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Recycling of Neodymium Iron Boron Magnet Scrap

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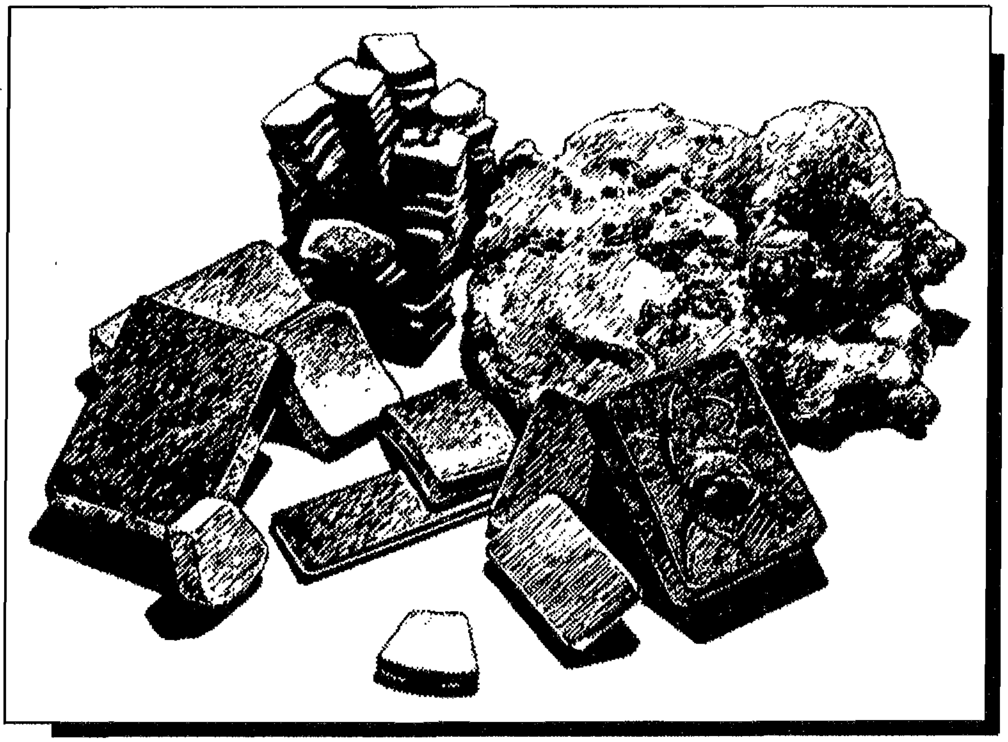
By J. W. Lyman and G. R. Palmer



UNITED STATES DEPARTMENT OF THE INTERIOR

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Cover: Examples of neodymium iron boron (NdFeB) magnet scrap that are recycled.

Report of Investigations 9481

Recycling of Neodymium Iron Boron Magnet Scrap

By J. W. Lyman and G. R. Palmer

UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	L	liter
°C	degree Celsius	*M*	molarity
cps	count per second	min	minute
ft	foot	mL	milliliter
g	gram	mL/min	milliliter per minute
g/L	gram per liter	mol pct	mole percent
h	hour	mt	metric ton
K	kelvin	pct	percent
kcal/mol	kilocalorie per mole	st	short ton
kg	kilogram	vol pct	volume percent
kJ/m^3	kilojoule per cubic meter	wt pct	weight percent
km/h	kilometer per hour		

RECYCLING OF NEODYMIUM IRON BORON MAGNET SCRAP

By J. W. Lyman[1] and G. R. Palmer[2]

ABSTRACT

The U.S. Bureau of Mines investigated methods of separating valuable rare-earth materials from Fe in neodymium iron boron (NdFeB) magnet scrap. A selective oxidation treatment of the scrap oxidized the rare-earth portion while leaving elemental Fe. Magnetic and leaching procedures were tried for separating the metallic Fe and rare-earth oxides, but the extremely fine grain size of the oxidized scrap prevented recovery by either technique. The best separation of rare earths from bulk NdFeB magnet scrap was obtained by dissolution with H_2SO_4 followed by precipitation of recyclable rare-earth salts. By precipitating neodymium-alkali sulfate double salts as an intermediate that can be converted to a variety of useful products, many materials-handling and economic disadvantages found with direct precipitation with fluoride or oxalate were avoided. Iron was removed from magnet leach solutions by precipitation as a jarosite, eliminating a major disposal problem. Research was also conducted with contaminated mixed $SmCo_5$ and NdFeB swarf. Using a flotation-leaching technique allows the $SmCo_5$ to concentrate in the froth, while the grinding-medium contaminant sinks and is removed as tailing. The NdFeB is dissolved by H_2SO_4 during the process.

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[1] Chemical engineer.

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INTRODUCTION

The U.S. Bureau of Mines (USBM) is developing technology to treat a variety of waste streams that contain valuable and strategic metals. Economic recovery from such streams ensures cost savings for industry and reduces the degree of U.S. dependence on foreign imports. As part of this effort, the separation of the valuable neodymium from relatively worthless Fe in NdFeB magnet scrap has been studied. Since this scrap typically contains nearly 30 wt pct Nd, and since the demand for Nd is constantly increasing (*1-3*),[3] cost-effective methods for scrap treatment will have a significant impact on industrial expenditure and materials supply in the expanding area of magnet manufacture.

Neodymium is a metal in the family of elements known as rare earths, which encompasses the elements of the periodic table from lanthanum to lutetium (lanthanides) and sometimes includes yttrium owing to similarity of properties. The term "rare earths" probably originated in the 19th century when these elements were first isolated as mixed oxides from rare-earth minerals, but they are not, in fact, rare at all, constituting the largest naturally occurring group of elements in the periodic table. All but one are more abundant than gold, silver, mercury, and tungsten (*4*). Samarium concentration in the Earth's crust is 2.5 times that of lead, and yttrium is 20 times more abundant than boron (*5*).

The lanthanide metal industry began with the manufacture of mischmetal-iron lighter flints made from mixed rare earth oxides (*6*). Mischmetal, in production for over 80 years, is also used in the ductile iron and steel industry. Another major usage for rare earths has been in the manufacture of fluid cracking catalysts for the petroleum industry (*7*). Because the rare-earth metals are chemically similar owing to their identical valence electron configurations, the technology to separate them from each other was not refined until the 1950's, at which time individual metals became available in large enough quantities for research (*4*, *8*). In the past, well over 90 pct of rare-earth consumption involved mixtures of metals or oxides, but the current trend is toward the use of specific lanthanides (*3*, *9-10*). Individual lanthanides are used as glass additives for cathode ray tubes and lasers, as lighting phosphors, as ceramics additives, as hydrogen storage alloys, and in new superconducting materials. The permanent magnet industry has also become a major user of specific lanthanides (*2*, *6*).

Permanent magnets are indispensable components of electromechanical and electronic devices such as computers, printers, motors, microwaves, and audiovisual components. An average home contains about 40 magnets, and a fully equipped car contains more than 30 (*2*, *8*, *11*). In 1979, with the advent of miniaturized portable stereo headphones and tape players, which utilized small but powerful $SmCo_5$ magnets, rare-earth-alloy magnet manufacture began. Consumption of samarium oxide in the United States was 165 st in 1982, whereas this market was nonexistent in 1978 (*9*). As the demand for permanent rare-earth magnets increased, and because of unrest in Africa, which threatened to affect the supply of cobalt, research was undertaken to develop other rare-earth transition-metal compounds that could combine improved magnetic capabilities with lower raw materials costs (*8*).

The lanthanides exhibit an unusual electronic structure in which the 4f electron shell is partly filled, producing magnetic moments that can favorably interact with the magnetic moments of first-transition-series metals such as Fe and Co. The resultant alloys have superior ferromagnetic properties, as indicated by the maximum energy product, which is the product of the flux density and the magnetic intensity (*12-14*). The fortuitous discovery of a stable $Nd_2Fe_{14}B$ phase met the demand for a lower cost, more readily available material with improved magnetic properties. Ordinary ferrite magnets have a maximum energy product of 36 kJ/m^3, whereas $SmCo_5$ magnets have products over 200 kJ/m^3. NdFeB magnet material has achieved the highest energy product of all, over 250 kJ/m^3. NdFeB material is also much more resistant to demagnetization at normal operating temperatures (*15-17*). Because of its improved magnetic properties, coupled with its lower cost, NdFeB magnet production has surpassed that of $SmCo_5$ magnets, as shown in figure 1.

The improved magnetic properties of NdFeB alloy have made possible the manufacture of smaller and more

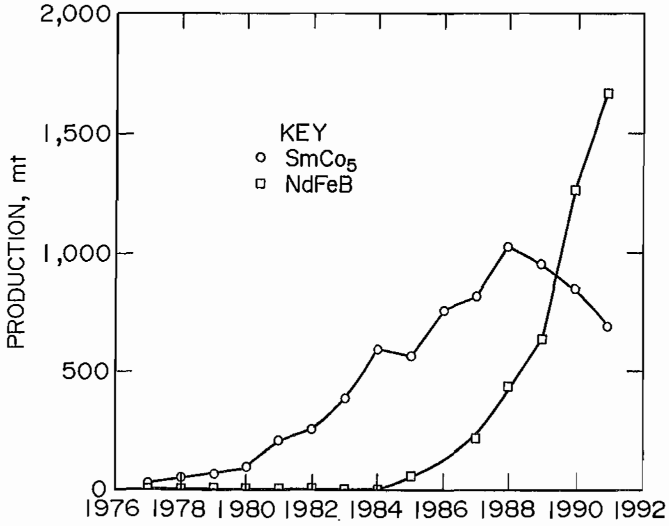

Figure 1.—Production of NdFeB magnet alloy relative to $SmCo_5$ since 1977.

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

efficient magnets that are now used in a variety of applications, including automotive starting motors, servo and other motors, meters, computers, audiovisual components, handheld portable tools, and other permanent-magnet devices requiring reduced size and weight (*2*, *8*, *10*, *18*). NdFeB magnets are also used in magnetic separators, in military and aerospace systems, and in magnetic levitation railway systems that will allow cruising speeds of over 450 km/h (*19-21*).

Currently, large amounts of scrap from NdFeB magnet manufacture are stockpiled owing to the lack of a cost-effective processing method. Because of the growing new market for individual rare-earth metals such as Nd, which was valued at $280/kg at yearend 1988, and owing to the likely continuing increase in demand for permanent magnets, scrap treatment will undoubtedly become an important alternative materials source (*2*). Development of a viable method to process NdFeB scrap will aid domestic manufacturers economically and reduce the necessity of importing rare-earth materials.

The two major methods currently used to manufacture NdFeB magnets are rapid solidification and powder metallurgy techniques. In rapid solidification, a melted alloy is supercooled by generating melt-spun ribbon, which is then crushed and treated in further processing steps such as polymer bonding or hot pressing. This process yields, material with extremely fine grain size and uniformity of microstructure; it has excellent magnetic properties. Typical scrap types generated by this process are slag and spillage materials from alloy melting, discarded ribbon material, and discarded finished magnets in a variety of forms. Powder metallurgy processing involves sintering a powder that is aligned in a magnetic field. This process generates sludge from grinding stages as well as discarded sintered and unsintered (green compact) magnet pieces (*1*, *8*). Some sintered magnet scrap bears a protective plastic outer coating as well.

The composition of scrap from powder metallurgy processing was found to be similar to that of scrap from rapid solidification. Both types had the following average composition in percent: 67.3 Fe, 26.3 Nd, 1.85 Pr, and 0.84 B. Some of the scrap samples also contained small percentages of Al or Co, which are added to improve the demagnetization resistance of the alloys. Because scrap compositions were quite uniform, economical treatment methods were sought that could efficiently separate rare-earth metals from Fe in all types of scrap despite variations in scrap geometry and surface oxidation. The two main methods investigated to accomplish this were (1) selective oxidation of rare earths and (2) acid dissolution and precipitation of rare-earth salts.

SELECTIVE OXIDATION

The purpose of performing selective oxidation was to oxidize the Nd in the scrap while keeping Fe in metallic form, thereby making the scrap amenable to rare-earth recovery either by magnetic separation or by dilute acid leaching of rare-earth oxides.

Previous research efforts have shown that it is possible to generate a stability region diagram for the Fe-H_2-H_2O system based on thermodynamic data for the various Fe oxidation-reduction reactions (*22*). For example, FeO reacts with H_2 according to the following reaction to give elemental iron:

$$FeO + H_2 = Fe + H_2O. \qquad (1)$$

The equilibrium constant (K_{FeO}) for this reaction can be expressed as

$$K_{FeO} = PH_2O/PH_2. \qquad (2)$$

Knowing that the combined pressures (P) of H_2 and water vapor are equal to 1 atm, it is possible to express the H_2 pressure as a function of temperature according to the following relationship:

$$P_{H_2} = 1/(1 + K_{FeO}) = 1/(1 + e^{-\Delta G/RT}), \qquad (3)$$

where in $e^{-\Delta G/RT}$, ΔG = free engery change of reaction,

R = gas constant,

and T = Absolute Temperature.

By plotting the H_2 pressure versus the temperature for each Fe oxidation reaction and superimposing the Nd oxidation reaction, it is possible to generate a diagram that shows the region in which metallic Fe and Nd_2O_3 can coexist. This combination stability diagram is shown in figure 2. For the reaction

$$Nd_2O_3 + 3H_2 = 2Nd + 3H_2O, \qquad (4)$$

thermodynamic data indicate that ΔG is on the order of +400 kcal/mol for temperatures between 298 and 1,000 K (*23*). When a value of this magnitude is substituted into equation 3, it is clear that for this temperature range, P_{H_2} will effectively be equal to 1. This means that Nd_2O_3

is stable throughout the Fe-H_2-H_2O diagram and that selective oxidation can be accomplished as long as the operating conditions are chosen to lie within the stability region for metallic Fe.

EXPERIMENTAL PROCEDURE

For this test work, the ratio of H_2 to water vapor was chosen to be 4:1, and all tests were run at 600° C. Ribbon material ground to minus 400 mesh was used in all tests except one in which unground ribbon material was employed. The experimental apparatus used is shown in figure 3. A sample was suspended from a balance into an Astro 1000A[4] muffle furnace through which high-purity helium gas flowed during sample heat-up to prevent oxidation. When the desired temperature was reached, the helium was turned off and a reactant gas of the required hydrogen-water vapor ratio was injected into the furnace.

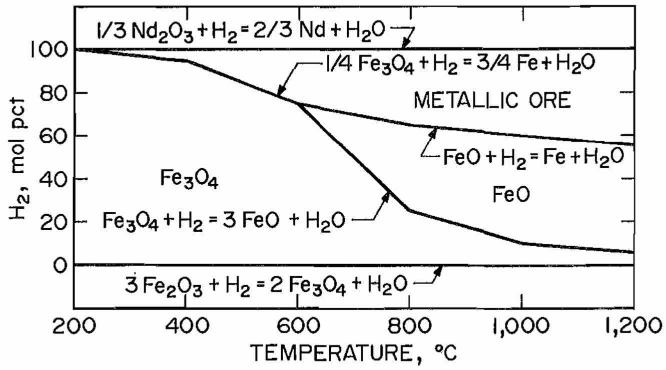

Figure 2.—Stability region diagram for Nd and Fe.

