SULFATION ROASTING AND LEACHING OF SAMARIUM-COBALT

MAGNET SWARF FOR SAMARIUM RECOVERY

by

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ABSTRACT

During production of samarium cobalt magnets, a large amount of magnetic swarf is generated due to milling and cutting. This can accrue up to 30% of input materials. Recycling end-of-life magnets is equally important as these materials are critical components of aging green energy systems and a variety of electronic components. Samarium is currently listed as one of the semi-critical materials by the Critical Materials Institute and the Department of Energy. This report describes a novel sulfation, roast and leaching process for the recycling and reuse of samarium from samarium-cobalt magnet waste.

Three stages are necessary for this process. The steps begin with sulfate conversion during acid roasting, selective thermal decomposition at higher temperatures, and leaching in demineralized water. This process is capable of separating samarium from cobalt, iron, and copper into a greater than 95% purity samarium sulfate leach solution.

Several factors were tested to identify the parameters that exert the highest effect on samarium sulfate grade and overall recovery in the leach solution. These include acid addition, temperature, residence time, mixing, gas flow rate, and gas composition. Preliminary muffle furnace tests produce a samarium sulfate product with over 99% purity. Rotary kiln experiments were conducted to better control mixing and atmospheric conditions within the reactor vessel. Complete sulfate conversion was achieved with 40% excess sulfuric acid at 400°C and a 15 minute residence time. Several stages of acid-roasting, residue recycling, and leaching may increase the final leach solution samarium sulfate grade and recovery. Better control of sulfur dioxide partial pressure in the reactor may also enable more selective roasting conditions.

This process is only viable if built with or alongside an existing sulfur recovery system such as an acid plant. Net present value after five-years with an acid plant is $2.2 million whereas the project is unfeasible without sulfur recovery. This is based on a two stage roasting process and treatment of 1000 tonnes per year of samarium-cobalt magnet waste. Based on the success of the results from this study, this process is highly recommended for immediate pilot-scale testing.

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CHAPTER 1

INTRODUCTION

Sulfation roasting and leaching is a process which begins by converting metals, oxides, or sulfides into sulfates. These sulfates are then roasted at specific temperature ranges to preferentially oxidize certain species before cooling and leaching in water. Most metal oxides are insoluble in neutral water and are thereby separated from the sulfates during leaching. Occasionally, the final products of this process include dissolved metal sulfates with similar decomposition temperatures which require further processing through ion exchange or solvent extraction to produce pure products.

Samarium and cobalt represent a major expense to magnet manufacturing companies due to their scarcity and high costs. This makes them ideal materials for recycling. The most common types of Sm-Co magnets consist of 1:5 or 2:17 samarium to cobalt ratios. During production, a large amount of magnetic swarf is generated due to milling and cutting accruing up to 30% of input materials. Recycling end-of-life magnets is equally important as these materials are critical components of aging green energy systems such as wind turbines and a variety of electronic applications. It is reasonable to assume that demand for cost effective recycling process will increase in the coming years.

The behavior of cobalt and iron in sulfation-roasting-leaching processes is well documented in the literature (Gallagher et al., 1970; Guo et al., 2009; Kar et al., 2000). However, the application of this process for samarium and the rare earth metal recovery has received little attention. Several studies have investigated the thermal decomposition of individual rare earth sulfates (Poston et al., 2003), but few have examined this process for complex ores and alloys. This study will investigate the sulfation-roast and leaching process for samarium-cobalt magnet swarf and determine the effects of acid addition, roasting temperature and time, pulp density, gas composition and flow rate, and mixing on samarium product quality and recovery.

1.1   Overview of Sulfation Roasting

Sulfation roasting is a pyrometallurgical process used in the beneficiation of metal oxide ores through conversion of oxides to sulfates before subsequent leaching in water. Magnet swarf typically consists of sintered alloy fragments created through cutting and grinding which may be impermeable

to SO_3 diffusion or incompletely oxidized. In order to react with these materials, the physical structure of the material must first be altered and the metal converted to an oxide. In one reaction mechanism, metals are first converted to oxides then with $SO_3(g)$ to form sulfates through the following reactions:

$$Me + ½ O_2(g) = MeO$$

$$MeO + SO_3(g) = MeSO_4$$
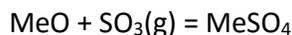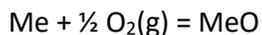
These reactions are spontaneous at temperatures above 300°C for samarium and cobalt and complete sulfation is possible. In another mechanism, sulfates are formed as precipitates during drying of saturated metal sulfate solutions.

$$MeO + H_2SO_4 = MeSO_4 + H_2O$$
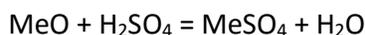
Sulfuric acid first dissolves metal oxides into their sulfate ion complexes. This is followed by drying to form metal sulfate precipitate. The solid product can be further purified through selective thermal decomposition. In the roasting stage, sulfates are placed in a furnace with temperatures exceeding 700°C. The selective oxidation of iron and cobalt is possible in this temperature range while samarium sulfate remains stable (Error! Reference source not found.).

There is a difference in the decomposition temperature between samarium and cobalt resulting in the possibility to preferentially oxidize cobalt sulfate from samarium above 740°C. Effective separation of samarium from the base metals is theoretically possible at baking temperatures between 740-800°C. Experiments performed in this study are based on the differences in thermal stability of samarium, cobalt, copper, and iron sulfates.

1.2   Case Study –Sulfation-Roast and Leaching of Nickel-Cobalt Laterite

Sulfation-roast-leaching has been utilized on a variety of ore types but is most commonly known for its treatment of nickel-cobalt laterites. A valuable case study of this process is presented by Guo et al. (2009). This process is much less expensive to treat iron-rich ores than smelting or high-pressure acid leaching methods. Operating temperatures in sulfation-roast and leaching processes are much lower than in smelting operations (above 1000°C) and the capital and operating costs are lower than high pressure acid leaching.
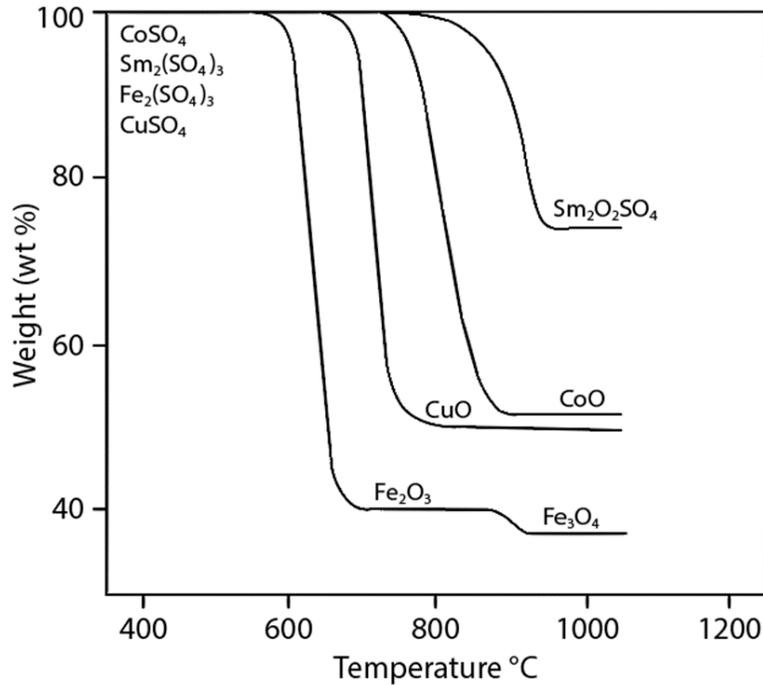
Figure 1.1: Thermogravimetric analysis of pure compounds: (1) $CoSO_4$, (2) $Sm_2(SO_4)_3$, (3) $CuSO_4$, and (4) $Fe_2(SO4)_3$. Modified from (Kolta and Askar, 1975; Paama et al., 2005).

