition...weight-percent..	62.1	3.1	6.0	7.2	2.2	0.6	0.5	NAp	NAp	NAp	16.9	1.4	NAp
	Distribution.......kilograms..	44.2	2.2	4.3	5.1	1.6	0.4	0.3	NAp	NAp	NAp	12.0	1.0	71.1
9	Non-magnetics:													
	Composition...weight-percent..	38.9	21.3	2.1	2.4	3.0	1.0	1.4	0.3	NAp	NAp	27.7	1.6	NAp
	Distribution.......kilograms..	20.9	16.9	1.7	1.9	2.4	0.8	1.1	0.3	NAp	NAp	22.0	1.3	79.3
10	Flotation product:													
	Composition...weight-percent..	65.2	4.3	3.1	4.0	1.6	0.4	NAp	NAp	NAp	NAp	21.7	1.4	NAp
	Distribution.......kilograms..	16.5	1.1	0.8	0.5	0.4	0.1	NAp	NAp	NAp	NAp	5.5	0.4	25.3
11	Flotation tails:													
	Composition...weight-percent..	26.7	29.2	1.6	2.6	3.8	1.3	2.0	0.6	NAp	NAp	30.5	1.8	NAp
	Distribution.......kilograms..	14.4	15.8	0.9	1.4	2.0	0.7	1.1	0.3	NAp	NAp	16.5	0.9	54.0
12	Blended primary leach feed:													
	Composition...weight-percent..	63.0	3.4	5.2	5.8	2.1	0.5	0.3	NAp	NAp	NAp	18.2	1.5	NAp
	Distribution.......kilograms..	60.7	3.3	5.1	5.6	2.0	0.5	0.3	NAp	NAp	NAp	17.5	1.4	96.4

See footnotes at end of table.

TABLE 24. - Material balance for integrated flowsheet--Continued

Key[1]	Stream	Ni	Cr	Co	Fe	Mo	W	Cb	Ta	Al	Ti	S	Other	Total, kilograms
13	Raffinate primary leach:													
	Composition..grams per liter..	156	0.5	13.0	14.6	3.7	0.5	NAp	NAp	NAp	NAp	1.0	NAp	[5]369
	Distribution.......kilograms..	57.6	0.2	4.8	5.4	1.4	0.2	NAp	NAp	NAp	NAp	0.4	NAp	70
14	Primary leach residue:													
	Composition...weight-percent..	11.2	11.2	1.1	0.7	1.7	1.2	1.1	NAp	NAp	NAp	64.7	5.0	NAp
	Distribution.......kilograms..	3.1	3.1	0.3	0.2	0.6	0.3	0.3	NAp	NAp	NAp	17.1	1.4	26.4
15	Raffinate cleaner leach:													
	Composition..grams per liter..	140	5.2	2.6	3.9	9.0	NAp	NAp	NAp	NAp	NAp	1.3	NAp	[5]77.1
	Distribution.......kilograms..	10.8	0.4	0.2	0.3	0.7	NAp	NAp	NAp	NAp	NAp	0.1	NAp	12.5
16	Cleaner leach residue:													
	Composition...weight-percent..	8.7	37.1	1.7	3.7	3.1	1.7	2.7	0.7	NAp	NAp	39.5	2.2	NAp
	Distribution.......kilograms..	3.6	15.4	0.7	1.1	1.3	0.7	1.1	0.3	NAp	NAp	16.4	0.9	41.5
17	Blended raffinates:													
	Composition..grams per liter..	160	1.4	11.7	13.3	4.9	0.4	NAp	NAp	NAp	NAp	1.1	NAp	[5]427.5
	Distribution.......kilograms..	68.4	0.6	5.0	5.7	2.1	0.2	NAp	NAp	NAp	NAp	0.5	NAp	82.5
18	Nickel carbonate:													
	Composition...weight-percent..	30.2	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	69.8	NAp
	Distribution.......kilograms..	5.1	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	11.8	16.9
19	Hydrolysis liquor:													
	Composition..grams per liter..	165	NAp	11.6	NAp	NAp	NAp	NAp	NAp	NAp	NAp	1.2	NAp	[5]411.5
	Distribution.......kilograms..	67.9	NAp	4.8	NAp	NAp	NAp	NAp	NAp	NAp	NAp	0.5	NAp	73.2
20	Hydrolysis filter cake:[6]													
	Composition...weight-percent..	3.4	4.2	1.4	18.8	14.6	1.4	NAp	NAp	NAp	NAp	NAp	35.4	NAp
	Distribution.......kilograms..	0.5	0.6	0.2	5.7	2.1	0.2	NAp	NAp	NAp	NAp	NAp	5.1	NAp
21	Nickel electrolyte:													
	Composition..grams per liter..	166	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	[5]378.3
	Distribution.......kilograms..	62.8	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	62.8
22	Spent nickel electrolyte:[7]													
	Composition..grams per liter..	86.3	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	[5]382
	Distribution.......kilograms..	33.0	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	33.0
23	Cobalt electrolyte:													
	Composition..grams per liter..	NAp	NAp	80	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	[5]60
	Distribution.......kilograms..	NAp	NAp	4.8	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	4.8
24	Blended leach residues:[6]													
	Composition...weight-percent..	9.8	27.2	1.4	1.9	2.8	1.4	2.0	0.4	NAp	NAp	49.3	3.4	NAp
	Distribution.......kilograms..	6.7	18.5	1.0	1.3	1.9	1.0	1.4	0.3	NAp	NAp	33.5	2.3	67.9