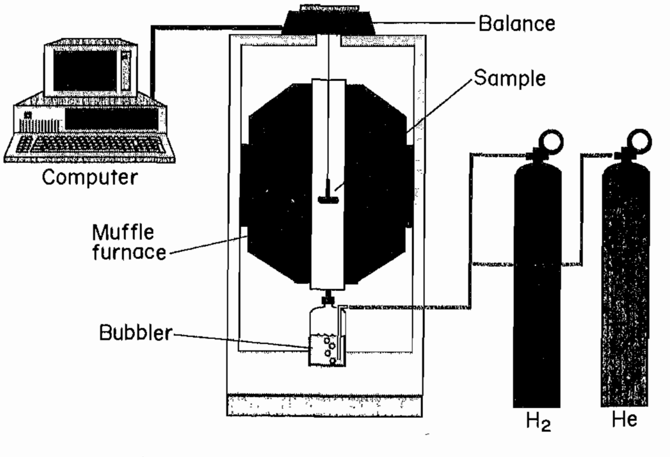

Figure 3.—Selective oxidation apparatus.

The hydrogen-water vapor ratio was controlled by injecting H_2 gas at a known rate through a bubbler apparatus that was maintained at a temperature sufficient to generate the appropriate amount of water vapor.

The progress of the reaction was monitored by means of sample weight gain, and weight versus time data were recorded with a computer interfaced with the balance.

RESULTS

A plot of weight gained versus time for a typical test run is shown in figure 4. The amount of weight gained correlated very well with that expected for Nd oxidation alone. X-ray diffraction (XRD) data helped to confirm that selective oxidation had in fact occurred. Figure 5 is an XRD scan of material that was oxidized selectively. The only Fe phase present in any quantity is metallic Fe, small amounts of Nd_2O_3 are also evident. By comparison, figure 6 shows the same material after nonselective

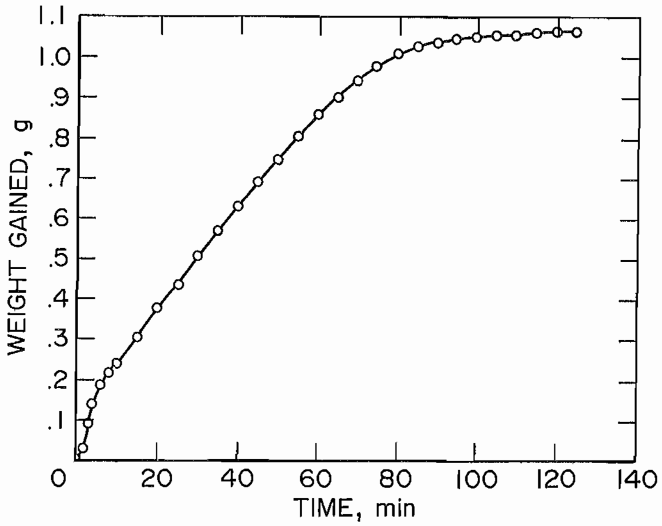

Figure 4.—Weight gained versus time in selective oxidation.

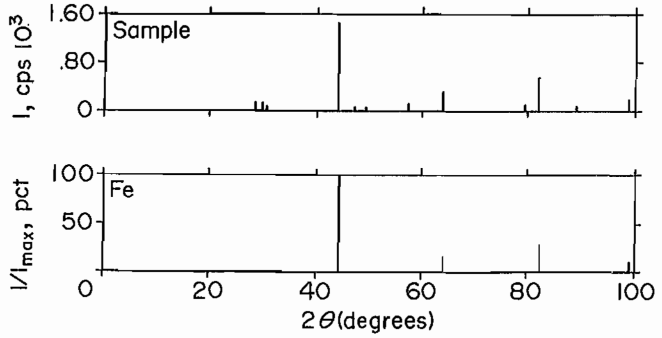

Figure 5.—XRD scan of selectively oxidized material.

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[4] Reference to specific products does not imply endorsement by the USBM.

oxidation in an excess of oxygen. It is clear that hematite (Fe_2O_3) and magnetite (Fe_3O_4) are present in significant quantities along with traces of an iron-neodymium oxide phase. To optimize the selective oxidation process, tests were carried out to study the effects of particle size, gas flow rate, and annealing on the reaction rate.

Effect of Particle Size

The effect of particle size is depicted in figure 7, which shows plots of weight gained versus time for unground ribbon and for minus 400-mesh material. It is evident that particle size does not play a significant role at this gas flow rate and reaction temperature.

Effect of Gas Flow Rate

Without changing the overall ratio of H_2 to water vapor in the reactant gas, the flow rate was varied to determine the effect of mass transport through the gas phase to the reaction surface. It was found that gas flow rate significantly affected the reaction rate, as shown in figure 8. A flow rate of at least 350 mL/min is required to overcome the effect of mass transfer through a gas boundary layer.

Effect of Annealing

Ribbon material is characterized by extremely fine equiaxed grains of the $Nd_2Fe_{14}B$ phase surrounded by a thin, intergranular, amorphous phase, which is rich in Nd. A $Nd_{1.11}Fe_4B_4$ phase has also been characterized. The excess Nd compound, which may actually be a $Nd_{70}Fe_{30}$ eutectic phase, presumably segregates to the grain boundaries during solidification (*16*, *24-29*). Because the material is multiphasic, it was thought that annealing, with its attendant grain growth, might enhance the reaction rate by aiding diffusion of the reactant gas within the sample particles. Figure 9 is a plot of the percent of Nd oxidized versus time for annealed and nonannealed material. Annealing does enhance the reaction rate slightly, but the effect is too small to be significant.

DISCUSSION

Selective oxidation was carried out with the hope that the sample morphology following reaction would lend itself to some type of separation of rare earths from Fe. Because of the fine grain size of the predominant $Nd_2Fe_{14}B$ phase and because of the initial presence of the Nd-rich

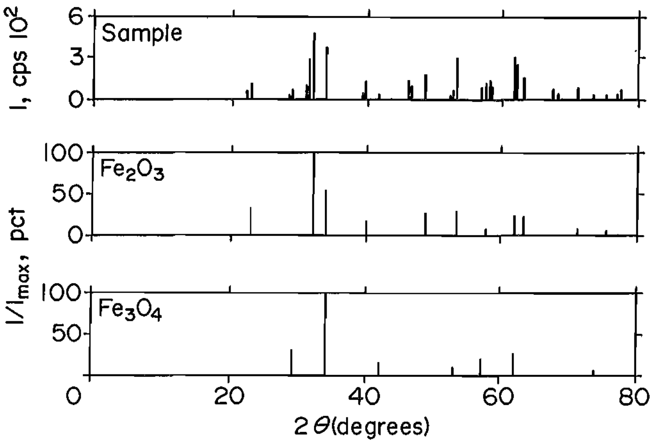

Figure 6.—XRD scan of nonselectively oxidized material.

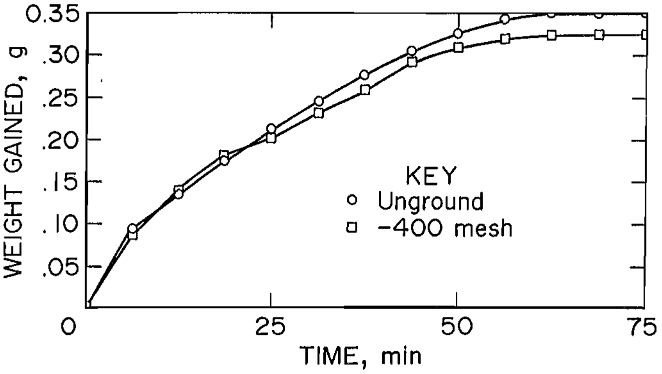

Figure 7.—Effect of particle size on selective oxidation.

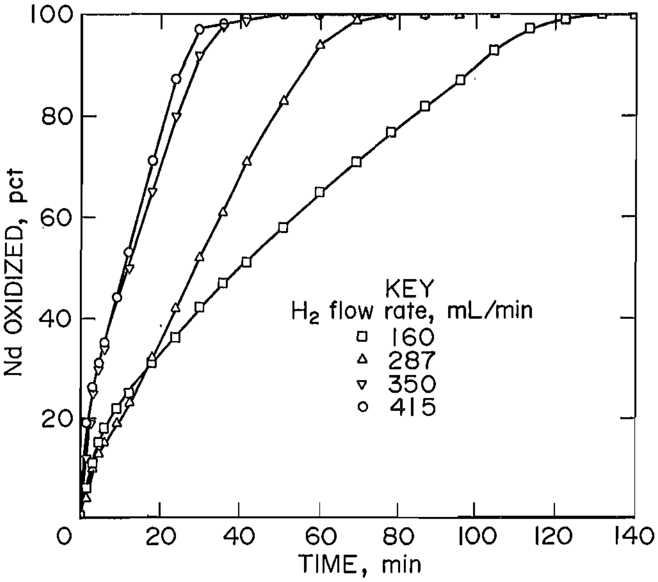

Figure 8.—Effect of gas flow rate on selective oxidation.

phase, interstitial growth of Nd_2O_3 grains that would be amenable to a dilute acid leach was hoped for. Dilute acid leaching under a variety of conditions was employed but was ineffective at selectively leaching rare-earth oxides out of the Fe matrix. As has already been noted, ribbon material has a complicated phase structure to begin with, and evidently the Nd_2O_3 that forms remains intimately mixed with Fe. If selective leaching had been shown to be effective, further grinding of selectively oxidized material might have been carried out to physically separate Nd_2O_3 from Fe. Magnetic separation of the two phases could then have been performed. Wet and dry magnetic separation was attempted, but, as expected, was ineffective at achieving any separation. Selective oxidation does accomplish the oxidation of Nd alone while leaving Fe in metallic form, but separation of the two metals still remained problematic. For this reason, it was decided to pursue a different processing scheme: total acid dissolution of the sample in stronger acid concentrations than those used for the dilute leach, followed by rare-earth precipitation in a variety of forms.

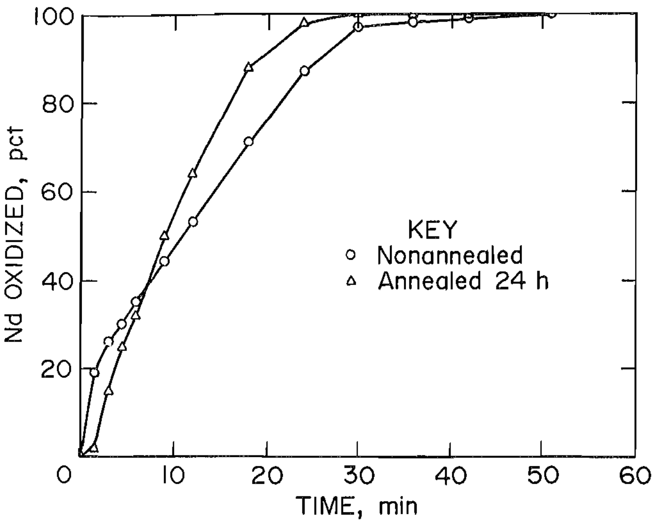

Figure 9.—Effect of annealing on selective oxidation.

ACID DISSOLUTION

Although H_2SO_4 and HCl were equally effective for scrap dissolution, H_2SO_4 was used in the bulk of tests owing to its lower cost and because it is widely employed in industry for rare-earth concentrate leaching. Precipitation of rare-earth salts and double salts from sulfate systems has been extensively studied and forms the basis for many industrial practices (*30-31*). All types of scrap dissolved readily without heating or agitation. Beneficiation of large scrap pieces positively influences the time needed for complete dissolution but is not required. Plastic-coated scrap needed to be crushed prior to leaching to render it amenable to attack by the acid. Tests were conducted to determine the typical acid requirements for scrap dissolution and to examine the leaching behavior of different types of scrap.

ACID REQUIREMENTS

Tests showed that a critical factor for scrap dissolution was the weight ratio of H_2SO_4 to scrap to be dissolved. For all scrap types tested except those containing an epoxy binder, a weight ratio of acid to scrap of 2:1 or higher was sufficient both to totally dissolve the scrap and to keep the solution pH low enough to prevent the oxidation of ferrous ion to ferric. It is known that acid solutions of ferrous ion oxidize less rapidly with increasing acidity (*32*). Ferric ion is undesirable because it forms precipitates in solution that can contaminate a process stream. For 1*M* acid solutions and an acid-to-scrap weight ratio of 2:1, the pH of the final, clear-blue solution was approximately 1.0, and no Fe precipitates formed. When the acid-to-scrap ratio was 1:1, the final pH was 3, dissolution was incomplete, and Fe precipitated out of the greenish filtrate over time.

EFFECT OF DIFFERENT SCRAP TYPES

Dissolution behavior for ribbon scrap and for hot-pressed ribbon scrap can be seen in figures 10 and 11, respectively. These figures show that despite differences in leach behavior, complete dissolution occurs when the acid-to-scrap weight ratio reaches 2.

One hundred grams of coarsely crushed pieces of epoxy-bonded ribbon material were leached in 1 L of 2*M* H_2SO_4. This is enough acid to dissolve 100 g of any other type of scrap, but in this case, 25 g remained undissolved. Visual and scanning electron microscope examination of leached pieces revealed that metal was still present in the center of each piece, so fine grinding may be required to leach this material efficiently. Other techniques, such as fluxing with an organic solvent followed by magnetic separation, were not studied, but it is clear that epoxy-bonded material will require additional processing.

Tests were carried out to determine the leaching behavior of slag, spillage, and green compact materials. All

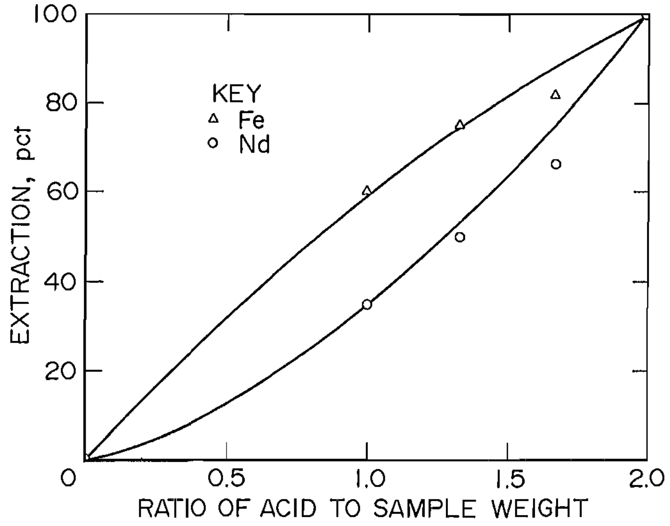

Figure 10.—Acid dissolution of ribbon scrap.