The first step of any sulfation-roasting process is to first convert the targeted metals into sulfates. This process can be accomplished through one or more of the following reactions:

$$MeO + H_2SO_4 = MeSO_4 + H_2O$$

$$Me + 1/2\ O_2 = MeO \quad or \quad 2Me + 3/2\ O_2 = Me_2O_3$$

$$MeO + SO_3 = MeSO_4 \quad or \quad Me_2O_3 + 3SO_3 = Me_2(SO_4)_3$$
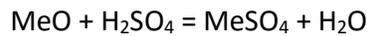
where *Me* represents the metal species in question. This process is thermodynamically favorable and highly exothermic for cobalt, nickel, and iron. The major limiting factors in sulfation are the amount of sulfuric acid or sulfur trioxide gas that is added.

1.2.1   Effects of Acid Addition

In the study by Guo et al. (2009), the effect of acid addition, roasting temperature, and roasting time were compared against metal extraction as sulfates. Extraction was calculated based on head grade of the starting material versus the amount of metal sulfate ions present in the leach solution. Leaching was conducted in demineralized water. The first experiment was designed to

determine the effect of acid addition on the overall recovery (extraction %) of metal sulfates in the final leach solution (Figure 1.2).
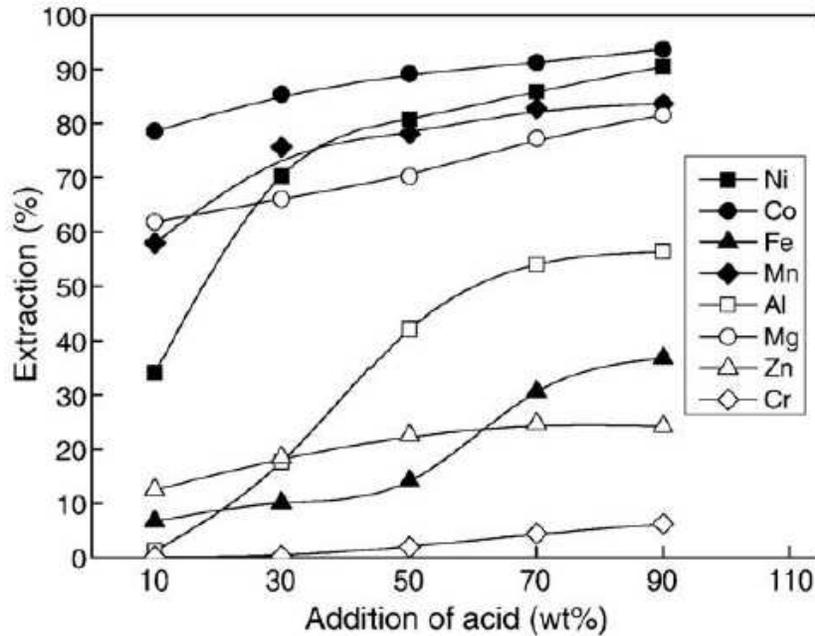
Figure 1.2: Effect of addition of sulfuric acid on metal extractions (roasted 700°C for 30 min; leach solid/liquid ratio: 50 g/L). From Guo et al. (2009).

It is shown that for nickel and iron, higher acid concentrations resulted in higher amounts of extraction while cobalt recovery remained high regardless of acid addition. This suggests that the sulfate phase of cobalt may be more thermodynamically favorable and stable than nickel or iron sulfate.

There are multiple possibilities as to why more iron and nickel were recovered with higher acid molarities. It may have been due to higher initial conversion rates of metal oxides to sulfates with higher acid addition. Larger amounts of sulfur in each test may also result in higher partial pressures of sulfur dioxide in the reactor vessel preventing metal sulfate conversion to oxides.

These tests failed to test several important variables involving sulfation including mixing of the initial slurry and gas composition during sulfation. They also failed to determine the exact mechanism for sulfation. Samples from each test were first mixed with acid and allowed to dry overnight before insertion into a pre-heated muffle furnace for roasting tests. It is possible that the

initial material formed a sulfate precipitate during overnight drying or formed sulfate due to high partial pressures of sulfur dioxide or trioxide gases during roasting. Both mechanisms are thermodynamically feasible but the exact process is unknown.

The author briefly attempts to explain the ability of concentrated sulfuric acid to oxidize elemental metals in the starting material thereby allowing subsequent sulfation. However, the testing of this theory appears less than comprehensive. Likewise, no attempt was made to determine any high-temperature sulfation processes that may have occurred. Reactor conditions are also poorly controlled with little regulation of gas composition or mixing of the samples. A more detailed description of the reaction mechanism and greater control over reactor conditions could greatly improve the results from this study. An accurate sulfation reaction model could lower acid requirements and the time required for sulfation.

1.2.2 Effects of Temperature and Time

Roasting temperature and time are the two most important factors during roasting of sulfate concentrates. The decomposition of metal sulfates can be simply represented as below:

$$1/n \ Me_2(SO_4)_n = 1/n \ Me_2O_n + SO_3 \ (n = 2 \ or \ 3)$$

The theoretical decomposition temperature of iron is between 600-650°C, which is lower than other valuable base metals in laterites such as nickel or cobalt (700-800°C). By controlling the temperature of the reaction vessel to be approximately 700°C, it is possible to selectively oxidize iron while nickel and cobalt remain as sulfates (Figure 1.3). Recoveries of cobalt and nickel between 80-90% are possible with minimal iron recovery (<10%) after 30 minutes of roasting. The effect of time on this process appears to be the most effective up to 60 minutes resulting in complete oxidation of iron (Figure 1.4). Other species such as nickel, cobalt, manganese, magnesium, and zinc do not indicate any major changes in overall extraction with time at 700°C. This indicates that the decomposition temperatures for these metals is higher than 700°C. Aluminum, chromium, and iron sulfates appear to have decomposition points below 700°C.

The extraction of iron as insoluble oxide is further supported by XRD analysis of the residue (Figure 1.5). It is shown that the formation of hematite becomes the dominant phase beginning at 700°C and is completed at 800°C after a roasting duration of 30 minutes at each temperature. The