See footnotes at end of table.

25	Roaster feed:													
	Composition...weight-percent..	13.2	36.4	1.9	2.5	3.5	1.9	2.7	0.6	NAp	NAp	32.9	4.5	NAp
	Distribution.......kilograms..	6.7	18.5	1.0	1.3	1.9	1.0	1.4	0.3	NAp	NAp	16.7	2.3	50.7
26	Sintered chromium concentrate:[8]													
	Composition...weight-percent..	16.2	44.6	2.4	3.1	4.3	2.4	3.3	0.7	NAp	NAp	NAp	25.8	NAp
	Distribution.......kilograms..	6.7	18.5	1.0	1.3	1.9	1.0	1.4	0.3	NAp	NAp	NAp	10.7	41.4
27	Aluminum reductant:													
	Composition...weight-percent..	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	100	NAp	NAp	NAp	NAp
	Distribution.......kilograms..	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	15.5	NAp	NAp	NAp	15.5
28	Flux:													
	Composition...weight-percent..	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp
	Distribution.......kilograms..	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	21.2	21.2
29	Chromium alloy:													
	Composition...weight-percent..	22.4	61.3	3.4	4.4	5.8	3.1	1.4	NAp	NAp	NAp	NAp	NAp	NAp
	Distribution.......kilograms..	6.6	18.1	1.0	1.3	1.7	0.9	0.4	NAp	NAp	NAp	NAp	NAp	29.5
30	Slag:[9]													
	Composition...weight-percent..	0.2	0.8	NAp	NAp	0.4	0.2	2.0	0.6	NAp	NAp	NAp	63.7	NAp
	Distribution.......kilograms..	0.1	0.4	NAp	NAp	0.2	0.1	1.0	0.3	15.5	NAp	NAp	31.0	48.6

NAp Not applicable.

[1] Stream designations refer to figure 27.

[2] Not reduced; included with "other."

[3] Includes 18.5kg rechcled sulfur and 15.8 kg makeup sulfur.

[4] Allows for sulfur losses and oxidation.