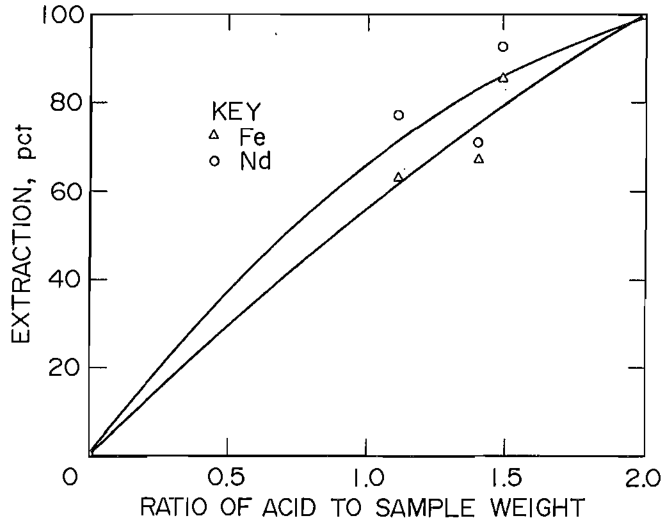

Figure 11.—Acid dissolution of hot-pressed ribbon scrap.

exhibited the same leaching behavior as ribbon and hot-pressed ribbon materials with regard to the amount of acid required for total dissolution.

In addition to determining the amount of acid required for effective dissolution, it was necessary to study the effect of acid concentration while maintaining the acid-to-scrap weight ratio at 2. One hundred grams of ribbon material was completely dissolved in 1 L of 2*M* (200 g) H_2SO_4, yielding a solution that analyzed 33 g/L Nd and 78 g/L Fe. (Analyses appear higher than those in the original scrap owing to loss of water volume from exothermic heating and H_2 evolution during dissolution.) One hundred and fifty grams of ribbon material was dissolved in 1 L of 3*M* (300 g) H_2SO_4, but large amounts of Fe and rare-earth sulfate salts precipitated out of solution. Although the original scrap contained approximately 40 g of Nd and 100 g of Fe, the filtrate contained only 23 g/L Nd and 77 g/L Fe. It was evident that sulfate solubilities were exceeded for both Fe and Nd when the H_2SO_4 molarity was 3 owing to the decreased amount of water used. Operating the system at a molarity of 2 was adequate to effect total sample dissolution while minimizing the water requirement.

ALUMINUM DISSOLUTION IN H_2SO_4 AND HCl

Small amounts of Al are sometimes added to magnet alloys during magnet fabrication to improve the resistance of the alloy to demagnetization at elevated temperatures. Unfortunately, Al is an undesirable element in final recycle products owing to the difficulty of reducing it to its metallic state. A series of tests was carried out in which the dissolution of Al from pure Al_2O_3, bulk magnet scrap, and NdFeB swarf was investigated in H_2SO_4 and HCl. For all materials except swarf, Al concentration is higher in the HCl system. This fact supports the necessity of performing scrap leaching in the H_2SO_4 system.

RARE-EARTH PRECIPITATION

Once scrap was dissolved in an acid solution, separation of the rare earths from Fe was achieved by precipitation of a rare-earth salt. For acid dissolution to be a viable method for treating NdFeB scrap, a rare-earth precipitation product must be generated that can be recycled for use in existing processes that use Nd salts as feed materials. Pure Nd fluorides and oxides are used in laser, glass, and ceramics manufacture, but by far the largest demand for Nd salts is in metallothermic or electrolytic reduction to produce Nd metal and alloys for magnet manufacture.

In metallothermic reduction, Nd chloride, fluoride, or oxide is reduced with calcium, sodium, or lithium metal (*33*). The purest and best characterized metal is produced by Ca reduction of NdF_3 generated either by precipitation from aqueous solution or by reaction of the oxide with HF gas or NH_4F at low temperatures (200° to 500° C). Prior to Ca reduction, the NdF_3 is melted under a dynamic atmosphere of HF and Ar, a process known as topping, to dehydrate it and remove residual O_2, which would contaminate the metal product (*31*, *34-36*). Any Fe present in the fluoride is carried over into the final metal product (*36*).

In electrolytic reduction, an electrolytic cell is employed to reduce Nd chloride, fluoride, or oxide to Nd metal using fused-salt electrolysis. The electrolytes used are multicomponent melts of either chlorides or fluorides. Aqueous solutions are not suitable electrolytes because at a decomposition potential electronegative enough to deposit Nd, H_2 gas is evolved. The advantages of a fluoride system are (1) fluorides are less hygroscopic than chlorides, leading to purer final products, and (2) fluorides can dissolve rare-earth oxides directly, whereas chlorides cannot. Work has also been carried out in which master alloys suitable for magnetic purposes were produced by fused-salt electrolysis of fluorides using transition-metal cathodes (*35-38*).

Both NdF_3 and Nd_2O_3 would be suitable precipitation products for recycle to current industrial operations. Fluorides can be precipitated directly from aqueous solutions; in fact, this is a recommended practice when large amounts of Fe are also present in solution (*31*). Rare-earth oxides are generally obtained by roasting rare-earth oxalates; although the presence of large amounts of Fe is known to inhibit their precipitation, rare-earth oxalates are one of the most important rare-earth salts (*31*, *33*). Residual Fe present in the precipitates would not be problematic for either metallothermic or electrolytic reduction, particularly if the Nd metal product were intended for magnet alloy manufacture.

Fluoride and oxalate precipitation, however, have associated problems. Fluoride precipitates tend to be gelatinous and difficult to filter, while oxalates are costly to produce and must be roasted to generate an oxide product suitable for recycle. A possible solution to the problems associated with the direct precipitation of fluorides and oxalates is to generate an intermediate precipitate that could then be converted to either a fluoride or an oxalate product, depending on industrial demand. An example of such an intermediate precipitate is the double sulfate salt of Nd and Na, which is used industrially for the precipitation and storage of rare-earth materials (*31*). The present work examined the precipitation of fluorides, oxalates, neodymium-sodium, and neodymium-ammonium sulfate double salts from dissolved scrap.

DIRECT PRECIPITATION

Neodymium Fluoride

Tests were carried out to study precipitation of NdF_3 from acid solutions of dissolved scrap using HF as the F^- source. For clarity, the term "extraction" refers to the percentage of an element originally present in the scrap that reports to the fluoride product. It is therefore obvious that low Fe extraction values are desirable. Table 1 gives compositions of leach solutions for several scrap types along with the extraction values of Fe and Nd in the fluoride product. All leach solutions were obtained by dissolving scrap in 1*M* H_2SO_4 except that 2*M* H_2SO_4 was used in the last ribbon test. The number of times the stoichiometric amount of HF used is also included in the table. It is clear that precipitation of NdF_3 can achieve very efficient separation of Nd from Fe.

Table 1.—HF precipitation

Scrap type	Nd in leach, g/L	Fe in leach, g/L	HF addition, times stoichiometry	Recovery, pct		F^- in effluent, g/L
				Nd	Fe	
Hot pressed	21.01	45.9	2.73	99.61	4.80	11.0
	15.07	38.6	3.84	98.58	3.52	14.0
	20.79	46.1	.16	13.93	1.06	.25
Ribbon	6.38	43.5	2.62	98.69	.98	2.34
	15.40	37.3	.97	59.57	.09	1.51
	18.04	46.7	.77	66.67	.06	.31
	18.04	46.7	1.54	98.85	.65	3.27
	18.04	46.7	2.31	99.43	.21	6.70
	18.04	46.7	3.09	98.89	.20	9.15
	18.04	46.7	4.63	91.67	.21	18.8
	18.04	46.7	5.40	65.00	.43	19.2
	18.04	46.7	6.17	58.89	.85	25.8
	[1]32.8	[1]77.9	[1]1.61	[1]99.45	[1]3.60	[1]7.29
Slag	18.50	48.5	1.52	99.00	2.55	2.79
	18.50	48.5	2.28	99.50	2.05	7.33
	15.30	37.3	.91	69.23	.34	1.08
	15.30	37.3	1.82	93.90	2.50	5.06
	15.30	37.3	2.72	95.64	.62	9.90

[1] This test was carried out using 2*M* H_2SO_4, compared with 1*M* H_2SO_4 in the previous tests.

The amount of HF added appears to have the greatest effect on Nd recovery. Iron extraction is influenced more by scrap type and Fe concentration in leach liquor. Figure 12 is a plot of selected data from table 1 and represents a test series in which the same leach solution was divided into equal portions to which varying amounts of HF were added. It is evident that HF additions of about 1.5 times the stoichiometric amount are required for complete Nd extraction. Iron extraction remained below 1 pct in each precipitate from this series. Adding more than four times the stoichiometric amount of HF caused Nd extraction to fall off markedly. This decrease is probably due to the formation of suspensions of extremely fine nuclei of NdF_3 that are not amenable to filtration.

The last ribbon entry in table 1 represents a test carried out using 2*M* H_2SO_4 (hence, the higher concentration values for Nd and Fe). When the precipitate from this test was washed with hot water and refiltered, two effects were noted. First, the Fe extraction value decreased to 0.18 pct Fe, and second, the precipitate recrystallized in a form that was easily filtered. Washing was effective in removing residual Fe from the precipitate. As previously stated, fluorides typically form gelatinous precipitates that entrain residual Fe, causing slow filtration. Filtration rate remains the most serious impediment to rare-earth recovery by direct fluoride precipitation from aqueous solutions (*31*). The amount of F^- remaining in solution depends on the amount of HF initially added. Even when less than the stoichiometric amount of HF is used, some F^- remains in solution. Since F^- is extremely corrosive in an operating system, it is necessary to keep its addition to a minimum. Using 50 pct excess F^- is reasonable since the Nd recovery is high while F^- content remains around 3 g/L.

Table 2 shows results obtained from precipitation using several sources of F^-. NaF achieves Nd extraction as efficiently as HF, and NH_4F performs nearly as well. Other reagents tried were not as effective. It appears that using NaF as the ion source keeps the F^- concentration to a minimum in the final filtrate.

Temperature effects on NdF_3 precipitation and filtration were also studied. Precipitation tests were carried out with two identical leach solutions to determine the effect of temperature. One solution was heated to 70° C prior to precipitation, and the other was left at room temperature. Precipitation was also carried out in one set of tests using HF, while NaF was used in another. Temperature did not have any appreciable effect on the rate of filtration.

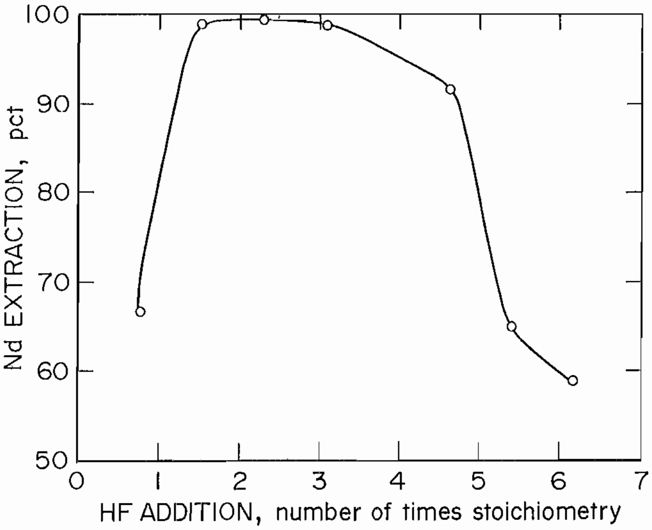

Figure 12.—Nd recovery in NdF_3 versus number times stoichiometric HF addition.

Neodymium Oxalate

The presence of large amounts of Fe tends to interfere with oxalate precipitation. Test work indicated that when oxalic acid is added in stages, only 90 pct Nd is recovered before the precipitate becomes contaminated with Fe. Iron oxalate begins to precipitate as the concentration of Nd in solution becomes lower. Washing the precipitate with a solution of dilute H_2SO_4 helped to remove residual Fe, leading to recovery values for Nd and Fe of 97.76 and 0.24 pct, respectively. Neodymium oxalate can be precipitated by this method, but reagent costs may be prohibitive. Since oxalates must be converted to oxides by roasting, and since the value of the oxide was only $17.50/kg at yearend 1991, it is unlikely that this procedure would be economically justifiable (*2*).

Table 2.—Other reagents used to generate NdF_3

Reagent	Nd in leach, g/L	Fe in leach, g/L	HF addition, times stoichiometry	Recovery, pct Nd	Recovery, pct Fe	F^- in effluent, g/L
HF	32.8	77.9	1.61	99.45	3.60	7.29
NaF	21.5	57.9	1.50	99.29	.35	1.25
	33.5	79.4	1.50	98.35	1.83	1.57
NH_4F	33.5	79.4	1.50	96.73	4.21	4.9
Na_2SiF_6 ...	33.5	79.4	1.50	67.38	.91	9.29

INTERMEDIATE DOUBLE-SALT PRECIPITATION

Neodymium-Sodium Sulfate Double Salt

Because of the difficulty of NdF_3 filtration and the expense and nonselectivity of Nd oxalate production, precipitation of a neodymium-sodium sulfate double salt was investigated. This double salt serves as an intermediate product and allows inexpensive separation of rare earths from Fe without filtration problems. Sodium hydroxide was added to acidic leach solutions of magnet scrap to raise the pH to 1.5. A light-purple, easily filtered, neodymium-sodium sulfate double salt precipitated from solution. Such double salts are very common, although the composition is variable and few have been fully characterized. Double neodymium-sodium sulfates are listed as having formulas such as $Nd_2(SO_4)_3 \cdot Na_2SO_4 \cdot 6H_2O$ or $NaNd(SO_4)_2 \cdot nH_2O$, where n is 0 or 1 (*17*, *39*). The precipitate contained, in percent, 35 Nd, 2 Pr, 6.5 Na, 50 SO_4, and only 0.2 Fe. Note that the molar amounts of Nd and Na are roughly equivalent, corresponding to the formulas above.

Table 3 presents data for a test series on generation of neodymium-sodium double salt in which varying amounts of a saturated NaOH solution were added to 400-mL samples of bulk magnet scrap leach solutions. Figure 13 shows the recovery of Nd and Fe in the neodymium-sodium double sulfate salt as a function of pH. The recovery of Nd exceeds 95 pct and reaches its maximum between pH values of 1.5 and 2, while Fe recoveries remain low. At pH values above 5, significant amounts of Fe begin to precipitate out of solution. When the precipitate was dissolved, the resulting liquor analyzed by inductively coupled plasma to contain 35.3 pct Nd, 1.97 pct Pr, and only 0.317 pct Fe, indicating that an effective separation was made between Nd and Fe. Twenty milliliters of NaOH solution per 400 mL of leach solution provided optimum neodymium-sodium double-salt precipitation. XRD data on hydrated neodymium-sodium double salts was not available in the literature, but the XRD pattern for the hydrated double salt of potassium (similar to sodium) closely corresponds to that for the neodymium-sodium double salt obtained in this work.