presence of iron sulfate at 700°C is due to the fact that the samples were run for only 30 minutes instead of the 60 minutes required to completely oxidize the iron.
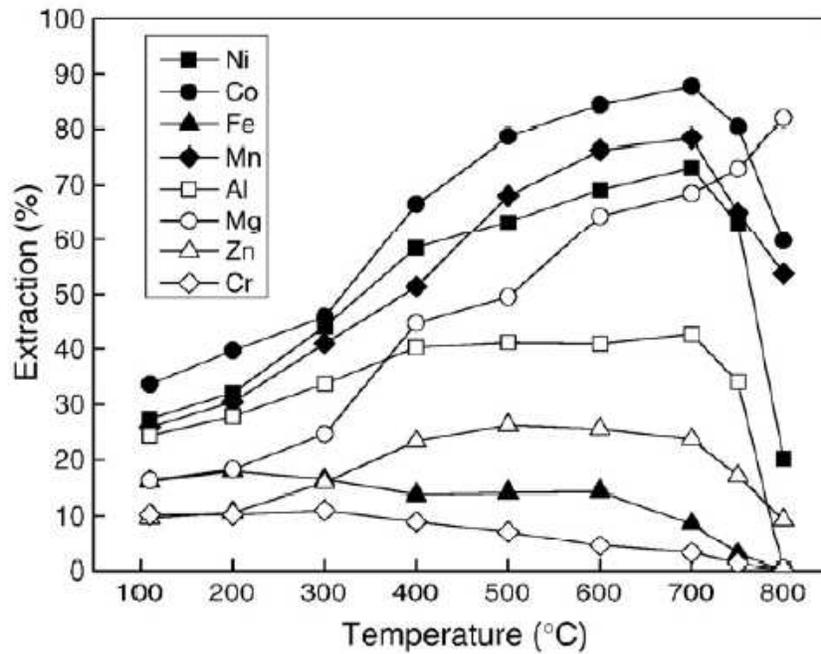
Figure 1.3: Effect of addition of temperature on metal extractions (roasted for 30 min; leach solid/liquid ratio: 50 g/L). From Guo et al. (2009).
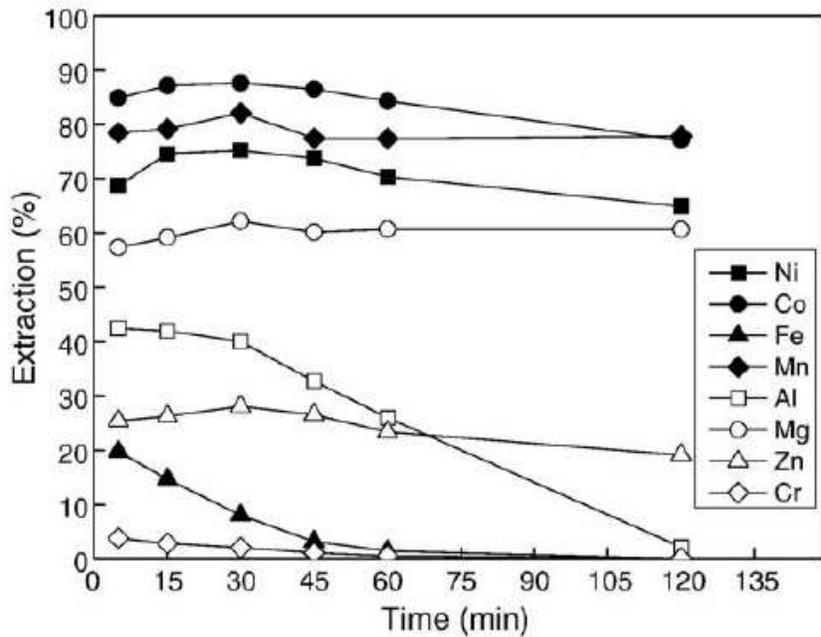
Figure 1.4: Effect of roasting time on metal extractions (roasted 700°C; leach solid/liquid ratio: 50 g/L). From Guo et al. (2009).
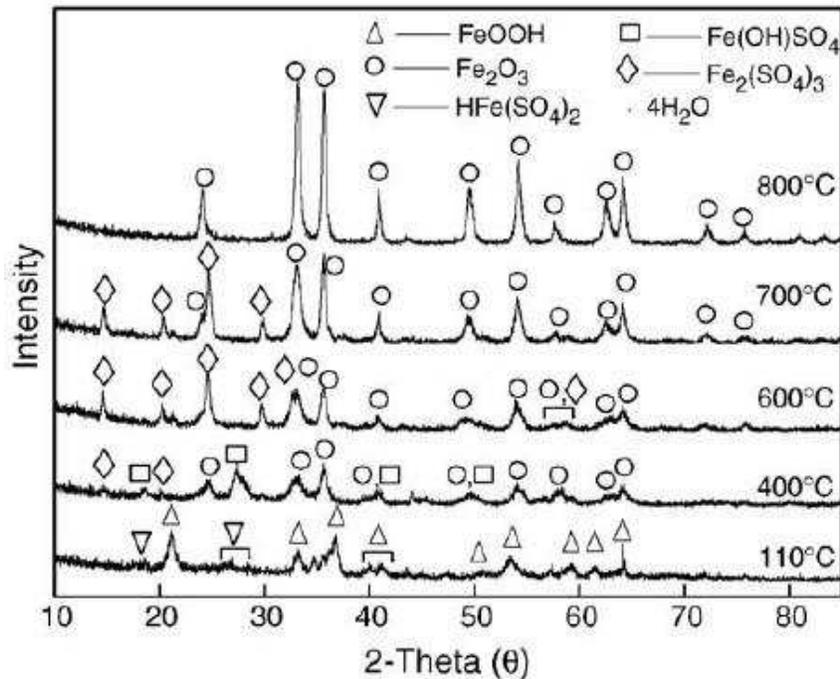
Figure 1.5: XRD patterns of roasted samples at different temperatures for 30 min. From Guo et al. (2009).

The leaching process is relatively simple. Roasted product is first placed in a mixing vessel with water where dissolution of the sulfates is fairly rapid (less than 30 minutes). A solid-liquid separation step is required to separate the insoluble oxides from the pregnant leach solution. Leach solutions are analyzed with ICP-MS and XRD.

1.2.3 Conclusions

The sulfation-roast-leaching process used on a limonitic laterite ore resulted in metal extraction of about 90% Ni and Co. A block-flow diagram of this process is presented below (Figure 1.6). This process was mainly influenced by the amount of acid added, the roasting temperature, and the time of roasting. Acid addition resulted in increased metal extraction for all the species involved but had the greatest effect on iron and nickel recovery. Increasing roasting temperatures to 700°C and roasting times to 60 minutes greatly improved the removal of iron as insoluble hematite while nickel and cobalt remained as soluble sulfates.

Further research into the conditions of roasting may be required to determine what type of roasting vessel and roasting gas conditions are optimal for this process. For this case study, a muffle

furnace was utilized with little control over the chemical or physical conditions of roasting. Samples were placed in crucibles with little or no gas diffusion or mixing capabilities. Reaction time could be improved if this process took place in a reaction vessel such as a rotary kiln or multiple hearth furnace where adequate mixing of material and heat could speed up reaction kinetics. Reducing the amount of time to treat these materials could greatly improve capacities and energy costs of this process.

The reaction mechanism for the formation of sulfates in this process was described as simple acid dissolution followed by sulfate precipitation during drying. However, higher-temperature sulfation roasting conditions may exist as sulfur dioxide and trioxide are released during decomposition of excess sulfur in the system. It will be important in any future research to describe the sulfation mechanism before this process can be controlled or optimized.
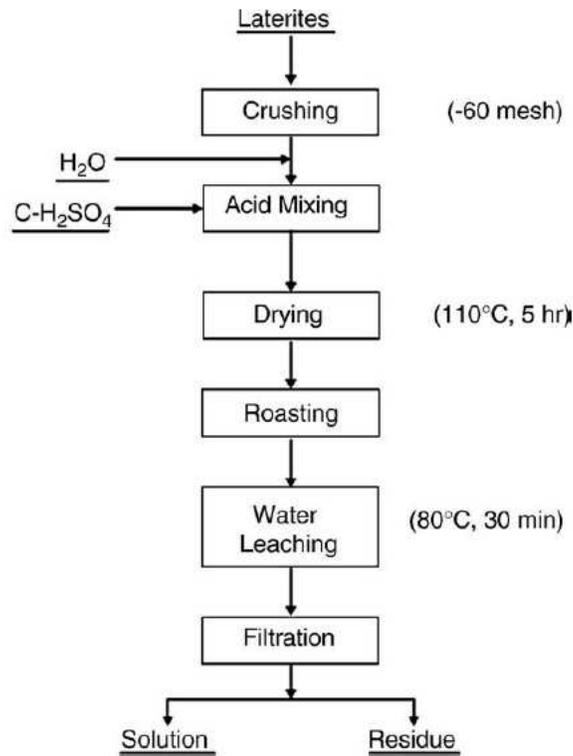
Figure 1.6: Flow sheet for the sulfation-roasting-leaching process for limonitic laterite ores. From Guo et al. (2009).

1.3   Case Study –Sulfation-Roasting and Leaching of NdFeB Magnets

In a similar process to that proposed in this current study, a sulfation-roasting process has been proposed for NdFeB magnets as an effective recycling strategy for this material. These magnets

typically consist of 30-40 wt% rare earth metals (REMs) of which 15-30 wt% is neodymium. Other REMs include Pr, Tb, Gd, and Eu. The remaining material consists primarily of iron and boron with trace amounts of the base metals.