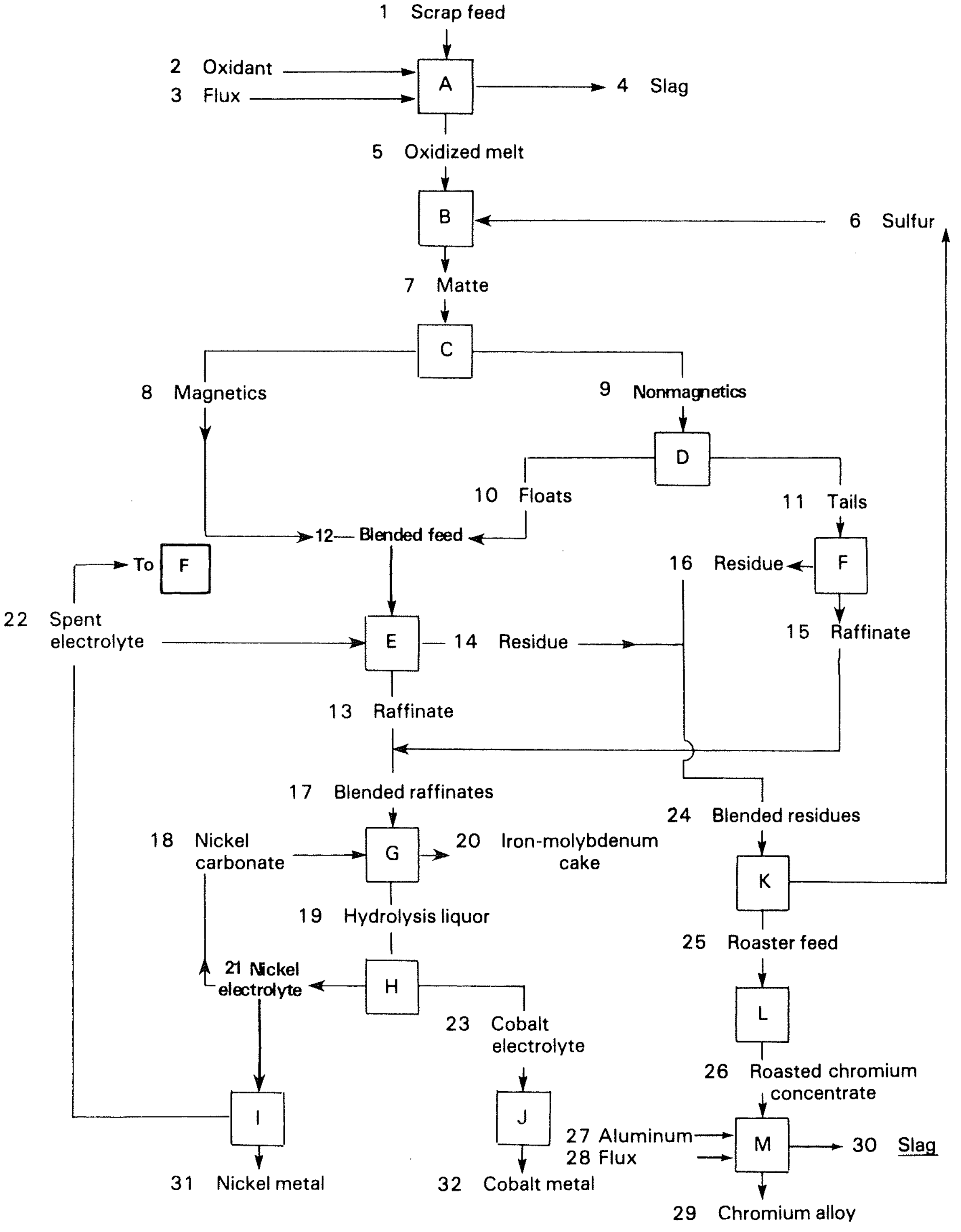
[5] Liters.

[6] Dry weight.

[7] Disposition of spent electrolyte: 703 liters to primary leach, 167 liters to cleaner leach.

[8] Other, primarily oxygen.

[9] Other, primarily calcium and oxygen.



KEY

A Oxidation
B Sulfidation
C Magnetic separation
D Flotation
E Primary leach
F Cleaner leach
G Hydrolysis
H Solvent extraction
I Nickel electrowinning
J Cobalt electrowinning
K Sulfur flotation
L Roast
M Aluminothermic reduction

FIGURE 27. - Process flowsheet for materials balance. Numbers key to tables 24 and 25.

Obviously some variation in feedstock composition would occur for a commercial plant. Owing to the complexity of the process, it is difficult to predict the effect at the various intermediate stages of the process. The role of iron in altering the structure of the chromium-rich sulfide phases was discussed earlier, and an upper limit of 15 percent iron in the composite feed was suggested. There are probably limits for the concentration of most of the elements present in the feed beyond which the separation efficiency and quality of the products will decline. One objective of a pilot plant operation would be to identify these limits or to show that composition variations within the expected operating range do not cause difficulties.