Neodymium-Ammonium Sulfate Double Salt

Instead of NaOH, NH_4OH was added to metal-rich H_2SO_4 leach solutions to raise the pH to 1.5. A light-purple precipitate formed, which again filtered very easily. This precipitate was characterized using XRD and found to consist of the two phases $Nd_2(NH_4)_2(SO_4)_4 \cdot 8H_2O$ and $(NH_4)Nd(SO_4)_2 \cdot 4H_2O$. The precipitate was analyzed to contain, in percent, 34 Nd, 2 Pr, 5 NH_4, 45 SO_4, and 0.5 Fe. Again, molar amounts of Nd and NH_4 are equivalent. Table 4 shows data from a test series in which the neodymium-ammonium double salt was formed from bulk magnet scrap. Four-hundred-milliliter samples of leach solution were reacted with varying amounts of reagent-grade NH_4OH. Significant amounts of Fe appear in the residue when over 25 mL of NH_4OH are added per 400 mL of original leach solution. Precipitation of Fe is undesirable and can be minimized by maintaining a pH of less than 2. Maximum Nd recoveries appear to be about 80 pct at a pH of 2, probably owing to water solubility of the neodymium-ammonium double salt.

Figure 14 shows the recovery of Nd and Fe as a function of pH. As in the Na system, significant amounts of Fe do not precipitate until the pH is well above 2.0.

Effect of Temperature

Increasing the temperature had very little effect on Nd recovery in the neodymium-ammonium double-salt system. Recovery of other elements, such as Fe and Co, was unaffected as well.

Table 3.—Sodium double-salt production from bulk magnet scrap

NaOH, mL	Double salt				Filtrate		
	Weight, g	Nd, pct	Fe, pct	Overall Nd recovery, pct	Nd, g/L	Fe, g/L	pH
0	0	NAp	NAp	NAp	30.7	76.8	~0.1
5	29.51	38.7	1.02	93.03	2.48	74.8	.35
10	32.09	37.7	1.14	98.54	.47	77.0	.79
15	34.51	35.2	1.69	98.91	.34	75.4	1.13
20	37.81	32.3	2.91	99.47	<.17	73.9	1.63
25	38.04	32.5	2.70	99.47	1.64	76.7	5.55
30	54.15	22.4	10.3	99.51	<.17	63.2	7.27

NAp Not applicable.

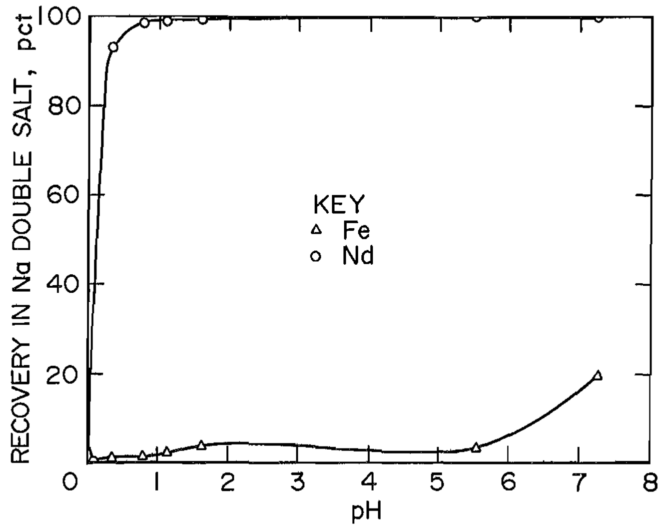

Figure 13.—Nd and Fe recovery in sodium double salt.

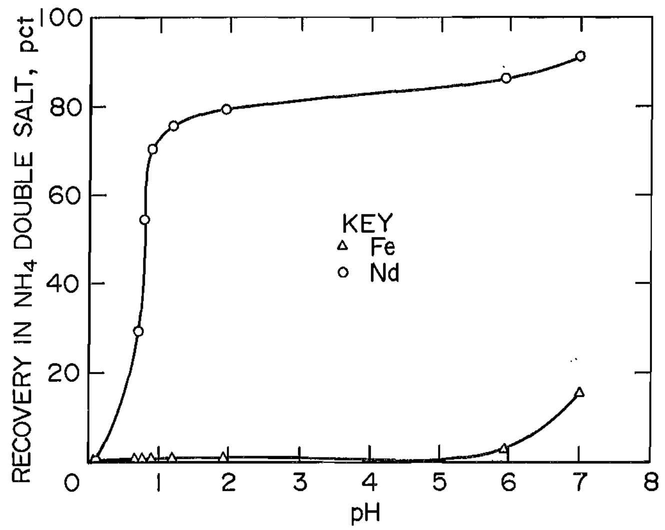

Figure 14.—Nd and Fe recovery in ammonium double salt.

Table 4.—Ammonium double-salt production from bulk magnet scrap

NaOH, mL	Double salt				Filtrate		
	Weight, g	Nd, pct	Fe, pct	Overall Nd recovery, pct	Nd, g/L	Fe, g/L	pH
0	0	NAp	NAp	NAp	29.4	78.1	~0.1
5	9.80	35.0	0.50	29.18	24.0	77.7	.70
10	18.20	35.0	.50	54.20	13.3	75.7	.78
15	23.20	35.5	.63	70.11	8.90	76.4	.89
20	25.66	34.6	.60	75.54	7.19	75.7	1.20
25	27.34	34.1	.89	79.22	6.11	74.9	1.94
30	33.46	30.3	2.20	86.23	4.10	71.2	5.93
35	46.14	20.7	9.02	91.08	2.59	62.8	7.00

NAp Not applicable.

Effect of Solution Age

Recovery of Nd was higher when a fresh leach solution was used. At 25° C, Nd recovery was 14 pct higher from a fresh solution than from a solution that had aged prior to treatment. At 75° C, Nd recovery in the fresh solution was 8 pct higher. This effect may be caused by the degree of oxidation of the transition metals, which may affect the solubility of the double salt. More B remained in solution when a fresh leach solution was used, a fact that could be important for potential B recovery.

Secondary Precipitation

Because Nd recovery in the neodymium-ammonium double salt is only about 80 pct under ordinary circumstances, several tests were carried out in which a second precipitation product was obtained to try to maximize overall recovery. Table 5 shows overall recoveries for several different secondary precipitation tests. It can be seen that oxalate precipitation is not selective for Nd over Fe and Co when the Nd recovery is high. Additional Nd can be recovered by adding more H_2SO_4 to spent leach solutions, with the attendant advantage of low additional Fe and Co recoveries. It is important to remember that the amount of Co present in this scrap is very small—a recovery of 5 pct represents an almost negligible amount.

Addition of $(NH_4)_2SO_4$ and Additional Acid

A series of tests was run in which varying amounts of additional H_2SO_4 and $(NH_4)_2SO_4$ were added to 250-mL magnet scrap leach solution samples prior to precipitation with NH_4OH. The leach solution head analysis was 30.3 g/L Nd and 73.1 g/L Fe. Neodymium recovery values are presented in figure 15. The plots are fairly level

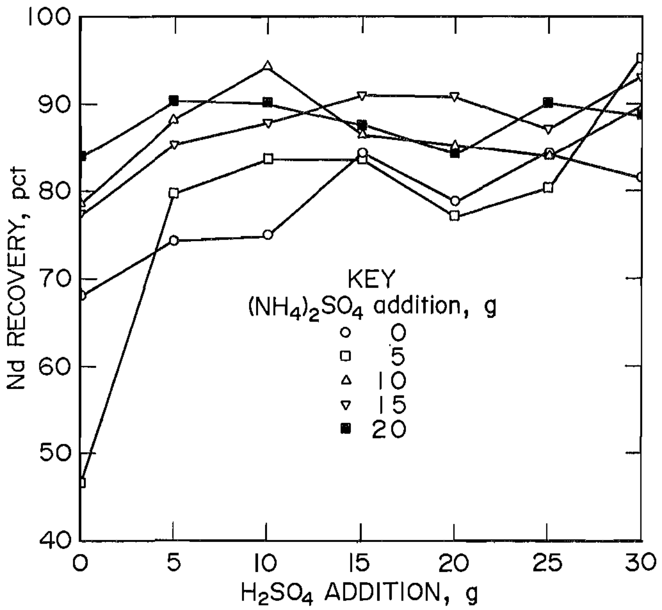

Figure 15.—Effect of additional H_2SO_4 and $(NH_4)_2SO_4$ on Nd recovery in the ammonium double salt.

above about 15 g added acid, and more than 10 g of $(NH_4)_2SO_4$ does not significantly enhance the Nd recovery. The maximum Nd recovery appears to be about 90 pct. This is a significant improvement over the 80-pct recovery obtained without $(NH_4)_2SO_4$ or additional acid.

Table 5.—Overall recovery following secondary precipitation

Reagent per 250 mL head	Recovery, pct				
	Al	B	Co	Fe	Nd
10 g HO_2CCO_2H	45.14	10.4	25.74	14.98	99.46
5 g HO_2CCO_2H	31.38	9.13	5.17	1.94	96.65
3.75 g HO_2CCO_2H	27.69	8.85	3.90	1.18	91.33
2.5 g HO_2CCO_2H	25.50	8.49	3.03	.65	84.97
1.25 g HO_2CCO_2H	23.50	8.28	2.51	.49	74.28
20 mL H_2SO_4	31.96	2.75	5.26	.08	89.75
20 mL H_2SO_4 followed by 24-h evaporation ...	32.22	2.60	5.07	.16	89.63

When the combined weights of additional acid and $(NH_4)_2SO_4$ exceed 25 g, mohrite $[(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O]$ forms over time. As long as the combined weights of these components are less than 25 g, only additional purple neodymium-ammonium double salt continues to form.

Effect of Time

Table 6 represents the results of a series of precipitation tests on bulk solid scrap solutions in which the time between reagent addition and filtration was varied from 5 to 120 min. Several of the tests were repeated at a higher temperature to determine the effect of temperature on the precipitation kinetics. Ten milliliters of additional H_2SO_4 was added in each test prior to precipitation to enhance the overall Nd recovery. These tests show that Al, B, Co, and Fe recoveries are basically unchanged after about 10 min of precipitation time, while Nd recovery continues to increase up to about 60 min. Temperature does not have any appreciable effect on the precipitation rate and, in fact, appears to be slightly detrimental.

Table 6.—Effect of time and temperature on recovery from ammonium double-salt precipitation

Time, min	Recovery, pct				
	Al	B	Co	Fe	Nd
	At 25° C				
5	31.00	2.27	3.59	0.33	74.50
10	36.53	2.54	7.31	.18	79.28
15	35.16	2.52	7.37	.24	77.18
30	31.97	2.58	5.56	.25	77.91
60	39.02	2.90	6.57	.18	87.84
120	37.25	2.85	6.36	.22	88.18
	At 50° C				
5	28.08	2.13	6.23	0.25	69.76
10	27.59	2.07	5.19	.22	70.89
15	28.56	2.20	5.62	.22	75.56
60	32.91	2.56	6.88	.35	84.45

Neodymium-Potassium Sulfate Double Salt

A similar, easily filtered purple salt was also formed by the addition of KOH to pregnant leach solutions of dissolved magnet scrap. Ninety-three percent of the Nd was recovered in this salt, which analyzed, in percent, 30 Nd, 2 Pr, 9 K, 50 SO_4, and 0.2 Fe. The molar K content is equivalent to that of Na and NH_4 in other double-salt species previously discussed.

DOUBLE-SALT CONVERSION

Tests were performed to determine whether the neodymium-sodium and neodymium-ammonium double-salt precipitates could be converted to pure fluoride products by leaching with HF solution. It was found that both Na and NH_4 double salts could be readily converted to NdF_3 with no loss of Nd. Because of their similarity to Na double salts, K double salts were not included in this phase of the research.

SODIUM DOUBLE SALT TO NdF_3

Table 7 shows results from conversion of 7-g Na double-salt samples to NdF_3. If all Nd is converted to NdF_3, the final product weight would be expected to be 3.42 g, analyzing 71.68 wt pct Nd. Residual amounts of SO_4^{2-} and Na^+ were found in the NdF_3 products, which varied depending on the amount of HF and water used in the leach. The SO_4^{2-} content in the NdF_3 varied inversely with the HF-double salt ratio. When the F^- concentration is very high, as in the 10 mL HF-25 mL H_2O test, the presence of Na_2SiF_6 was noted by XRD. This can be avoided by performing the conversion in Nalgene or Teflon reactor vessels. Washing the NdF_3 in a 10-vol-pct HF solution significantly lowered both Na^+ and SO_4^{2-} concentrations.

Effect of Wash Time Prior to Conversion

A series of tests was carried out to determine what effect washing the Na double salt in water prior to fluoride conversion might have on the purity of the final product. Identical samples of the Na double salt were agitated in water for varying lengths of time before the HF was added. The results are presented in table 8.

Washing prior to fluoride conversion has a deleterious effect on the SO_4^{2-} and Na^+ content of the final NdF_3 product. Iron content remained largely unaffected. Despite differences in the SO_4^{2-} and Na^+ concentrations in the final products, XRD scans were identical.

Effect of Conversion Time

Another series of tests was set up to study the effect of conversion time on the purity of the NdF_3 product. Samples of neodymium-sodium double salt weighing 27 g were reacted for varying lengths of time in a solution of 10 mL HF and 100 mL H_2O in Nalgene reaction vessels. There was no initial wash. It can be seen from table 9 that 15 min is adequate for complete conversion of the double salt while keeping SO_4^{2-} and Na^+ impurities at acceptable values.

AMMONIUM DOUBLE SALT TO NdF_3

Similar results were obtained for conversion of the NH_4 double salt to NdF_3 except that the purity of final products was higher than in the Na system. Table 10 shows data from the conversion of the NH_4 double salts to NdF_3 by reacting the double salt with various combinations of HF and water. Fifty grams of double salt, which analyzed 34.8 pct Nd, was converted in each test. If all Nd is converted to NdF_3, the final product should weigh 24.35 g and should contain 71.68 pct Nd. Twenty-five grams of HF is approximately 1.67 times the stoichiometrically required amount to effect complete conversion. Neodymium losses were negligible, and XRD showed high purity of all fluoride products.

Table 10 shows that several combinations of conditions produce similar results. Judging from the weight of product obtained and from the Nd analyses, the best results are obtained by using 50 g or more HF for a 50-g double-salt sample. The amount of water used must be between 10 and 20 times the weight of double-salt sample.

Fluoride generated from neodymium-ammonium double salt is not always easily filtered. It was determined that the HF must be added to the water prior to addition of the NH_4 double salt for a filterable product to be obtained. When double salt is added first to water, the salt dissolves, and the NdF_3 that forms upon addition of HF is gelatinous and difficult to filter, as in direct NdF_3 precipitation. When HF is already present in solution, conversion to fluoride occurs before the double-salt dissolution, producing coarser crystals.

For both the Na and the NH_4 systems, the purest products are obtained at an HF-double salt ratio of 1.43 or higher and at a water-HF ratio of 10. Residual Fe content was independent of the conversion conditions, depending instead on the amount of Fe originally present in the double salt. Fluorides obtained from conversion of the double salts are easily filtered—one major advantage to this method of processing NdFeB scrap.