Magnets in this study were milled down to <40, <125, and <200 µm size fractions before mixing with 12-16M acid solutions in cylindrical alumina crucibles. Acid addition was controlled by comparing the acid-to-magnet ratio (g/g) while adding demineralized water to maintain a constant pulp density. Slurries were mixed with a silica glass rod then allowed to dry at 110°C overnight. The addition of acid was conducted to cause sulfation of the starting material.

Roasting was conducted in a preheated electric muffle furnace between 650-850°C for a duration of 15-120 minutes. Experiments were conducted to show the effects of roasting temperature, acid addition, and roasting duration. The final residue was removed from the crucibles and mixed with 25-50 mL demineralized water in 50 mL PE plastic bottles for 15 min to 24 hours at 225 rpm. Solutions were analyzed with ICP-OES while solid samples were characterized through XRF, XRD, SEM and EPMA.

1.3.1   Effect of Acid Concentration on Rare Earth Metal Recovery

The effect of acid concentration is shown in Table 1.1 for the four major REMs and iron. This table is used to demonstrate the amount of acid required to convert the starting metal oxides into their respective sulfates. Roasting temperatures in this initial experiment at 650°C were below that needed to selectively roast any of the five metal sulfates into oxides. Fixed conditions: <40 µm particle size, 24-hr drying duration, 110°C drying temperature, 650°C roasting temperature, 1-hr roasting duration, 25°C leaching temperature, 24-hr leaching duration, and 0.02 g/mL magnet-to-water ratio. The acid-to-magnet ratio was modified in successive experiments between 2.15-8.60.

It is demonstrated from Table 1.1 that complete sulfation of the REMs was possible with a 16M acid slurry. However, near complete sulfation occurred at 14.5M or an acid-to-magnet ratio of 4.3:1.0. This study did not account for mixing of the starting material during sulfation. Other factors not included in this study were the effects of gas composition or gas diffusion through the samples. The proposed reaction mechanism is acid dissolution followed by precipitation during the overnight drying period.

Table 1.1: Extraction efficiencies of REMs and Fe with different acid concentrations. Table from Onal et al., 2015.

Acid concentration (M)	12	13.5	12	13.5	14.5	16
Stirring		No	No	Yes	Yes	No	No
Element	Extraction (%)					
Nd	43.4	76.3	90.0	90.9	98.6	100
Pr	45.3	71.6	90.6	91.2	99.5	100
Dy	43.7	68.2	87.2	90.7	99.2	100
Gd	21.2	63.0	89.6	91.2	100.0	100
Fe	41.0	61.5	64.2	72.2	88.9	90.0

1.3.2 Effect of Temperature on Metal Recovery

The sulfate samples were further roasted between 650-850°C to determine the effect of temperature on the final recovery of the metals in the leach solution as well as the terminal pH after 24-hrs of leaching Figure 1.7. Fixed conditions for the roasting temperature study: 1-hr roasting duration, 25°C leaching temperature, 24-hr leaching duration, and 0.02 g/mL magnet-to-water ratio.

It was found that rare earth sulfates were stable below 750°C while higher temperatures of 800-850°C resulted in lower recoveries of these metals in the final leach solution. Meanwhile, recoveries of cobalt, copper, and iron all begin to decrease below 725°C. This suggests that there is a feasible decomposition temperature range for separation of rare earth metal sulfates from base metal oxides between 725-750°C. Terminal pH is shown in this figure to demonstrate the removal of iron from the system. This is due to oxidation of soluble ferrous iron to ferric iron over time in water which is accompanied by a decrease in pH.

1.3.3 Effect of Time on Metal Recovery

A series of tests were conducted at 750°C and 800°C while varying roasting duration between 15-60 minutes (Figure 1.8). The final leach solutions were tested through ICP-OES to determine the recoveries of base and rare earth metals. Fixed conditions for the roasting temperature study: roasting temperature of 750° or 800°C, 25°C leaching temperature, 24-hr leaching duration, and 0.02 g/mL magnet-to-water ratio.

It was found that the final recovery of the rare earth metals (Nb, Nd, Pr, and Dy) was above 98% for roasting residence times below 60 minutes at 750°C but decreased as low as 88% at 800°C

after 60 minutes. The overall recoveries of base metals was lower at 800°C than 750°C. Rare earth metal recovery did not decrease at 750°C while recoveries were lower at 800°C. This suggests that the decomposition point for the rare earth sulfates studied in this paper is between 750-800°C.
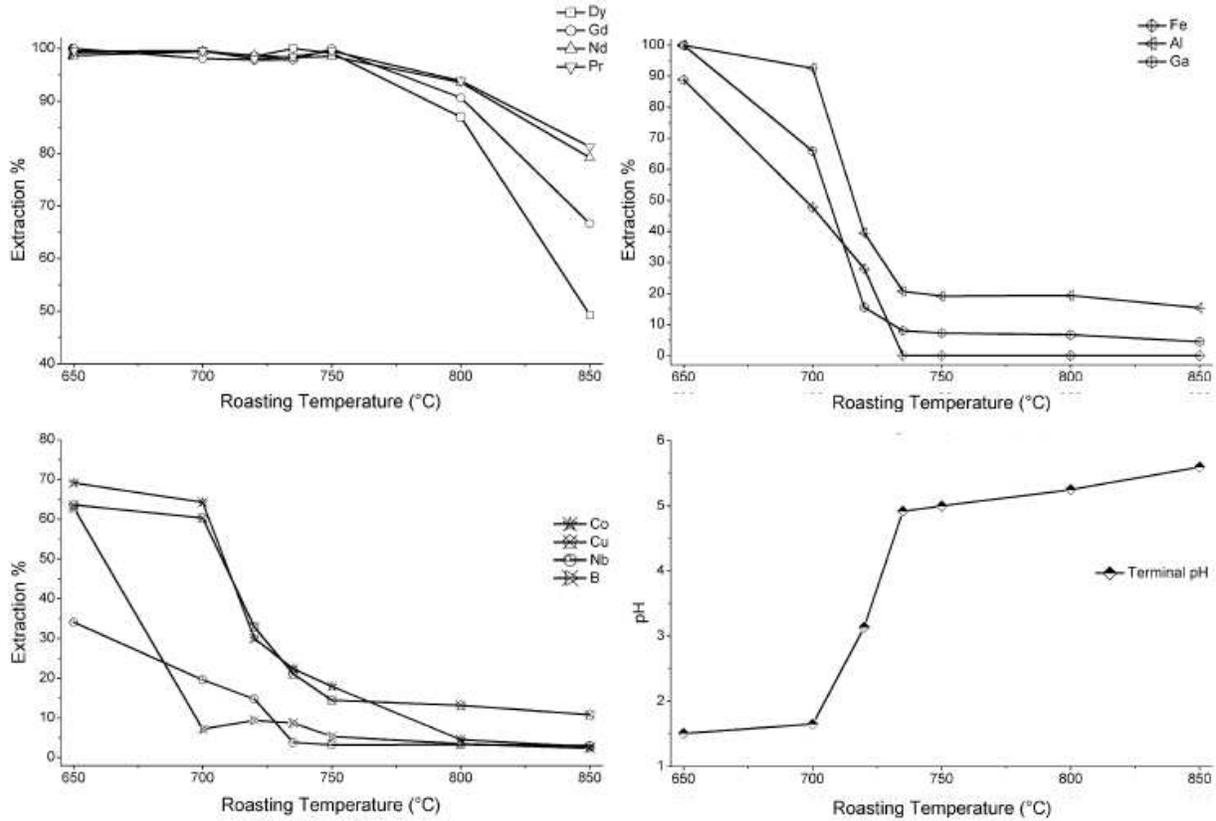
Figure 1.7: Effect of roasting temperature on terminal pH of the solution and leach recovery (extraction %) of the tested metals. Figure from Önal et al. (2015).