Recovery of Metals

The material balance shown in table 24 provides the basis for predicting the recovery of metals in the overall process. It also provides a means for judging the efficiency of each step of the operation. The projected recovery of metals in the various products, byproducts, and wastes is shown in table 25. In this determination, as well as for the material balance, it was assumed that 100 kilograms of metallic scrap of "aim" composition was treated. The oxidant was 33 kilograms of fully oxidized scrap (flue dust, mill scale, or chemical process sludge) of the "aim" composition. Thus the weight of the feed of 133 kilograms includes 17.2 kilograms of unrecovered material such as O_2, Al, and Ti. The three principal products are pure electrolytic Ni (90 percent of Ni in feed), pure electrolytic Co (80 percent of Co in feed), and Cr alloy ingot (93 percent of Cr, 9 percent of Ni, and 16 percent of Co in the feed). It is assumed that each of these products will be of a quality suitable for reuse by superalloy melters.

TABLE 25. - Projected recovery of metals

Key[1]		Ni	Cr	Co	Fe	Mo	W	Cb	Ta	Other	Total
1,2	Feed:										
	Distribution.kilograms..	75.7	19.5	6.0	7.0	4.0	1.2	1.7	0.7	17.2	133
31	Electrolytic nickel:										
	Distribution.kilograms..	67.9	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	67.9
	Recovery.......percent..	90	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp
32	Electroytic cobalt:										
	Distribution.kilograms..	NAp	NAp	4.8	NAp	NAp	NAp	NAp	NAp	NAp	4.6
	Recovery.......percent..	NAp	NAp	80	NAp	NAp	NAp	NAp	NAp	NAp	NAp
29	Chromium alloy:										
	Distribution.kilograms..	6.6	18.1	1.6	1.3	1.7	0.9	0.4	NAp	NAp	29.5
	Recovery.......percent..	9	93	16	18	43	75	57	NAp	NAp	NAp
4	Induction furnace slag:										
	Distribution.kilograms..	0.6	0.4	NAp	NAp	NAp	NAp	0.3	0.4	16.8	18.5
	Recovery.......percent..	<1	2	NAp	NAp	NAp	NAp	18	57	NAp	NAp
20	Hydrolysis filter cake:										
	Distribution.kilograms..	0.5	0.6	0.2	5.7	2.1	0.2	NAp	NAp	5.1	14.4
	Recovery.......percent..	<1	3	4	82	52	17	NAp	NAp	NAp	NAp
30	Aluminothermic reduction slag:										
	Distribution.kilograms..	0.1	0.4	NAp	NAp	0.2	0.1	1.0	0.3	46.4	48.6
	Recovery.......percent..	<1	2	NAp	NAp	5	8	59	43	NAp	NAp

NAp Not applicable.

[1] Stream designation refers to figure 27.

The fourth valuable product is the roasted hydrolysis filter cake, which will contain at least 50 percent of the molybdenum in the feed. This Fe-Mo oxide also contains some Ni and Cr. This cake could be processed to further concentrate the molybdenum, or it could be used directly as an additive for stainless or alloy steel production.

Recovery of metals in the four products in which their full value would be realized is Ni--99 percent, Cr--93 percent, Co--96 percent, and Mo plus W--92 percent. The losses of these metals are either in the slag or in a product where the full value would not be recovered, such as cobalt in the hydrolysis cake.

Columbium and tantalum are largely present in the induction furnace and aluminothermic reduction slags. The concentration of these metals in the slag will be on the same order as their concentration in the scrap feed. It may be possible to recover these elements through further processing; however, it is assumed that the byproduct value of these metals will be very low.