Table 7.—Effect of fluoride addition on products from conversion of sodium double salt

Test	Solution composition		Fluoride product					Filtrate analysis, g/L	
			Weight,	Analysis, pct					
	HF, mL	H_2O, g	g	Nd	Fe	SO_4	Na	Nd	Fe
1	1	100	4.77	48.8	0.121	27.6	3.68	0.356	0.469
2	2	100	3.81	65.0	.125	5.4	2.30	.005	.391
3	5	100	3.63	67.3	.202	2.3	2.14	.155	.322
4	5	50	4.11	57.1	.159	2.2	4.13	.033	.504
5	5	25	3.93	60.2	.257	2.4	2.93	.012	.615
6	10	25	4.99	46.6	.435	1.3	7.58	.004	.739
7	10	100	3.85	66.6	2.12	1.1	1.81	.004	.059

Table 8.—Effect of wash time prior to fluoride conversion on final sodium composition of sodium double salt

Wash time, min	Analysis, pct					
	Nd	Pr	SO_4^{2-}	Na	F^-	Fe
0	66.4	0.938	5.1	1.64	25.9	0.206
10	62.6	.939	7.5	1.84	25.0	.183
20	63.9	.917	10.7	1.97	24.3	.262
30	65.2	.827	10.3	1.82	24.8	.181

Table 9.—Effect of conversion time on final fluoride product composition

Conversion time, min	Weight, g	Analysis, pct				
		Nd	Fe	Pr	SO_4^{2-}	Na
5	10.71	66.1	0.190	1.08	5.5	0.92
15	10.64	68.1	.241	1.02	4.8	.84
75	10.80	67.1	.292	1.06	6.7	.97
150	10.57	67.7	.453	1.09	4.8	1.05
300	10.51	66.8	.668	1.08	5.4	.81

Table 10.—Conversion of neodymium-ammonium double salt to fluoride

Test	Solution composition, g		NdF_3 product				
			Weight, g	Analysis, pct			
	HF	H_2O		Nd	Al	SO_4^{2-}	NH_4^+
1	25	125	30.85	58.5	<0.274	11.4	1.1
2	25	250	27.67	63.2	.302	10.1	.8
3	25	375	28.49	61.4	.281	9.8	.7
4	25	500	28.86	60.5	.280	16.3	1.3
5	25	750	27.70	63.2	.317	7.8	.5
6	25	1,000	26.97	63.2	.303	9.4	.6
7	50	125	30.22	53.9	<.273	11.2	1.0
8	50	250	27.54	64.2	.325	9.3	.8
9	50	375	25.67	64.6	.349	7.5	.7
10	50	500	25.63	68.9	.357	6.3	.5
11	50	750	25.66	68.2	.343	4.9	.5
12	50	1,000	23.82	70.9	.353	4.7	.4
13	75	125	26.15	62.8	.331	8.5	.8
14	75	250	25.24	66.4	.352	7.6	.3
15	75	375	24.92	71.1	.363	7.1	.7
16	75	500	24.48	70.6	.362	5.7	.6
17	75	750	24.43	70.1	.369	4.2	.5
18	75	1,000	22.70	71.9	.373	4.4	.4

PURIFICATION OF FLUORIDE PRODUCTS

Multiple Washes of Fluoride

Neodymium-sodium and neodymium-ammonium double salts were converted to NdF_3 and then washed in HF solutions three additional times to reduce the concentration of SO_4^{2-} and Na^+ or NH_4^+ in the fluoride product. The HF wash solution consisted of a 1:2:10 weight ratio of HF to NdF_3 to water. Results from the Na system are presented in table 11, and those from the NH_4 system are presented in table 12.

Three washes are sufficient to reduce Na^+ and NH_4^+ levels significantly, and one additional wash evidently decreases the SO_4^{2-} content in the Na system as well. The apparent increase in SO_4^{2-} and NH_4 concentrations for the fourth wash in the NH_4 system could be due to experimental error.

Table 11.—Effect of multiple washes on NdF_3 (sodium system) product

Wash	Analysis, pct				
	Nd	Fe	F	NH_4^+	SO_4^{2-}
1	67.0	0.18	28.5	1.17	4.29
2	69.5	.19	29.6	.80	3.52
3	69.3	.19	29.7	.65	3.45
4	70.7	.21	28.6	.59	2.11

Table 12.—Effect of multiple washes on NdF_3 (ammonium system) product

Wash	Analysis, pct				
	Nd	Fe	F	NH_4^+	SO_4^{2-}
1	68.8	0.15	24.7	1.10	11.2
2	73.4	.14	29.2	.10	3.01
3	68.9	.13	29.0	.06	<2.05
4	68.8	.13	29.4	.35	3.04

Analysis of Topped Fluoride Product

A sample of NdF_3 produced from the neodymium-ammonium double salt was sent to a magnet alloy producer and put through the HF furnace to "top off" the sample prior to thermite reduction. A sample of the topped material was returned and analyzed. The sample was very pure, containing, in percent, 70.2 Nd, 29.2 F, <0.2 Al, <0.01 NH_4, 0.18 Fe, and <0.2 SO_4. The purity of this material was sufficient to enable Nd alloy to be produced with the same recovery as that obtained when virgin raw materials were employed (approximately 80 pct). An actual metal biscuit was produced by the above-mentioned fabricator using thermite reduction, showing that the recycle process could be carried to completion.

DOUBLE-SALT CONVERSION TO OXALATE

Oxalate products were also obtained by reacting Na and NH_4 double salts with 0.2*M* oxalic acid. The double salt-oxalic acid weight ratio was 0.72. Fifteen minutes was adequate for complete conversion. Losses of Nd were negligible in the conversion process, and the weights of Nd and Pr in the final products indicated that nearly pure oxalate precipitates were obtained. These oxalates could be roasted to yield pure oxides if desired. The purity of oxalate products was confirmed by XRD. It was concluded that Nd double salts may be treated with either HF or oxalic acid to generate fluoride or oxide products, respectively.

IRON JAROSITE PRECIPITATION

Following rare-earth precipitation, the spent leach solution, which still contains as much as 77 g/L Fe, must be treated by an Fe removal process prior to disposal or recycle. Because ordinary neutralization leads to the formation of iron hydroxides, which cannot be easily filtered, it was decided to investigate precipitation of a jarosite to facilitate solid-liquid separation. Jarosites are compounds of the type $MFe_3(SO_4)_2(OH)_6$, where M is K^+, Na^+, NH_4^+, or a metal ion such as Ag^+ or one-half Pb^{2+}. Iron is present in the ferric oxidation state. Jarosite precipitation chemistry is well understood and widely used in the zinc industry for removal of Fe in the most economical manner possible (*40-42*). Jarosites are easily filtered, exhibit good stability, and can be formed directly from spent leach solutions following double-salt precipitation. In addition, jarosites can be converted to hematite for use in cement production, pigmentation, and iron manufacture (*43*).

Spent solutions were placed in a reaction kettle through which oxygen was bubbled and allowed to react for 6 h at 90° C to form a yellow jarosite, which was then removed by filtration. The presence of oxygen ensures oxidation of ferrous to ferric ion. The amount of jarosite formed depended on (1) the presence or absence of an oxidant, (2) reagent addition, (3) pH of spent solution, and (4) the hydroxide species used.

EFFECT OF OXIDANT ADDITION

Tests showed that addition of hydrogen peroxide (H_2O_2) positively affected jarosite formation in both the Na and NH_4 systems, probably owing to improved kinetics for the oxidation of ferrous to ferric ion. Figure 16 shows a plot of Fe extraction as a function of H_2O_2 addition at a pH of 1.5. It was possible to form jarosites from both Na and NH_4 spent leach solutions without H_2O_2, but the amount of jarosite formed was much greater when H_2O_2 was present. Iron recovery in the ammonium jarosite was slightly higher than in sodium jarosite. Recovery of Fe did not increase dramatically for either system beyond an H_2O_2 addition of 30 g (50 pct) when the pH was 1.5. Table 13, however, shows that increasing the H_2O_2 addition to 100 mL/L (30 pct H_2O_2) and raising the pH to 2.0 led to an Fe recovery of nearly 90 pct in sodium jarosite. It is evident that both H_2O_2 addition and pH are extremely important for jarosite precipitation.

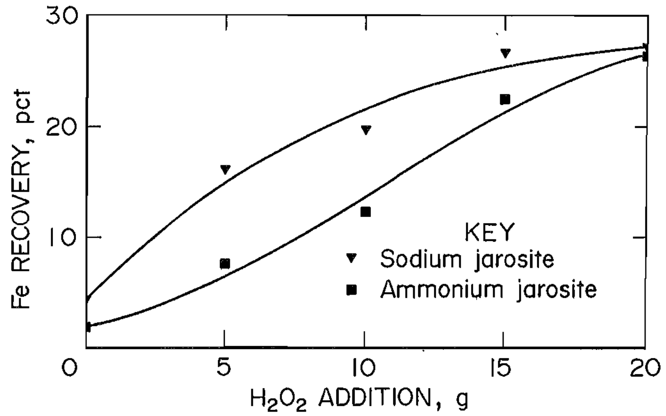

Figure 16.—Effect of H_2O_2 addition on sodium and ammonium jarosite formation.

Table 13.—Effect of H_2O_2 on sodium jarosite formation

H_2O_2 addition per L	pH	Fe recovery as jarosite, pct
None added	1.56	1.88
30 g of 50 pct	1.64	22.59
None added	2.0	2.36
30 g of 50 pct	2.0	72.41
100 mL of 30 pct ..	2.0	89.85

SEQUENCE OF REAGENT ADDITION

Two tests were performed to determine exactly what effect the sequence of H_2O_2 addition had on the amounts of Nd double salt and iron jarosite that form. Thirty grams of 50-pct H_2O_2 was added prior to double-salt precipitation in one test and after it in the other. The same feed solution was used in both tests. Analyses showed that Nd precipitation differs greatly depending upon when the H_2O_2 is added. Table 14 shows a comparison of Nd and Fe weights in grams reporting to the double-salt and jarosite products for these two tests.

Clearly, it is important to add the H_2O_2 after precipitation of the double salt to maximize Nd recovery. Iron recovery is largely unaffected by the sequence of reagent addition.

Table 14.—Effect of H_2O_2 addition on Nd and Fe precipitation, grams

Sequence	Double salt		Jarosite	
	Nd	Fe	Nd	Fe
1	12.73	0.77	10.13	32.85
2	22.16	.70	1.07	32.84

EFFECT OF Na_2SO_4 ADDITION AND pH

Table 15 shows iron recoveries obtained as a function of Na_2SO_4 addition and pH. It can be seen that the critical factor for jarosite formation is pH. Sodium sulfate only enhances jarosite formation up to an addition of 30 g at pH 1.5. Addition of higher amounts is detrimental. Sodium sulfate addition is not beneficial when the pH is 2.0.

EFFECT OF TIME

A test series was carried out to study the behavior of jarosite formation over time. The pH of the initial solution was 1.83, and the 30-pct H_2O_2 addition was 50 g /L. At 1-h increments, samples of the jarosite slurry were removed from the reactor and submitted for analysis. XRD showed no variation in the jarosite crystal structure over time. The varying composition of the solution over time is shown in figure 17. After 2 h of reaction time Fe removal slows dramatically. This time interval corresponds also to an abrupt drop in pH due to the consumption of OH$^-$ as jarosite forms. Below a pH of approximately 1.0, there is insufficient concentration of OH$^-$ to form more jarosite. This indicates that to remove more Fe, the pH must be adjusted upward after 2 h of reaction time. The increase of dissolved species concentrations at 5 to 6 h was caused by water evaporation from the reactor.

Table 15.—Effect of Na_2SO_4 addition and pH on Fe recovery in jarosite

Na_2SO_4 addition, g/L	pH	Jarosite weight, g/L	Fe recovery in jarosite, pct
0	1.52	4.81	1.16
10	1.50	30.09	9.84
20	1.55	28.44	10.98
30	1.39	53.66	24.78
40	1.41	40.98	15.09
50	1.44	27.82	10.98
50	2.00	168.7	69.51
20	2.00	164.5	71.90
0	2.00	167.5	72.41

EFFECT OF pH ADJUSTMENT

When spent leach solutions at pH 2 were placed in the jarosite reactor for 6 h using a 30-pct H_2O_2 addition of 50 g/L, approximately 70 pct of the Fe present was recovered as jarosite. Additional tests were performed in which the spent jarosite solution was readjusted to pH 2 and placed in the reactor for a second time. Only 5 to 6 pct more of the Fe was recovered during the second treatment, giving an overall Fe recovery of ~75 pct.

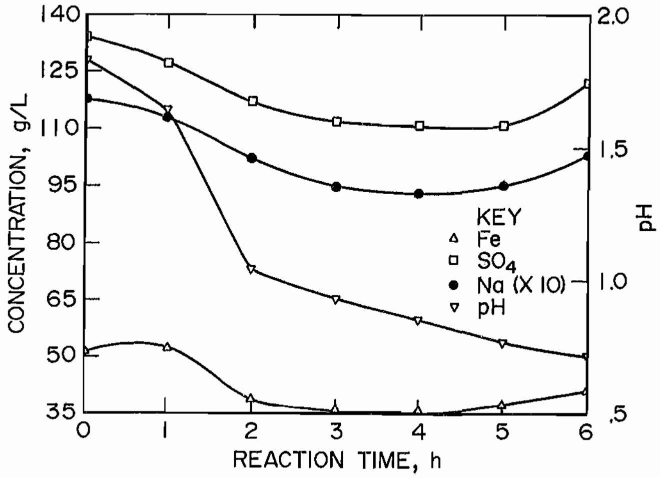

Figure 17.—Variation in jarosite solution composition over time.

In another set of tests, the pH was adjusted during the jarosite process. Known quantities of NaOH were added at varying intervals. The assumption was made that by adding NaOH and replenishing the supply of OH^-, improved Fe extraction could be obtained. Table 16 shows a summary of results obtained from this series. The starting pH in each test was 2.0, and tests ran for 4 h.

Table 16.—pH adjustment during jarosite formation—different additions of NaOH

Test	Sample treatment		Fe recovery, pct
	NaOH addition, g	Time interval, min	
1	0	NAp	62.1
2	25	120	65.4
3	25	60	68.9
4	25	30	84.0

NAp Not applicable.

In the fourth test, in which 25 g NaOH was added after each 30-min period, the precipitate was dark brown, indicating the possible presence of $Fe(OH)_3$, but filtration was rapid. XRD revealed that much of the Fe in this material was present in the form of goethite (FeOOH).