1.3.4   Conclusions

Sulfation roasting and leaching was determined to be a viable process for the treatment of neodymium iron boron magnet waste and scrap. The major factors influencing this process are acid addition, roasting temperature, and roasting residence time. An acid to magnet ratio (g:g) of 4.3:1.0 was found to be optimal for complete sulfation during these experiments. However, the experiments failed to determine the total extent of sulfation during initial mixing and drying of the acid-magnet slurry. This paper reports on XRD patterns and SEM analysis of the residues after roasting and leaching but makes no mention of sulfation before roasting. A more accurate study of the sulfation mechanism of rare earth and base metals would improve the accuracy of the results from this paper.

Roasting temperature and duration were found to follow expected trends with higher recoveries at lower temperatures but higher grade with increased temperature. The results suggest a thermal decomposition point between 750°C and 800°C for the rare earth metals considered. Meanwhile, the decomposition point of the base metals was at or below 725°C. This suggests that a temperature window above 725-750°C is feasible for separation of base metals as oxides from the rare earth sulfates.
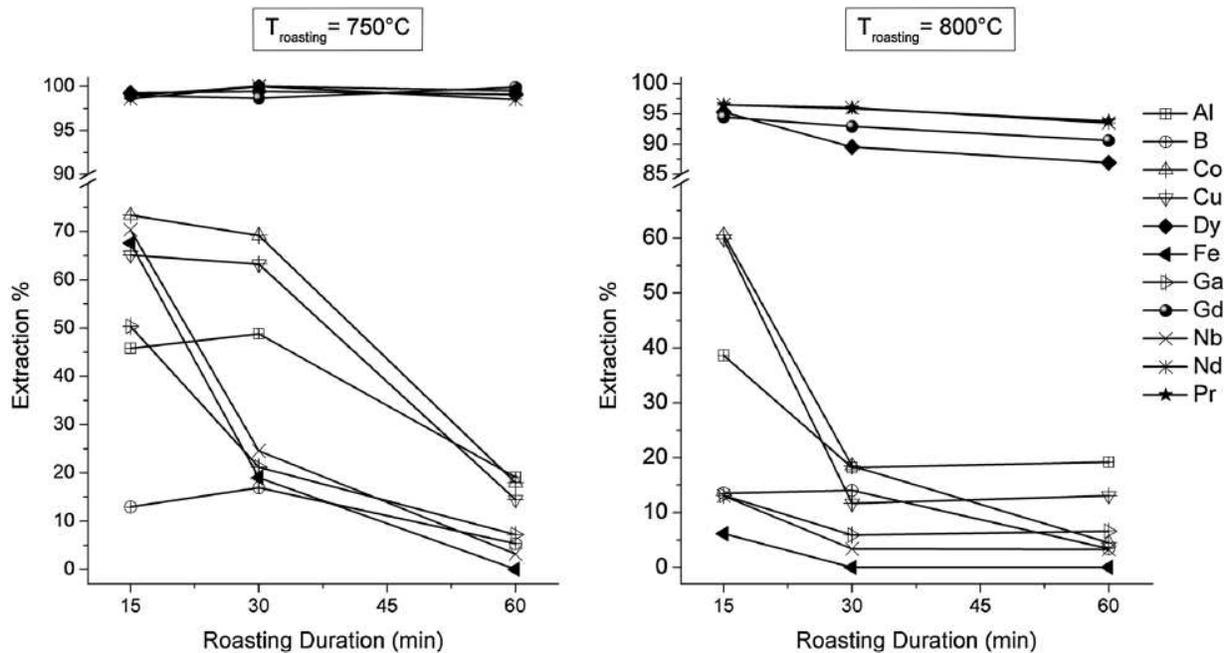
Figure 1.8: Effect of roasting time on metal recovery in the leach solution. Figure from Önal et al. (2015).

Further research into the sulfation mechanism and roasting conditions would improve the results from this case study. Factors not considered in this study include gas composition in the roasting reactor, mixing of the samples, and the kinetic mechanism controlling thermal decomposition. It is possible that roasting duration could be greatly decreased with mixing if fluid-film or diffusion control the kinetics of the decomposition reaction. Controlling the atmosphere of the reaction vessel by venting sulfur dioxide could also improve kinetics if the reaction is diffusion controlled. Each of these factors should be considered for future experiments.

CHAPTER 2

OBJECTIVES AND EXPERIMENTAL METHODS

The primary goal of this research is to develop and optimize a recycling process for the recovery of samarium from samarium-cobalt magnet swarf and magnet waste. A secondary objective is to upgrade the cobalt value of the residue before sale and shipment to an industrial cobalt recovery plant.

2.1   Proposed Process Flow Diagram

A similar method to that described in Guo et al. (2009) was investigated as a treatment method for samarium-cobalt magnet waste. A diagram of this procedure is shown in Figure 2.1. This process begins by mixing sulfuric acid, water, and swarf material in the roasting reactor. Off-gases are scrubbed while the solid residue is sent to a leaching tank. After a period of leaching in the mixing tank, the insoluble oxides are filtered while the leachate is sent to a precipitation circuit to recover samarium as oxalate. This oxalate product can be calcined into a pure samarium oxide product that can be recycled into the magnet manufacturing process or sold at market value.
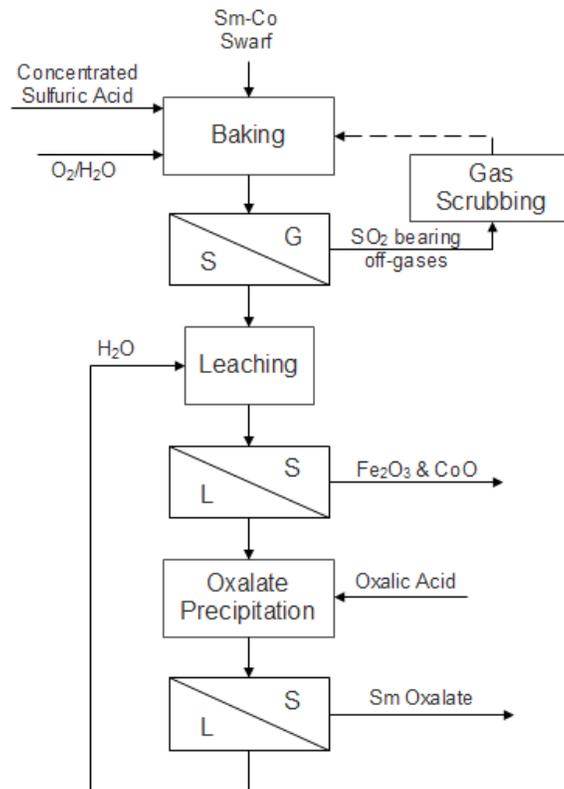
Figure 2.1: Flow sheet for the sulfation-roasting-leaching process for Sm-Co magnet waste.

2.2   Material Sampling and Preparation

Swarf material was collected from the Electron Energy Corporation based out of Pennsylvania as a byproduct of their samarium-cobalt magnet manufacturing process. The material utilized in muffle furnace experiments was washed in acetone, dried, and ground in a Spex Mill before passing 200 Tyler-mesh. Material from the rotary kiln experiments was roasted at 800°C in an air atmosphere with mixing at 10 rpm before crushing and grinding in a Spex Mill and passing 200 Tyler-mesh.

The sampling size was estimated utilizing Gy's Rule and the maximum particle size was 74 microns (200 Tyler-mesh). Based on this calculation, a sample size of 1.4 grams was necessary to properly represent the material in these tests. Due to the size and behavior of the muffle furnace crucibles utilized in this experiment, the sample sizes for those tests were smaller than that necessary for proper sampling. This may introduce some error into the results from muffle furnace experiments. However, all of the tests conducted in the rotary kiln experiments were above the minimum sample size needed for proper representation of the starting material.