Improvement in Operating Efficiency

The material balance and predicted distribution and recovery of elements are based on results achieved in laboratory work. Clearly there are a number of points in the overall operation where conditions could be varied to increase or decrease the recovery of specific elements. For example, the recovery of columbium and tantalum is influenced by the degree of oxidation of the molten metal bath. It may be possible to recover substantially all of these metals in the induction furnace slag at the expense of somewhat lower chromium recovery. Perhaps the most important variable is sulfur content of the matte. By lowering the sulfur content of the matte to about 18 percent, the Co, Fe, and Mo content of the chromium sulfide phase and the amount of free molybdenum sulfide are significantly reduced. The resulting Cr alloy would be more nearly a binary alloy of Cr and Ni, thus improving its acceptability, while the hydrolysis cake would be enriched in Mo. It is also known that a portion of the heavy metals in the leach residues are in the form of carbides and mixed heavy metal sulfides. It may be possible to remove these metals in a concentrate by floating the chromium sulfide after sulfur flotation. These points should be taken into consideration in any future studies to further develop the overall process.

Alternative Processing Methods

Although a few modifications were made, the viability of the basic flowsheet was demonstrated in the experimental program. One major modification that merits further consideration is the use of direct leaching of ground matte to separate nickel and chromium. This alternative procedure is based on the observation that dissolution of chromium sulfide can be suppressed by limiting the redox potential during leaching. The chromium-rich residue of such a direct leach process would be treated to produce chromium metal using fluidized-bed roasting and aluminothermic reduction. The major advantage would be elimination of the magnetic separation and froth flotation operations, which were found to be rather inefficient.

CONCLUSIONS

The technical viability of a novel process to recover chromium and other metals from superalloy scrap has been demonstrated. An experimental program using laboratory-scale equipment verified that the following processing steps were viable and capable of providing metal products suitable for reuse in superalloys.

1. Mixed alloy scrap was melted and homogenized, after which a solid reducible oxide was added to oxidize the reactive metals (Al, Ti, Hf, Zr, etc.) present in the charge. The slag was skimmed and reserved for possible recovery of Cb and Ta.

2. Sulfur was added to the bath to form a partial sulfide matte containing 17 to 25 percent sulfur. The matte was cast into an insulated mold for slow cooling to develop a coarse grain structure.

3. The solid matte was crushed and ground to liberate particles of the three phases (chromium sulfide, nickel sulfide, and nickel-rich metal).

4. Wet magnetic separation was applied to remove the magnetic portion of the aggregate. Nickel and chromium sulfides were separated using froth flotation. Owing to the friable nature of the sulfides and the difficulty in floating nickel sulfide fines, this portion of the flowsheet was found to be least efficient.

5. The magnetic fraction was combined with the nickel sulfide flotation concentrate and then was given a hydrochloric acid-chlorine leach under controlled redox potential. This resulted in nearly complete extraction of Ni, Co, Mo, and Fe and rejection of chromium as a sulfide in the residue.

6. The leachate was hydrolyzed by the addition of nickel carbonate to remove iron and molybdenum. In a commercial operation the resulting filter cake would be roasted to produce a granular oxide suitable for use in the stainless and alloy steel industries.

7. A tertiary amine solvent extraction system was used to separate nickel and cobalt from the chloride leach liquor.

8. Pure nickel metal was produced from the nickel-bearing solution by electrowinning.

9. Cobalt metal would be electrowon from the cobalt-rich solution in a commercial plant. Insufficient material was available to demonstrate this operation on the laboratory scale.

10. The chromium concentrate tails were also leached to remove any nickel sulfide not separated during flotation.

11. The chromium sulfide concentrate was roasted to the oxide in a fluidized-bed roasting system. A chromium oxide product containing 0.02 percent sulfur was produced.

12. The granular chromium oxide sinter was blended with aluminum powder and fluxes and reduced to a chromium alloy ingot. A fully metallic chromium-nickel ingot containing 0.033 percent sulfur was produced.

Based on laboratory work, the estimated recovery of the principal elements in a form that recovers their full value was Cr--93 percent, Ni--99 percent, Co--96 percent, and Mo--92 percent. Columbium and tantalum were contained in the melting furnace and aluminothermic reduction slags. Treatment of these slags to recover these elements may be possible.

An alternative scheme that could simplify the flowsheet was identified but not exhaustively investigated because of time limitations. This procedure is based on the observed inertness of chromium sulfide when the redox potential is carefully controlled during the leach. The feasibility of directly leaching a granulated matte was demonstrated on a bench-scale batch test. Further exploration of this promising approach appears justified.

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