EFFECT OF CONTINUOUS pH MONITORING AND ADJUSTMENT

Several (jarosite) precipitation tests were performed in which the pH was maintained at a set value using a pH controller. Ammonium hydroxide and H_2SO_4 were added as needed to maintain a pH of 2, and the reactor temperature was maintained at 90° C. One hundred milliliters of 30-pct H_2O_2 was used per liter of feed solution as an oxidant. The reaction was allowed to proceed for 5 h, after which the final solution was neutralized with $Ca(OH)_2$. Results are given in table 17. Feed samples were taken at room temperature and again after the desired reactor temperature of 90° C was reached. Examination of the data shows that jarosite precipitation had already commenced by the time the solution reached 90° C.

Table 17 shows that Co losses in the jarosite are minimal. Iron removal is nearly complete after 3 h. A significant amount of Nd remained in solution throughout the jarosite precipitation process. Over the course of the test, SO_4^{2-} and NH_4^+ levels rose owing to the continuous addition of H_2SO_4 and NH_4OH. Final solution after neutralization is very low in Nd, Fe, and Co, but an additional step to recover NH_4^+ would be necessary. For a batch test in which pH was not continuously monitored, the final NH_4^+ and SO_4^{2-} concentrations following neutralization were 2.2 and 3.6 g/L, respectively. The NH_4^+ concentration was significantly reduced in the batch test, although the Fe recovery was only 90 pct in the jarosite precipitate.

Table 17.—Effect of time during continuous jarosite production on solution

Sample description	Analysis, g/L				
	Nd	Fe	Co	NH_4^+	SO_4^{2-}
Head	7.57	59.7	0.267	10	163
Heated head, 90° C	7.49	37.3	.282	8.3	134
Time in reactor, h:					
1	4.49	7.91	.268	23	109
2	3.63	3.11	.302	28	118
3	3.44	1.20	.314	39	132
4	3.97	.93	.303	40	146
5	4.44	.35	.276	41	143
Final solution after neutralization	<.002	<.0003	.027	17	1.7

TOXIC CHARACTERISTIC LEACHATE PROCEDURE TESTING

TCLP tests were performed from which it was determined that ammonium jarosite and the solid product obtained from the neutralization of spent jarosite solutions can be classified as nonhazardous wastes.

BEHAVIOR OF RESIDUAL Nd

In the Na system, residual Nd precipitates with the jarosite and is lost, whereas in the NH_4 system, Nd is retained in the spent solution from jarosite precipitation processing and could potentially be recovered in a later step. As was shown previously, Nd recovery in the NH_4 double salt is only 80 pct. The rest remains in solution. It is advantageous that the Nd remaining in solution does not precipitate in the ammonium jarosite. Spent Nd-containing solution following Fe removal could be recycled to the original leach.

FLUORIDE ION INHIBITION OF JAROSITE FORMATION

Some jarosite precipitation tests were carried out on solutions from which Nd had been removed by direct precipitation with F^-, and it was found that jarosite failed to form in every test where F^- was present in solution. Instead, a white precipitate formed, which analyzed high in F^-. It is evident that the presence of F^- inhibits the jarosite process. Direct precipitation of NdF_3 from Fe-bearing leach solutions is therefore undesirable, due both to filtration difficulty and to the inhibiting effect of F^- on subsequent Fe recovery through jarosite precipitation.

BEHAVIOR OF BORON

Boron does not precipitate either with the rare-earth double salt or during subsequent jarosite formation, and its concentration in solution never exceeds approximately 1 g/L. Preliminary tests were carried out to determine the possibility of precipitating B.

CALCIUM BORATE PRECIPITATION

Two tests were performed in which 20 g and 40 g respectively of $Ca(NO_3)_2$ was added to 1 L of spent NH_4 leach solution to see if calcium borate could be formed. XRD analysis showed that the test residues consisted predominantly of gypsum, but residue analyses also showed B recoveries of 1.71 pct for the 20-g test and 7.33 pct for the 40-g test. Although the recoveries are low, these tests show that it is possible to precipitate the B.

ZINC BORON PRECIPITATION

Zinc metal powder was dissolved in spent jarosite solution from the ammonia system. The feed solution analyzed, in grams per liter, 0.449 Al, 1.2 B, 59.7 Fe, and 9.12 Nd before addition of the Zn. The pH was then raised in stages with concentrated NaOH. A greenish-grey precipitate formed around pH 5.0 that analyzed, in percent, 2.49 Al, 2.0 B, 11.5 Fe, 5.41 Zn, and 14.4 Nd. The remaining solution contained only 0.688 g/L B, indicating that a significant amount of the B was precipitated. The greenish residue was found by XRD to be a composite of neodymium-sodium double salt and any of several forms of hydrated zinc borate. Zinc borate hydrates are used commercially as flame retardants (*44*). Other salts, such as zinc fluoborate, could also be precipitated.

An overall processing flowsheet is shown in figure 18 delineating the stages required to separate and recover rare earths, Fe, and B.

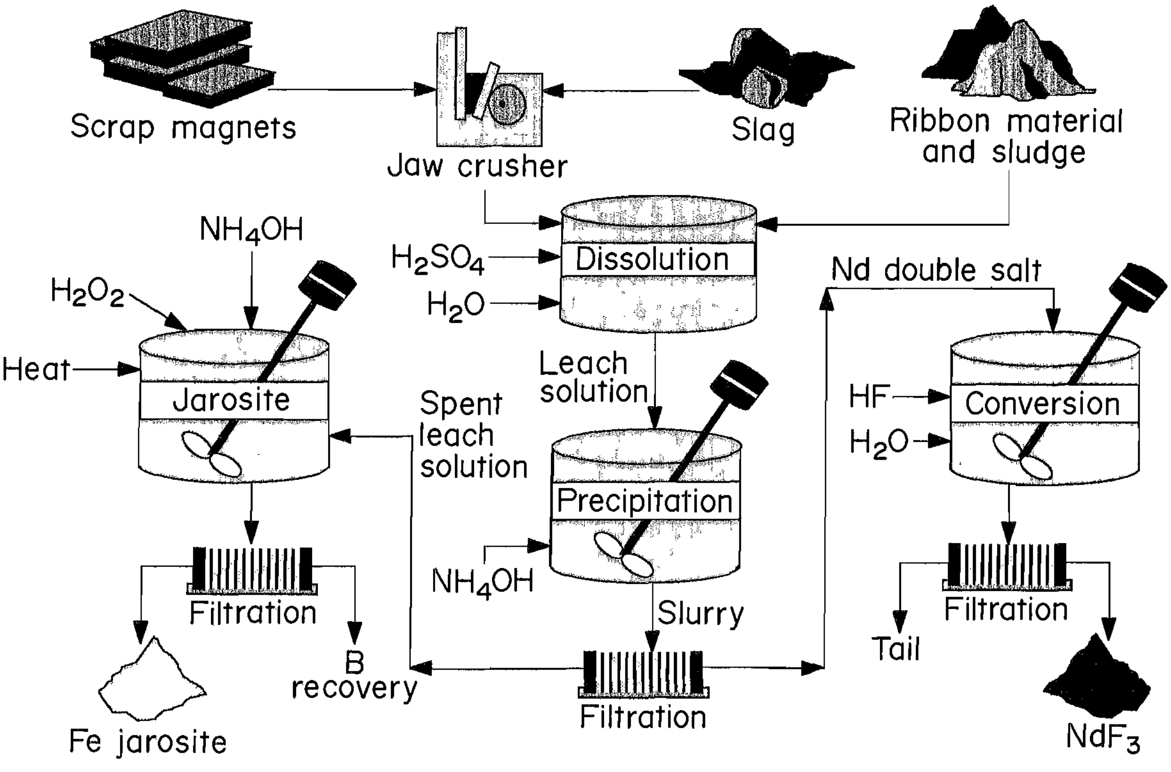

Figure 18.—Overall processing flowsheet.

TREATMENT OF GRINDING SWARF

In addition to the treatment of coated and uncoated bulk scrap pieces described in previous sections, an extensive investigation of grinding swarf generated during magnet fabrication was carried out. Two different varieties of swarf were studied: NdFeB swarf alone, and mixed swarf containing both NdFeB and $SmCo_5$ alloys. Mixed swarf is generated when grinding facilities do not have dedicated circuits for each type of alloy being handled. Both NdFeB swarf and mixed swarf contain cooling and lubricating oils, as well as grinding media such as Al_2O_3 and/or SiC.

NdFeB SWARF

Wet Versus Dry Leaching

Leaching, double-salt precipitation, and jarosite formation were carried out on two batches of NdFeB swarf that had not been degreased. In one test series, 100 g of wet swarf was leached; in the other, 100 g of wet swarf was first dried in air and then leached using the same amounts of acid and water as for the wet leach (1 L 2*M* acid). Results are presented in table 18.

Table 18.—Wet versus dry leaching of NdFeB swarf

Sample condition	Nd recovery in double salt, pct	Fe recovery in jarosite, pct	Fe remaining in leach residue, pct
Wet	98.07	27.11	15.76
Dry	98.33	30.14	24.28

Iron appears to be less amenable to leaching when the swarf material is dry. However, Nd leaches and precipitates effectively for both types of material. Drying is advantageous in that it reduces the amount of Fe that goes into solution and must be precipitated. Jarosite recovery also appears to be slightly enhanced when dried material is used.

Effect of Leach Time

A series of tests was carried out in 2*M* H_2SO_4 to study the effect of leach time on NdFeB swarf for the purpose of gaining data that could be applied to a continuous system. Table 19 represents results from these tests. The feed material analyzed, in percent, 2.94 Al, 0.767 B, 0.233 Co, 46.9 Fe, and 20.9 Nd. Traces of Ni, Sm, Mn, Cr, and Ga were also present. It can be seen from table 19 that a 5 min-leach time is adequate for complete leaching of unmixed swarf.

Table 19.—Effect of time on metal extraction during NdFeB swarf leaching

Time, min	Extraction, pct				
	Al	B	Co	Fe	Nd
2.5	20.96	93.07	11.93	95.45	97.95
5	13.04	97.09	15.73	97.13	98.91
10	15.13	98.85	33.55	98.67	99.42
15	18.15	98.30	27.01	98.94	99.32
20	19.42	98.94	46.06	98.67	99.60
30	17.98	99.01	57.31	98.68	99.59
60	16.38	99.34	93.54	99.07	99.86

MIXED SWARF

XRD analysis of mixed swarf head samples showed the presence of SiC, $Nd_2Fe_{14}B$, and $SmCo_5$. Some samples were merely air-dried, while others were washed in a variety of solvents. All samples gave identical XRD and X-ray fluorescence scans, indicating that the amount of grinding oil is minimal. A typical analysis, in percent, for swarf dried in air is 4.17 Al, 0.52 B, 14.00 Co, 7.01 Sm, 0.48 Cu, 37.20 Fe, 16.75 Nd, 0.40 Ni, and 0.18 Ga.

Single-Stage Leaching

Effect of Degreasing on Leach Behavior

Tests showed that degreased swarf material leached very differently from swarf material that was merely dried. When swarf was degreased with trichloroethylene in a Soxhlet extractor prior to leaching, the extraction percentages in 2*M* H_2SO_4 leach solution were 98.63 Nd, 98.67 Fe, 98.18 Sm, and 95.02 Co. When swarf was merely dried and not degreased, extraction percentages were 99.65 Nd, 93.02 Fe, 58.24 Sm, and 40.45 Co. Significant concentration of Sm in the leach residue occurs when the initial swarf material is untreated.

Effect of Acid Molarity

Untreated mixed swarf material was leached in H_2SO_4 solutions of varying concentrations. It was found that Nd and Fe leach quite effectively at all molarities of acid, but $SmCo_5$ does not. One hundred grams of swarf was added to 1 L of leach solution in each test, and the leach time was 24 h. The response of Nd, Fe, B, Sm, and Co is shown in figure 19, where the ordinate refers to the percent of material originally present that remains in the residue. The data conclusively show that the NdFeB portion of the scrap leaches as a discrete unit while $SmCo_5$ material responds differently. All of the scrap containing

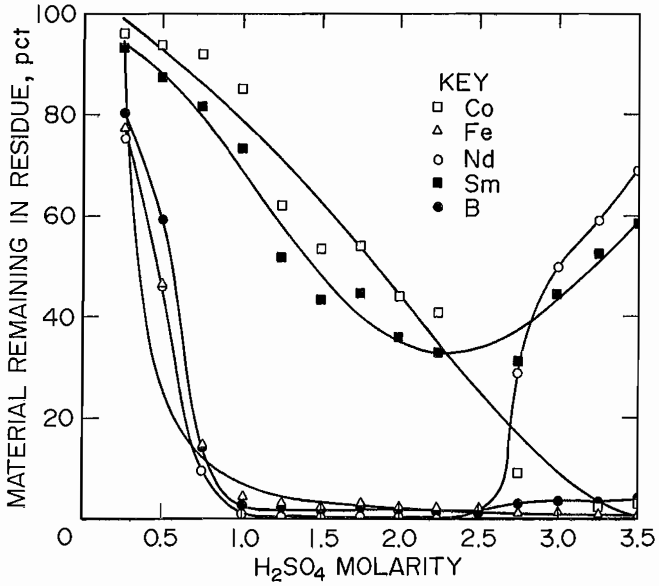

Figure 19.—Mixed swarf leaching behavior as a function of molarity (Co, Fe, Nd, Sm, B).

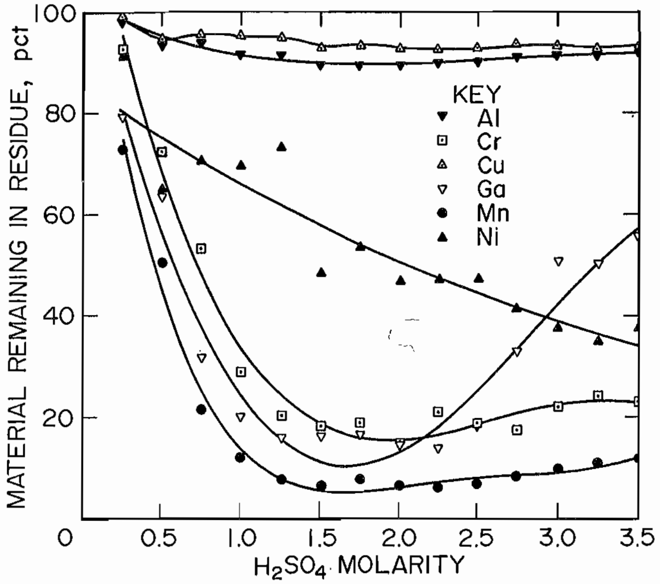

Figure 20.—Mixed swarf leaching behavior as a function of molarity (Al, Cr, Cu, Ga, Mn, Ni).

Nd can be effectively leached in 1*M* H_2SO_4, while over 80 pct of the $SmCo_5$ portion is unaffected. Both Nd and Sm begin to precipitate as sulfates above an acid molarity of about 2.5. The best separation of Sm from Nd is accomplished with acid concentrations between 0.75*M* and 1*M*. Figure 20 shows the leaching responses of Al, Cr, Cu, Ga, Mn, and Ni from the same test series. Aluminum and Cu show almost no variation with acid molarity despite the long leach time, while the other four elements are dramatically affected by the acid concentration.