2.3   Benefits and Limitations of Muffle Furnace versus Rotary Kiln Reactors

The two major methods utilized in this research included a series of experiments utilizing crucibles in a muffle furnace as well as rotary kiln trials. Major benefits of muffle furnace experiments include rapid testing and multiple sample repeats per run. The limitations of furnace testing are small sample size, higher risks of human error, sample loss due to expulsion during evaporation, minimal mixing, and little control over reactor atmosphere. This method has been used for the scoping study to determine the effects of acid molarity, roasting temperature, and roasting residence time.

Rotary kiln experiments greatly improve several system parameters including better control of the atmosphere in the reactor, better mixing during baking, and larger more representative sample sizes. This is possible because rotary kilns utilize However, rotary kiln tests are more time-consuming and are ill-suited for exploratory experimentation. A series of experiments are conducted to verify baking temperature and acid addition for larger samples than muffle furnace tests. It is also possible to test the effects of mixing, pulp density, and gas composition in rotary kilns.

2.4   Swarf Composition Determination

Analysis of the initial swarf composition was the first variable to be tested in this study. This was accomplished through several methods including QEMSEM, x-ray diffraction (XRD), x-ray

fluorescence (XRF), and ionically coupled plasma mass spectrometry (ICP-MS). The most accurate elemental mass balance for the starting material was calculated through ICP-MS analysis of the initial leach and residue.

Initial swarf composition was determined by analyzing leach solutions after the roasting stage then completely converting the remaining residue to metal sulfates in a secondary sulfation stage. These latter sulfates were leached in the same manner as the first stage and analyzed along-side the initial leach solutions via ICP-MS. In this manner, the metal gram values of the initial swarf material can be calculated by combining the initial and residue leach values. Additional calculations for determination of the initial swarf composition are presented in Appendix B.

Standards for swarf composition were created for muffle furnace experiments by mixing five 0.1 gram samples with 3 mL of 6.0 molar sulfuric acid. A standard was necessary in muffle furnace test due to the fact that the amount of residue was too small to be significantly separated from the filter paper after filtering. These samples were prepared by heating 0.1 gram samples with excess acid at 250°C for one hour before increasing temperatures to 350°C for another hour. This was accomplished to remove excess sulfuric acid from the system. Furnace standards were cooled over night before being dissolved in 50 mL deionized water. Leaching was conducted in a Multi-Therm Temperature Controlled Vortexer (Vortexer) at 900 rpm for five hours. Leach solutions were analyzed through ICP-MS.

Larger samples from the rotary kiln tests were converted to metal sulfates in a controlled sulfation study comparing mixing, pulp density, gas flow rate and composition, sulfation residence time and temperature, and acid addition. Samples from the rotary kiln trials were dissolved in 250 mL deionized water and mixed on a shaking table overnight. The solutions were filtered and analyzed through ICP-MS and averaged to create an elemental starting mass balance for the swarf material.

2.5   Muffle Furnace Experiments

A series of muffle furnace experiments are conducted as a scoping study to determine the effects of acid addition, roasting temperature, and roasting duration in sulfation roast and leaching studies utilizing samarium-cobalt magnet swarf.

2.5.1 Experimental Apparatus and Set-Up

A diagram showing the step-by-step procedures followed in muffle furnace experiments can be observed in Figure 2.2. In the muffle furnace experiments, samples were added to silica porcelain crucibles and mixed with water and sulfuric acid before insertion into an electric muffle furnace (Figure 2.3). The goal of the first set of experiments was to determine how to properly heat and treat these samples in a muffle furnace. It was found in early testing that rapidly heating the slurries often resulted in expulsion of material from the crucibles and decreased overall recoveries. This problem is solved by a multistage pre-baking process. Crucibles are first placed in the furnace at 100°C and heated to 250°C. They are slowly heated up to 350°C to prevent rapid boiling and expulsion of slurry from the crucible. After a period of 15-20 minutes, samples are ready to be heated to target baking temperatures between 700-800°C. Heat ramping duration in the muffle furnace is approximately 3 hours excluding residence time spent at the pre-baking or baking stages.
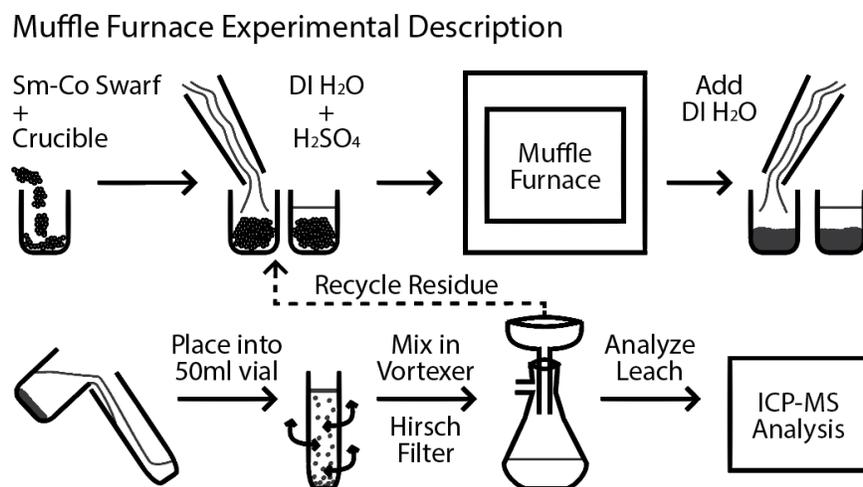
Figure 2.2: Step-by-step description of experimental procedures for muffle furnace experiments

2.5.2 Effect of Pre-Roasting Residence Time

The amount of time necessary for sulfation during pre-baking was tested by mixing 0.1 grams of sample with 4 mL of a 4.5 molar sulfuric acid solution in silica crucibles. Samples were then heated in a muffle furnace up to 250°C and removed every 5 minutes up to 25 minutes. These samples were then re-inserted into the furnace and heated to 750°C for one hour. Baked material was removed and mixed with 50 mL of deionized water before mixing for 30 minutes at 900 rpm in a vortexer. Solutions

were filtered and analyzed with ICP-MS and compared with the initial swarf composition for final gram recovery values. Results from these experiments can be found in Appendix C.

Figure 2.3: Thermolyne electric muffle furnace used in experiments for all lab-scale experiments

2.5.3   Effect of Roasting Temperature

It was found in an earlier study by (Guo et al., 2009) that cobalt recovery begins to decrease at 730°C while samarium decomposition is estimated to occur around 800°C (Poston et al., 2003). As a result of this previous work, a temperature of 750°C was chosen as a starting temperature for initial experimentation. The effect of temperature was tested by varying roasting temperature between 725-825°C in 25°C intervals with a fixed residence time of one hour. The pre-roasting conditions were fixed based on the procedure described in Section 2.5.2.

2.5.4   Effect of Acid Addition

Acid to water ratios were tested in a similar manner to the pre-baking experiments in which 0.1 gram samples were mixed with water and acid before insertion into the furnace. A range of acid molarities varying from 2.8-6.0 were tested at fixed residence times of 20 minutes at 250°C and 60

minutes at 750°C. Baked material was added to 50 mL deionized water and mixed for 30 minutes at 900 rpm. Solutions were filtered and analyzed through ICP-MS and compared with swarf composition for recovery values.

2.5.5 Effect of Roasting Residence Time

The next variable of consideration is to determine the required residence time at 750°C. An acid molarity of 4.8 was found to have the highest samarium recovery and grade from the previous round of experiments. This molarity was fixed in the residence time trials. Samples were heated for 20 minutes at 250°C before increasing temperatures to 750°C. At this baking temperature, samples were removed every 10 minutes for one hour and again at 90 and 120 minutes. Similar to previous experiments, samples were removed and added to 50 mL deionized water before mixing at 900 rpm for 30 minutes. Solutions were filtered and analyzed through ICP-MS to determine final grade and recovery.