Double-salt products were precipitated from each leach solution by raising the pH to 1.5 with NH_4OH. The amounts and colors of precipitates varied widely according to the initial concentrations of Fe and Co. Table 20 shows the precipitation results. It is obvious that above a molarity of 2, an additional pink salt begins to precipitate along with the rare-earth double salts. The formation of the additional salt appears to depend on both the solution concentration and the length of time during which solutions were allowed to settle prior to filtration. No pink salt formed at Fe and Co concentrations less than about 34 and 7 g/L, respectively, and the quantity of precipitate was very large in the 3*M* H_2SO_4 test, which was allowed to settle overnight. By contrast, the 3.25*M* H_2SO_4 test was filtered almost immediately, although it was noticed that pink salt did form in the sample bottle over time. The pink salt was characterized by XRD and found to consist of a combination of $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (mohrite), which have nearly identical scans.

Mixed Swarf Leaching With Added H_2SO_4 and $(NH_4)_2SO_4$

Tests were carried out to investigate the effect of reagent addition on double-salt production and eventual rare-earth recoveries. Varying amounts of H_2SO_4 and $(NH_4)_2SO_4$ were added to mixed swarf leach solutions, after which double salts were precipitated with NH_4OH. The formation of the pink salt was dependent upon the amount of reagents added. No pink salt formed at all when combined H_2SO_4 and $(NH_4)_2SO_4$ additions were less than 20 to 25 g. The formation of the pink salt was also investigated as a function of time. Purple double-salt products were collected immediately after settling (15 min), after which the spent leach solutions were allowed to stand. Pink precipitates were obtained after 24 h.

Reagent addition did enhance overall Nd recovery. The maximum Nd recovery obtained in this series of tests was between 75 and 80 pct. Neodymium did not continue to precipitate with the pink salt. In every case, the pink salt contained less than 1 pct Nd. The maximum Sm extraction was about 70 to 75 pct. Approximately 10 pct of the Sm precipitated in the pink salt at high acid and sulfate additions. Fifty-five percent of the Co and over 25 pct of the Fe were recovered in the pink salt at maximum H_2SO_4 acid and $(NH_4)_2SO_4$ additions.

Table 20.—Characterization of precipitates from solutions of different molarity

Molarity	Recovery, pct				Weight, g	Color
	Nd	Sm	Fe	Co		
0.5	0	0	0	0	NA	NA.
0.75	68.06	48.26	.05	.98	25.0	Purple.
1.0	71.97	58.51	.10	.61	33.1	Do.
1.25	75.83	59.50	.07	.29	36.8	Do.
1.5	76.46	65.35	.07	.22	42.4	Do.
1.75	75.97	63.81	.12	.24	38.1	Do.
2.0	78.54	68.41	19.37	42.91	106.2	Pink.
2.25	78.12	66.23	15.29	28.56	90.2	Do.
2.50	76.41	65.76	5.58	12.90	59.6	Purple-pink.
2.75	68.22	62.28	25.78	55.00	130.3	Pink.
3.0	82.63	77.42	50.69	84.00	217.8	Do.
3.25	45.66	37.92	.05	.06	12.2	Purple.
3.5	1.21	12.61	4.97	11.54	21.8	Pink.

NA Not available.

Effect of Leach Time

Figure 21 shows a plot of the percentages of Nd, Fe, Sm, Al, and Co that remain in the leach residue from 1*M* H_2SO_4 leaching as a function of time. After 1 h, over 80 pct of the Nd and Fe have leached, while over 80 pct of the Sm and Co remain in the residue. Leaching of Sm and Co was relatively unaffected by time. Results using 2*M* acid are shown in figure 22; it can be seen that Sm and Co leaching is significantly affected by time in 2*M* acid. Over 90 pct Al reports to the residues in these tests.

Effect of Agitation

Agitation of the leach solution was only marginally advantageous in increasing the extent of Al, Nd, Fe, Sm, and Co dissolution.

Two-Stage Leaching

Because the $SmCo_5$ alloy tends to concentrate in the leach residue when swarf is not degreased, it is possible to treat mixed swarf in a two-stage leach process whereby a

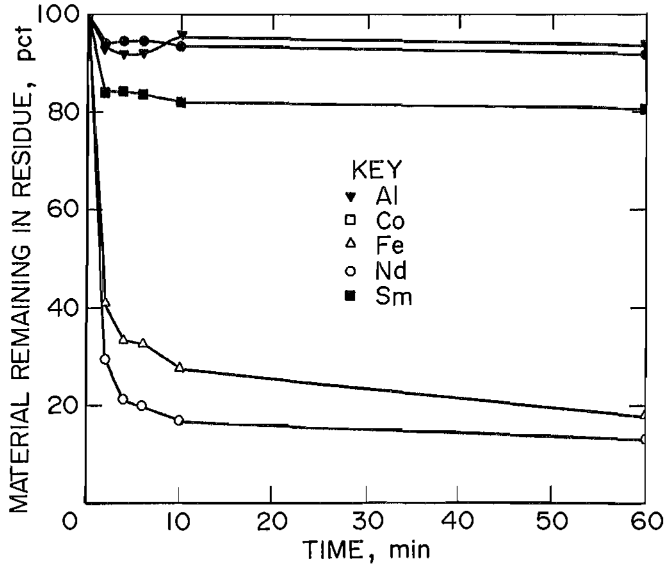

Figure 21.—Effect of time on leaching of mixed swarf in 1*M* H_2SO_4.

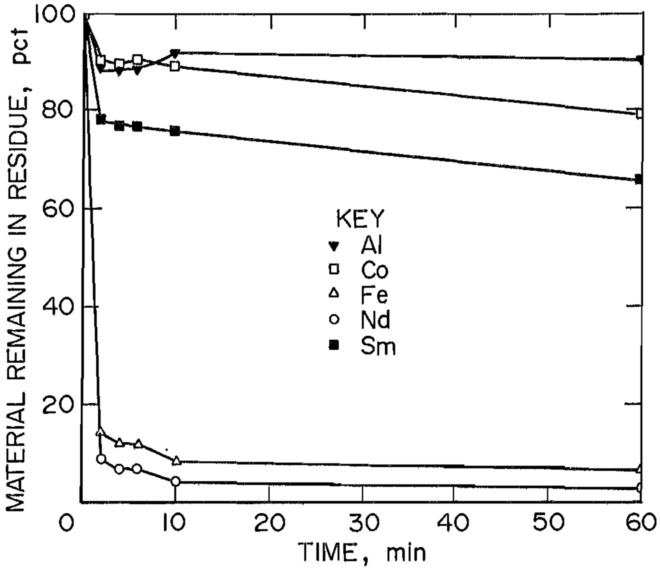

Figure 22.—Effect of time on leaching of mixed swarf in 2*M* H_2SO_4.

crude initial separation is made. In the first leach, raw, untreated swarf material was added to 2*M* H_2SO_4 to produce a Nd-Fe-rich leach solution (L1) and a $SmCo_5$-rich leach residue (R1). L1 was then treated with NaOH to produce a Nd-rich double salt precipitate (P1) and an Fe-rich spent solution (S1) from which a jarosite product was recovered (J1). This jarosite was very spongy and light in texture and was found by XRD to be metasideronatrite $[(Na_4Fe_2(SO_4)_4 \cdot 3H_2O)]$. The spent jarosite solution (SJ1) contained some dissolved Fe and Co. R1 was then degreased and leached to produce a Sm-Co-rich leach solution (L2) and a second leach residue (R2). A Sm-rich double salt (P2) was precipitated from L2 using NaOH. The spent solution (S2), which contained more Co than Fe, was subjected to jarosite processing to produce a second jarosite (J2) and a Co-rich solution (SJ2). A flowsheet of the overall process is shown in figure 23. A final, Co-rich precipitate (P3) and spent solution (S3) can also be obtained by neutralizing the SJ2 stream with NaOH, although they are not depicted in figure 23.

Table 21 shows the percentages of original material present that report to different final processing streams based on an original weight of 100 g. The number of grams of each element reporting to each stream was calculated and then totaled. These totals were found to be very close to actual head values and so were used in calculating the recoveries presented in table 21, in effect normalizing the data to 100 pct. Data in table 21 show that leaching and precipitation can quite effectively concentrate the various elements initially present into different final process streams. A two-stage process like this one would greatly reduce the number of solvent extraction stages needed to produce final Sm and Nd concentrates. In addition, it is clear that the bulk of the Co can be recovered separately from Fe.

A statistically designed test series was carried out to study main and interactive effects of leach time and acid molarity on leaching of mixed swarf. A two-level factorial design was used with acid molarity varying from 0.5 to 2.5 and with time varying from 2 to 32 min. Analysis of the head material, in percent, was 20.4 Nd, 45.6 Fe, 3.82 Sm, and 8.20 Co. Equations fitting the test results are shown below for Nd and Sm extractions:

$$\text{Nd ext. (pct)} = 27.6 + 28.6(A) + 0.51(B) - 0.20(A)(B), \quad (5)$$

and

$$\text{Sm ext. (pct)} = 3.33 + 12.3(A) - 0.03(B) + 0.16(A)(B), \quad (6)$$

where A is acid molarity and B is leach time in minutes. Such equations can be used to predict the best conditions for achieving the maximum Nd extraction while minimizing that of Sm. Neodymium and Sm extractions can be seen to depend most heavily on acid concentration, although the time factor also is important in regard to Nd extraction. The equations predict that a 1*M*, 1-h leach of mixed swarf would extract 74.2 pct Nd but only 23.4 pct Sm.

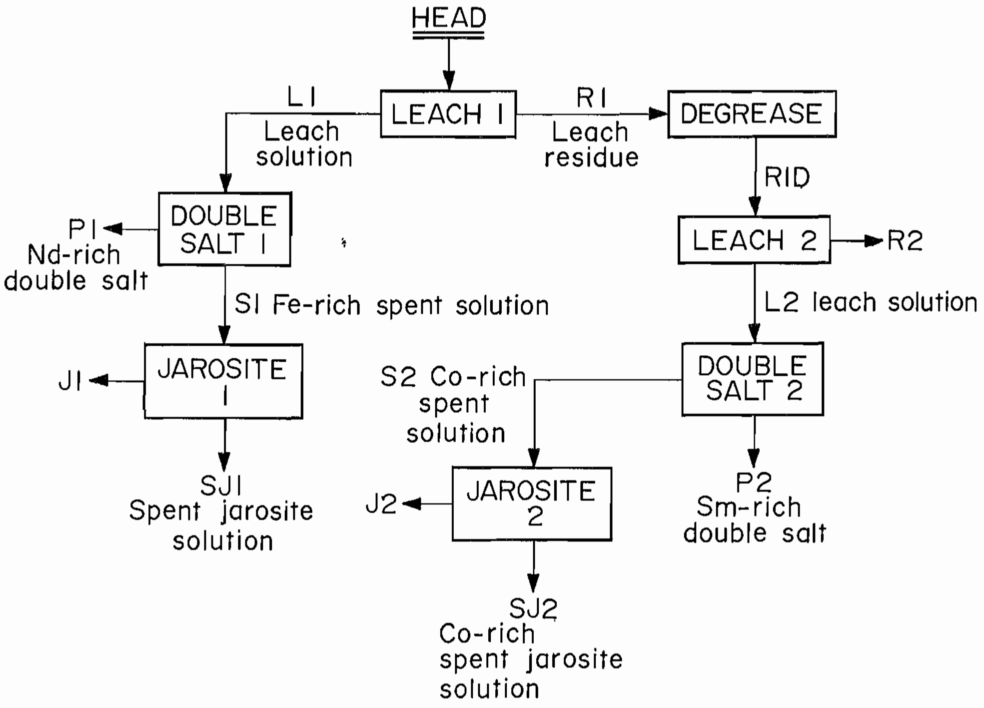

Figure 23.—Two-stage recovery scheme for treatment of mixed swarf.

Secondary Leaching of Leach Residues

A composite $SmCo_5$-rich leach residue was obtained from 1*M* leach tests. Half of this residue was degreased, and the other half was not. The untreated half analyzed, in percent, 13.3 Al, 26.8 Co, 0.039 Cr, 0.282 Cu, 1.98 Fe, 0.080 Ga, 0.59 Nd, 0.304 Ni, and 11.8 Sm. The degreased half analyzed, in percent, 10.1 Al, 31.1 Co, 0.044 Cr, 0.299 Cu, 1.75 Fe, 0.095 Ga, 0.548 Nd, 0.340 Ni, and 13.6 Sm. Both residues were leached at four different H_2SO_4 molarities for 24 h to determine the best conditions for producing a concentrated $SmCo_5$ leach solution.

The test results summarized in table 22 indicate that high extractions of Sm and Co cannot be achieved at the molarities studied unless the residue is first degreased. An acid molarity of 1 to 1.5 is adequate for maximum $SmCo_5$ recovery and also yields the best recovery for the remaining Nd and Fe. Aluminum and Cu leached very poorly under all test conditions studied, while Cr, Ga, and Ni were extracted more efficiently from the degreased material. Sodium double salt obtained from degreased-residue solutions contained 30 pct Sm and 2 pct Nd.

A second statistically designed test series was carried out to study the effects of leach time and acid molarity on secondary leaching of mixed swarf leach residues from which the bulk of the Nd and Fe had already been removed. The feed analysis, in percent, was 5.78 Al, 28.5 Co, 14.7 Fe, 3.84 Nd, and 13 Sm. The predictive equations are given below, where, as before, A is acid molarity and B is leach time in minutes.

$$\text{Nd ext. (pct)} = 36.4 + 22.1(A) + 1.20(B) - 0.42(A)(B), \quad (7)$$

and

$$\text{Sm ext. (pct)} = -0.29 + 5.67(A) - 0.02(B) + 0.21(A)(B). \quad (8)$$

Equations 5 through 8 show that a counter-current leach process could be designed that would be an effective way to process mixed swarf material; Sm would be extracted with strong acid and Nd with spent acid. Although the acid concentration would need to be very high to recover the remaining Sm (thereby leaching all of the remaining Nd), the resulting leach solution would be concentrated with respect to Sm.