2.6 Rotary Kiln Experiments

Rotary kiln trials were separated into two major types of experiments. These include a study to determine ideal sulfation conditions while the second set of experiments determined ideal roasting conditions. Sulfation was determined by investigating several categories including the effect of sulfation temperature, residence time, acid addition, pulp density, mixing speed, gas composition, and gas flow rate. Roasting experiments tested the effects of roasting temperature, residence time, and gas flow rate. The final roasting experiments utilized completely sulfated material determined from the sulfation study.

2.6.1 Experimental Apparatus and Set-Up

The rotary kiln consists of a silica glass reactor vessel designed by Allen Scientific in Boulder, CO, along with glass fittings and joints, fitting clamps, motor with chains and attachments to the reactor vessel, a five-gallon bucket for wet off-gas scrubbing, ¼" tubing for gas input, power supply, and a heating vessel (Figure 2.4). An overview of the experimental procedure can be seen in Figure 2.5.

Samples are inserted into the furnace via ½" plastic tubing connected to an elevated plastic funnel. Swarf is placed in the funnel and rinsed through the tubing into the center of the glass reactor with sulfuric acid solution then the tube is rinsed with DI H_2O. Any remaining liquid/slurry is expelled

from the tube and into the reactor with a rubber pipet bulb. A motor is then attached to the reactor vessel with a chain and gear fixed onto the surface of the glass reactor with a rubber fitting. Glass fittings and joints are connected using sealant grease and clamps while the off-gas is bubbled through 5% NaOH solution in the five-gallon bucket. Once the sample is inserted and all of the fittings are sealed, the heating vessel is closed and clamped down. The power supply and motor can be turned on to allow heating and mixing in the vessel. A makeshift hood covering consisting of vinyl floor-matting and clamps was used to prevent off-gases from escaping the hood and entering the room.

Figure 2.4: Rotary kiln furnace used in experiments for all bench-scale experiments

After the conclusion of each experiment, the hood covering was removed, the power supply and motor shut down, and the heating vessel was opened and allowed to cool with a fan for 30 minutes. The tubes on each end of the glass reactor were cleaned with a pipe scrubber and paper towels. This was necessary to remove unreacted material at the edges of the heating vessel where the reactor was significantly cooler than its center. The glass reactor is then removed from the heating vessel, filled with DI H_2O, mixed, and poured into 250 mL plastic bottles. Any remaining material inside the reactor washed by inverting the kiln reactor and pouring into the same 250 mL plastic bottles.

The beakers were mixed on a shaking table overnight and pressure filtered through a Hirsch Funnel and ash-less filter paper. Chemical analysis of the leach solution was conducted using ICP-MS analysis. Residues are recycled back into the rotary kiln and roasted under ideal sulfation conditions before leaching and pressure filtering. The initial and residue leach solutions are compared to determine final recovery. Filter papers were weighed before and after filtration and washing to determine mass loss from the system.

Rotary Kiln Experimental Description
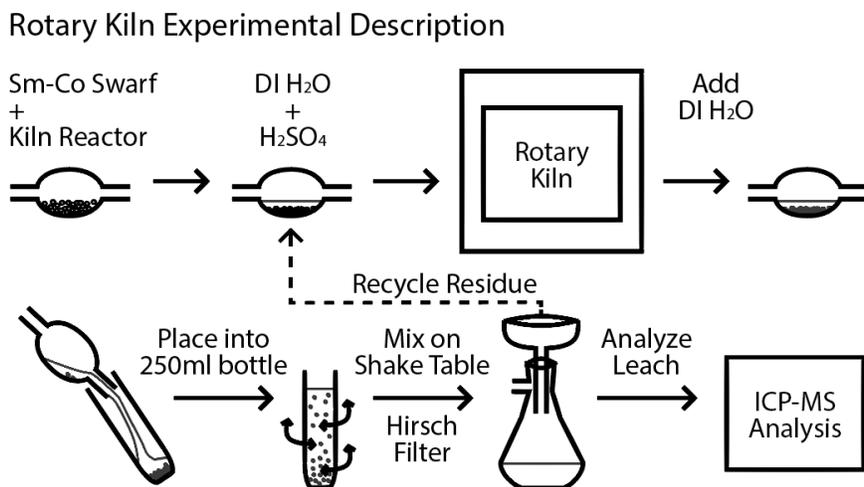
Figure 2.5: Step-by-step description of experimental procedures for rotary kiln experiments

2.6.2 Conditions for Complete Sulfation

The conditions for complete sulfation are determined through a series of experiments testing the effects of sulfation temperature, residence time, acid-to-swarf ratio, mixing, pulp density, gas composition, and gas flow rate. This experiment is designed with a partial factorial matrix utilizing Minitab statistical software to determine the significance of each factor on the overall recovery of cobalt, samarium, iron, and copper in the final leach solution. A quarter-factorial design consisting of 15 experiments is conducted utilizing one midpoint. The high and low conditions for each experiment are listed in Table 2.1 below. Experimental procedures listed in Section 2.6.1 were followed for each of the listed tests.

Table 2.1: Low and high values tested for factors from rotary kiln sulfation experiments

Factor	Temperature	Time	Acid:Swarf	Gas Flow Rate	Mixing	Pulp Density
Low	300°C	0 min	1.4 : 1	2 L/min	no mix	5% solid
High	400°C	60 min	2.8 : 1	9 L/min	mix	20% solid

2.6.3 Effect of Roasting Temperature

The effect of roasting temperature is determined by first utilizing optimal sulfation conditions found in Section 2.6.2. Once complete sulfation has occurred, the temperature of the rotary furnace is increased up to roasting temperatures between 740°C and 780°C. Concurrently the air flow rate is fixed at 2 liters per minute or increased to 9 liters per minute and mixing ceased. The primary purpose for altering these variables is two-fold. Mixing is prevented at high temperatures due to sample loss from the reaction chamber. Falling sample during the rotation of the kiln reactor vessel is observed to leave the main chamber and enter the tube on the outgassing end. Temperature variation is observed to decrease rapidly as the temperature probe is moved from the main reactor chamber to the tubes. For these reasons, the mixing of the reactor vessel is stopped after complete sulfation has occurred.

Overall heat ramping time is approximately 37 minutes in the rotary kiln reactor as opposed to 3 hours in the muffle furnace. A residence time of one hour is held constant for all roasting temperature experiments. All other operating procedures for these experiments are described in Section 2.6.1.

2.6.4 Effect of Gas Flow Rate and Composition

In order to better remove excess sulfur dioxide from the reactor vessel, a series of identical experiments to the roasting temperature study are conducted at a gas flow rate of 9 liters per minute compressed air. All other factors are held constant to those found in Section 2.6.3 including the variation of roasting temperature between 740-780°C in 20°C intervals. Higher gas flow rates are expected to drive out excess sulfur dioxide thereby prohibiting secondary sulfation from off-gases remaining in the reactor vessel. An additional experiment utilizing argon in the place of compressed air was conducted to compare the effects of gas atmosphere on roasting conditions.

2.6.5 Effect of Residence Time

The effect of residence time is determined by fixing roasting temperature at 780°C with a compressed air flow rate of 9 liters per minute. Sulfation conditions are optimized according to the procedures determined in Section 2.6.2. Residence time is varied from 15 to 60 minutes in 15 minute intervals. Additional tests are conducted at 780°C on larger samples from 1 to 3 hours in 1 hour intervals. Standard rotary kiln operating procedures were followed and are listed in Section 2.6.1.