Table 21.—Metal distribution reporting to different processing streams, percent

Stream	Nd	Sm	Fe	Co	Al	Ni	Cu	B
P1	86.58	28.10	0.30	0	0	0	0	0
J1	1.48	0	67.55	3.38	0	0	0	14.88
SJ1	.21	.38	18.40	16.53	2.54	18.70	0	72.33
R2	.59	2.64	.59	2.22	97.33	0	100	0
P2	10.82	64.96	.30	1.26	0	0	0	0
J2	.30	3.47	10.37	.96	0	0	0	0
P3	0	.50	2.49	75.61	0	81.30	0	0
S3	0	0	0	0	.17	0	0	12.79

Table 22.—Extraction of $SmCo_5$-rich residue (degreased and untreated) at different H_2SO_4 molarities, percent

Molarity	Sm	Co	Nd	Fe	Al	Cr	Cu	Ga	Ni
Untreated:									
0.5	51.2	48.3	76.9	81.8	0.8	41.8	3.9	44.1	46.8
1.0	81.3	78.4	89.1	89.9	1.3	62.8	7.9	58.6	67.5
1.5	89.0	90.9	90.2	85.6	1.4	67.0	6.2	63.5	72.4
2.0	79.6	94.8	85.5	88.7	1.4	67.9	6.5	61.4	74.1
Degreased:									
0.5	72.0	68.8	78.5	68.7	.8	42.4	3.9	56.9	63.8
1.0	97.3	96.0	93.0	92.8	1.4	71.4	9.3	72.1	77.8
1.5	98.7	97.8	99.7	99.4	4.0	84.1	15	88.8	81.1
2.0	90.1	96.9	82.8	92.0	1.3	61.1	7.4	53.9	72.5

Investigation of Double-Salt Solubilities

Double salts generated from mixed swarf contain both Nd and Sm, which need to be separated by a solvent extraction or ion exchange process. Before this can be accomplished, however, the double salt must be put into solution. The solubility of mixed double salts in a variety of media was investigated. Mixed Na and NH_4 double salts were quite soluble in 4*M* HCl. The solubility of the double salts in Na_2SO_4 solution was also investigated. The Na double salt was found to be insoluble, and the NH_4 double salt reacted with $NaSO_4$ solution to produce insoluble Na double salt.

Water leaching was also examined, and it was found that when 50 g of NH_4 double salt was added to 500 mL of H_2O, 24.12 g dissolved. When 10 g of Na double salt was added to 200 mL of H_2O, only 1.99 g dissolved. Owing to its greater solubility, the NH_4 double salt would be preferred industrially from the standpoint of eventual Nd and Sm separation.

Jarosite Production

Iron recoveries in the jarosite produced from mixed swarf leach solutions tend to be lower than for scrap, possibly owing in part to the presence of grinding oil and also owing to the lower Fe concentration in the starting solution. Direct comparisons of degreased versus untreated material show enhanced Fe removal from degreased material. Mixed swarf contains on average half as much Fe as regular scrap; thus, 50 mL of H_2O_2 per liter of spent leach solution should be adequate to oxidize all of the Fe. However, batch jarosite tests only produced Fe recoveries between 20 and 50 pct. The recovery was increased to 71 pct when 100 mL was used. It is apparent that increasing the amount of H_2O_2 aids jarosite formation, exceeding the requirements for adequate Fe oxidation.

FLOTATION-LEACH OF MIXED SWARF

When swarf is leached, the rapid dissolution of NdFeB particles generates vigorous bubbling action as H_2 gas is evolved. Tests were carried out in which the natural foaming properties of mixed swarf leach samples were utilized in a flotation cell to produce a concentrate and tail stream with widely different compositions.

Beaker Tests

Mixed swarf samples were slowly added to a 2*M* H_2SO_4 solution in a 900-mL beaker which had been placed in a collection pan. As the leach reaction proceeded, a concentrate of froth and entrained solids overflowed from the beaker. After all of the swarf had reacted, a concentrate product and solution were obtained from the pan, and a tail product and solution remained in the beaker. A materials balance for this test is given in table 23.

Table 23.—Metal distribution of beaker test products, percent

Stream	Al	Co	Fe	Nd	Sm
Solid:					
Concentrate	23.76	87.46	6.20	3.02	73.40
Tail	70.61	.63	.74	<.10	.49
Total	94.37	88.09	6.94	3.12	73.89
Filtrate:					
Concentrate	1.49	2.93	27.71	25.15	6.20
Tail	4.14	8.98	65.35	71.73	19.91
Total	5.63	11.91	93.06	96.99	26.11

Flotation-leach quickly accomplished a three-way preliminary separation of NdFeB, $SmCo_5$, and grinding media. XRD scans of the concentrate and tail materials showed that $SmCo_5$ concentrates in the froth, while SiC and corundum concentrate in the tail. NdFeB leaches rapidly and remains in the solution with a total recovery approaching 97 pct.

Several tests were performed in which acid was added to a swarf slurry. In these tests, 12 pct of the Co and 10.5 pct of the Sm reported to the tail solid product, and over 80 pct of the Al ended up in the concentrate. Evidently the sequence of processing is a critical factor. Swarf must be added to an acid-water mixture if efficient separation is to be achieved.

Conventional Flotation Cell

Mixed swarf was float-leached using a conventional Denver flotation cell. Swarf was added first to form a water slurry into which acid was introduced. It was hoped that the cell would promote the separation by enhancing particle mixing. Test results showed that increasing the acid molarity enhanced the recovery of Fe and Nd in the tails and concentrate filtrates, but the flotation cell was no more effective than the beaker in achieving a clean concentrate. The flotation cell is also undesirable in that it causes a much larger amount of $SmCo_5$ to be carried into the tail product, although it is more efficient in removing the Al. The tail recoveries of Sm, Co, and Al were 36.7, 39, and 76.5 pct respectively.

Several tests were performed in which mixed swarf was leached for different lengths of time at different acid molarities. During leaching, the froth that formed on the top of the solution was stirred periodically with a glass rod to ensure adequate exposure of all material to the acid. The froth was then removed using a suction device that consisted of a hose attached to a vacuum flask. Five hundred milliliters of water was placed in the vacuum flask prior to each test to neutralize the concentrate product as it was removed, thereby preventing further leaching of Co and Sm. Table 24 summarizes the results obtained from the concentrate product. Table 25 shows the behavior of elements reporting to the concentrate and tail solutions combined. In each test the tail products contained approximately 20 pct Al and very little pct Nd, Fe, Sm, and Co. Aluminum reports to the concentrate more readily in higher molarity acid. Cobalt dissolution is not greatly affected by time for 1*M* and 1.5*M* H_2SO_4, but it shows a more dramatic dissolution response in 2*M*. The same trend can be seen for Sm. Therefore, if 2*M* acid is used, residence times must be less than about 8 min to minimize $SmCo_5$ losses in solution. Neodymium and Fe behavior is most sensitive to acid molarity and is dramatically affected by time at lower acid concentrations.

Table 24.—Suction flotation leaching—concentrate recoveries

Acid molarity	Time, min	Recovery, pct				
		Al	Co	Fe	Nd	Sm
1	15	68.92	85.69	11.75	6.96	71.34
	12	57.47	89.54	21.21	12.72	78.23
	10	61.09	89.80	22.64	13.56	78.04
	8	53.14	91.14	28.56	17.43	79.00
	6	71.96	89.30	27.43	16.27	75.50
	4	52.99	90.78	25.69	16.06	79.58
	2	62.30	90.77	37.32	24.04	79.42
	0	58.89	91.82	49.13	33.46	80.53
1.5	12	74.80	86.70	10.18	5.65	78.28
	10	68.14	88.28	15.35	9.38	76.00
	8	72.35	88.43	15.64	9.71	76.10
	6	62.80	89.22	16.49	9.37	76.53
	4	67.70	89.97	19.09	11.31	82.00
	2	74.25	87.99	19.29	11.79	79.84
2	15	72.83	81.92	5.75	2.31	70.71
	12	79.93	84.69	6.63	3.24	71.22
	10	74.37	85.49	8.13	4.22	72.32
	8	81.07	86.42	7.18	3.15	73.30
	6	71.45	87.92	8.26	3.67	74.86
	4	70.63	89.65	9.66	4.38	76.46
	2	73.51	90.43	12.23	6.58	77.93
	0	61.44	90.04	10.22	4.97	77.24

Table 25.—Suction flotation leaching—combined filtrate recoveries

Acid molarity	Time, min	Recovery, pct				
		Al	Co	Fe	Nd	Sm
1	15	10.98	11.88	87.18	92.24	26.78
	12	8.00	6.88	76.73	86.27	19.52
	10	7.78	7.07	76.07	85.81	19.55
	8	8.40	6.52	70.55	82.12	19.11
	6	4.97	7.16	70.03	81.90	21.61
	4	9.82	7.03	73.16	83.21	18.75
	2	8.81	6.52	61.54	75.58	18.56
	0	5.46	6.84	50.26	66.39	18.55
1.5	12	10.79	11.77	89.34	94.20	20.57
	10	10.86	9.41	83.18	90.14	22.67
	8	9.73	9.86	83.80	89.97	22.42
	6	13.63	9.44	83.15	90.49	22.35
	4	8.25	8.55	80.38	88.46	16.66
	2	8.38	9.14	79.87	87.87	17.69
2	15	11.23	17.00	93.98	97.63	28.44
	12	8.49	14.32	93.10	96.70	27.98
	10	9.75	12.86	91.40	95.60	26.34
	8	7.24	10.93	92.48	96.74	25.73
	6	8.48	9.33	91.41	96.31	24.35
	4	7.58	8.33	90.10	95.60	22.74
	2	8.59	7.92	87.39	93.36	21.20
	0	12.53	2.04	89.34	94.90	21.06

Approximately equivalent results can be obtained with several sets of operating parameters: (1) 1*M* acid for 15 min, (2) 1.5*M* acid for 12 min, and (3) 2*M* acid for 8 min or less.

Column Flotation Leaching

Because previous test work showed that simultaneous leaching and floating of mixed swarf was an effective means of achieving efficient separation of $SmCo_5$ material from NdFeB, further tests were designed to investigate the system behavior in flotation columns. Tests were carried out using 3-ft, 4-ft, and 8-ft flotation columns. A 2*M* H_2SO_4 lixiviant was used in all of the column experiments. Figure 24 schematically portrays what was expected to take place within the operating columns. As a mixture of NdFeB, $SmCo_5$, and grinding-medium particles entered the column filled with leach solution, the NdFeB particles dissolved in the H_2SO_4 solution, producing H_2 bubbles. The bubbles attached to the hydrophobic $SmCo_5$ particles and caused them to float to the top of the column, where they were removed as a concentrate. The hydrophilic grinding-medium particles then settled to the bottom of the column, where they could be removed as a tailing.

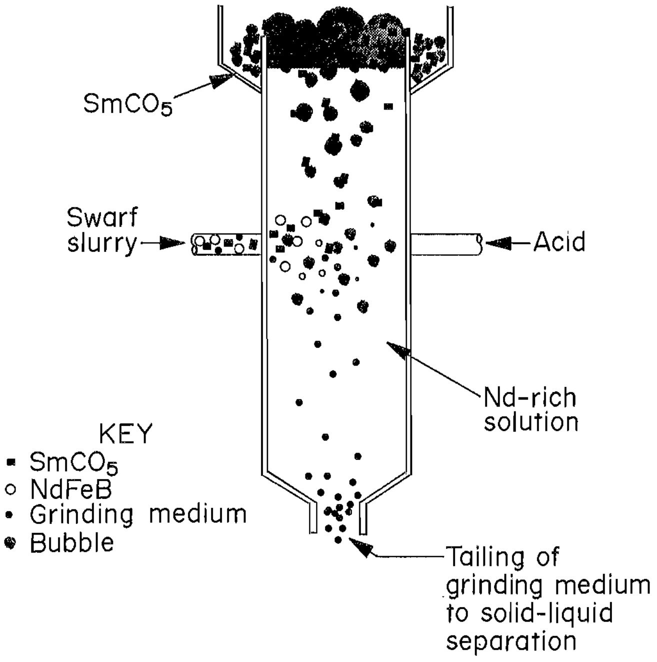

Figure 24.—Schematic of flotation-leach processing of mixed swarf.

During some of the experiments, makeup acid was continuously added at the same rate as the slurry feed to offset dilution of the system due to the slurry water. In one test, the acid line was divided, and makeup acid was added both above and below the swarf inlet. Impellers were used at the froth-slurry interface in each test. Table 26 shows what percent of original constituents report to the concentrate for a variety of tests.

Table 26.—Comparison of concentrate product recoveries from column tests

Reactor flotation column, ft	Makeup acid	Recovery, pct				
		Al	Co	Fe	Nd	Sm
3	None	39.09	73.31	8.83	2.44	63.53
4	4.5*M*	68.47	52.30	3.55	.59	44.66
	None	34.08	66.72	5.08	.82	58.53
8	None	50.68	60.67	4.85	.71	51.52
	2*M*	56.08	68.11	18.25	14.19	59.80
	2*M*	39.72	68.04	17.13	18.55	60.51

Examination of the data shows that the 3-ft column was as effective as any of the column lengths in achieving an efficient separation. The column tests using the 4-ft column with no makeup acid gave the best separation. Several important observations were noted during these tests:

1. $SmCo_5$ extractions were independent of initial concentration in the feed. Neodymium and Fe, however, leached more completely when their original concentrations were higher and those of $SmCo_5$ were lower.
2. Longer residence times aided Fe and Nd leaching. Aluminum reported to the tail stream more efficiently also.
3. Adding the swarf in slurry form achieved a more effective separation than adding it dry.
4. When a water wash was used on the flotation froth, all extraction values decreased, rendering the overall process less efficient.
5. Addition of an impeller at the top of the cell improved the Al separation, but it caused an increase in the leaching rate of $SmCo_5$, probably owing to enhanced diffusion of reactants through the organic coating on the surface of $SmCo_5$ particles in untreated swarf.

CONCLUSIONS

As a result of the experiments conducted to evaluate potential recycling schemes for rare-earth, transition metal permanent magnet scrap, the following conclusions were reached.

Selective oxidation with a controlled H_2-water vapor gas mixture successfully oxidized the Nd in NdFeB magnet scrap ribbon material while leaving Fe in metallic form. Separation of the Nd_2O_3 from the Fe phase, however, was not possible with dilute leaching or with magnetic separation techniques. The oxidized phase and the metallic Fe phase are too intimately mixed to be easily separable.

A process for leaching NdFeB scrap with H_2SO_4 was developed and refined. H_2SO_4 dissolution was easily accomplished, requiring neither heating nor agitation. An acid weight two times that of the scrap weight was needed for complete dissolution at a molarity of 2. Sodium and NH_4 double-salt precipitation of Nd from an H_2SO_4 solution was investigated and optimized. Precipitation of the Na or NH_4 rare-earth salt had no attendant filtration problem and effectively separated Nd from Fe. Conversion of the double salts to NdF_3 was studied, and the best conditions for product purity were determined. A filterable fluoride product was generated from both the Na and the NH_4 systems without introducing contaminating F^- into the Fe-rich stream resulting from Nd precipitation. Iron removal from spent leach solutions was accomplished through precipitation of a potentially useful jarosite product. Iron recovery values close to 100 pct were obtained. Finally, B can be recovered separately in a usable form such as zinc borate hydrate. Preliminary cost analysis showed the process to be economically viable.

Neodymium metal alloy could be produced from scrap using the USBM-developed process. A satisfactory metal biscuit was obtained using NdF_3 prepared by recycling NdFeB scrap. The Nd recovery was 80 pct, which is equivalent to that obtained using virgin raw materials. Production of this biscuit demonstrated that the recycle process can be carried to completion.

A flotation-leach process developed to treat mixed swarf shows excellent potential for returning a concentrated $SmCo_5$ product that would have high value.

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