CHAPTER 3

RESULTS AND DISCUSSION

A series of experiments were completed to provide information on magnet swarf composition and its behavior in acid-bake-leaching processes. Tested parameters of furnace operation and sample preparation include roasting residence time and temperature, acid-to-swarf ratio, sulfation residence time and temperature, pulp density, mixing, gas flow rate, and gas composition. Experiments are separated into muffle furnace and rotary kiln tests. Muffle furnace tests are conducted as a scoping study to determine which conditions

3.1 Magnet Swarf Composition

Analysis of samarium-cobalt swarf has revealed several key aspects of this material. Imaging analysis through QEMSCAN demonstrates that Sm-Co swarf is fairly homogeneous with distributed pockets of high cobalt and samarium value (Figure 3.1). High cobalt was defined as any pixels with greater than 60% Co, high samarium as greater than 30%, and high iron as greater than 25%. Typical ranges for cobalt, samarium, and iron are 50-60%, 20-30%, and 15-25%, respectively. There were no pockets of high or low concentration within each of these typical ranges and metal values were well distributed throughout each grain. Therefore, these were chosen as the typical ranges for cobalt, samarium, and iron. These are represented as gray particles in Figure 3.1. Higher concentrations well above the typical ranges were chosen either as high cobalt or samarium values.

3.1.1 Composition of the Muffle Furnace Swarf Material

Composition of the starting material is determined through acid digestion in both muffle furnace and rotary kiln tests. Standards are created for muffle furnace experiments through averaging of 15 repeated tests held at 350°C for 3 hours with 300% excess sulfuric acid. Solutions from these muffle furnace standards are filtered and do not reveal any solid material after 5 hours of leaching at 900 rpm. The 15 solutions are analyzed through ICP-MS and averaged to determine an elemental cobalt of 41.1 wt%, samarium of 20.9 wt%, iron of 14.1 wt%, and copper of 3.9 wt% as shown in Table 3.1. Standard deviations varied from 4.1-4.4%. These four major elements are determined to represent approximately 99.4% of the starting material (see Appendix B).

Table 3.1: Averaged cobalt, samarium, iron, and copper values for 100 mg of initial swarf material from muffle furnace experiments

Values	Cobalt	Samarium	Iron	Copper
Average (mg)	41.09	20.95	14.13	3.89
StDev (mg)	1.77	0.91	0.68	0.16
StDev (%)	4.31%	4.36%	4.79%	4.07%
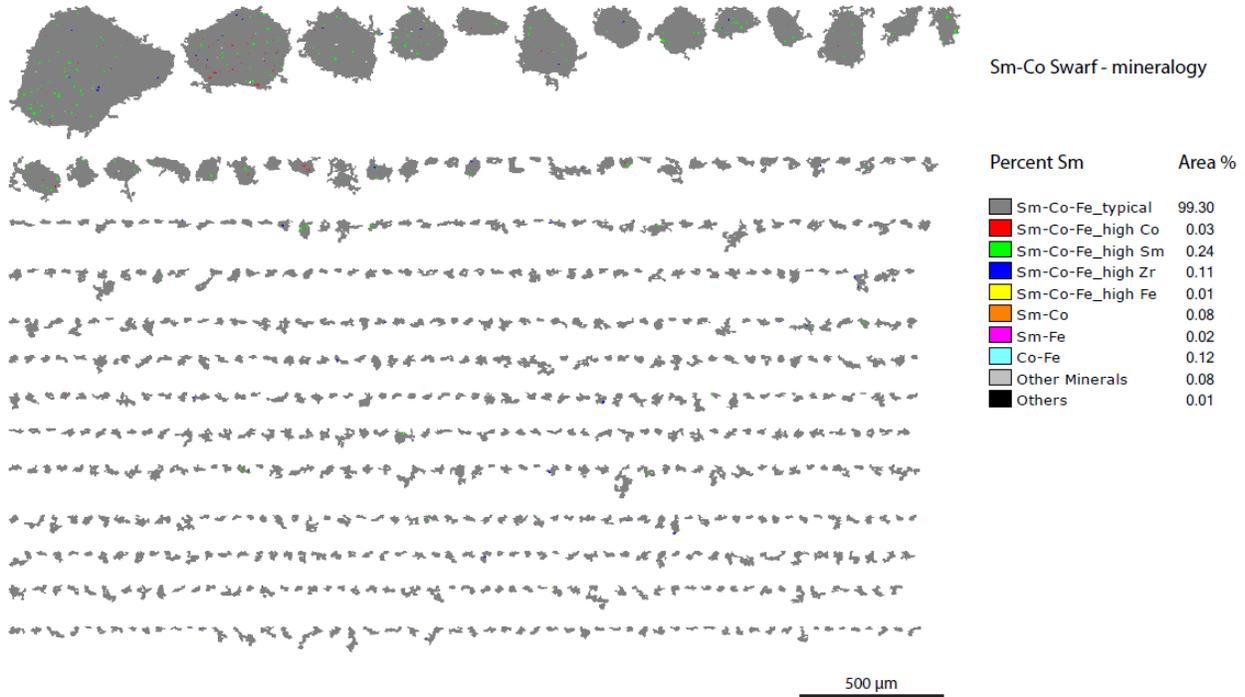
Figure 3.1: Mineralogy map on QEMSCAN imaging analysis of raw Sm-Co swarf sample.

3.1.2   Composition of the Rotary Kiln Swarf Material

Additional material was ordered from the Electron Energy Corporation due to a lack of supply after muffle furnace experiments. The initial leach and leached residue solutions from rotary kiln experiments were averaged to provide a compositional analysis of the new material. This is accomplished by performing a secondary sulfation roast on the residue from the initial experiments and analyzing the residue leach solution alongside the initial leach solution. An overview of the procedures can be found in Section 2.6.2. Both of the leach solutions from rotary kiln experiments are combined to calculate the head grade entering the system. Analysis of the leach and residue streams provide the initial gram values of the four major elements based on a 100 gram input (Table 3.2).

Table 3.2: Averaged cobalt, samarium, iron, and copper values based on 100 grams of starting swarf material for rotary kiln experiments

Values	Cobalt	Samarium	Iron	Copper
Average (g)	45.18	20.71	15.14	4.36
Stdev (g)	2.14	1.12	1.42	0.24
Stdev (%)	4.74%	5.41%	9.41%	5.51%

3.2   Muffle Furnace – Effect of Temperature

The first parameter tested in the muffle furnace experiments was the effect of temperature on the overall grade and recovery of samarium. Roasting temperatures were varied from 725-825°C (Figure 3.2). These ranges were based on the theoretical thermal decomposition point of cobalt, iron, copper, and samarium sulfate. Samarium sulfate should decompose between 755-800°C (Paama et al., 2005; Wilfong et al., 1964) while cobalt, iron, and copper decompose at or below 720°C (Kolta and Askar, 1975). Procedures for the muffle furnace temperature experiments can be found in Section 2.5.3.

It was found that the grade of the leach solution with respect to samarium increased sharply between 725-750°C while the recovery of cobalt, iron, and copper sharply decreased at and above 750°C (Figure 3.2). Samarium recovery decreased above 725°C and was near 50% at 750°C. There was no significant recovery of any of the four major elements at or above 775°C. Solutions were analyzed through ICP-MS and normalized against a five-sample standard consisting of fully dissolved swarf material.

It was found during temperature trials that the highest grade and recovery of samarium occurred at 750°C (Figure 3.3). Higher recoveries of samarium were measured at 725°C, but the grade of the final product was approximately 60%. Saleable samarium oxide is at least 99% pure with much better economics above 99.99% pure. The purity of the samarium sulfate solution was approximately 99.59±0.05% after baking at 750°C for one hour. The residence time does not account for heat ramping which is approximately 5 minutes for every 25°C. Therefore, the actual residence time for tests at higher roasting temperatures is as much as 20 minutes longer than those at the lowest residence times. This may cause higher roasting temperatures to exhibit lower recoveries due to heat ramping times.
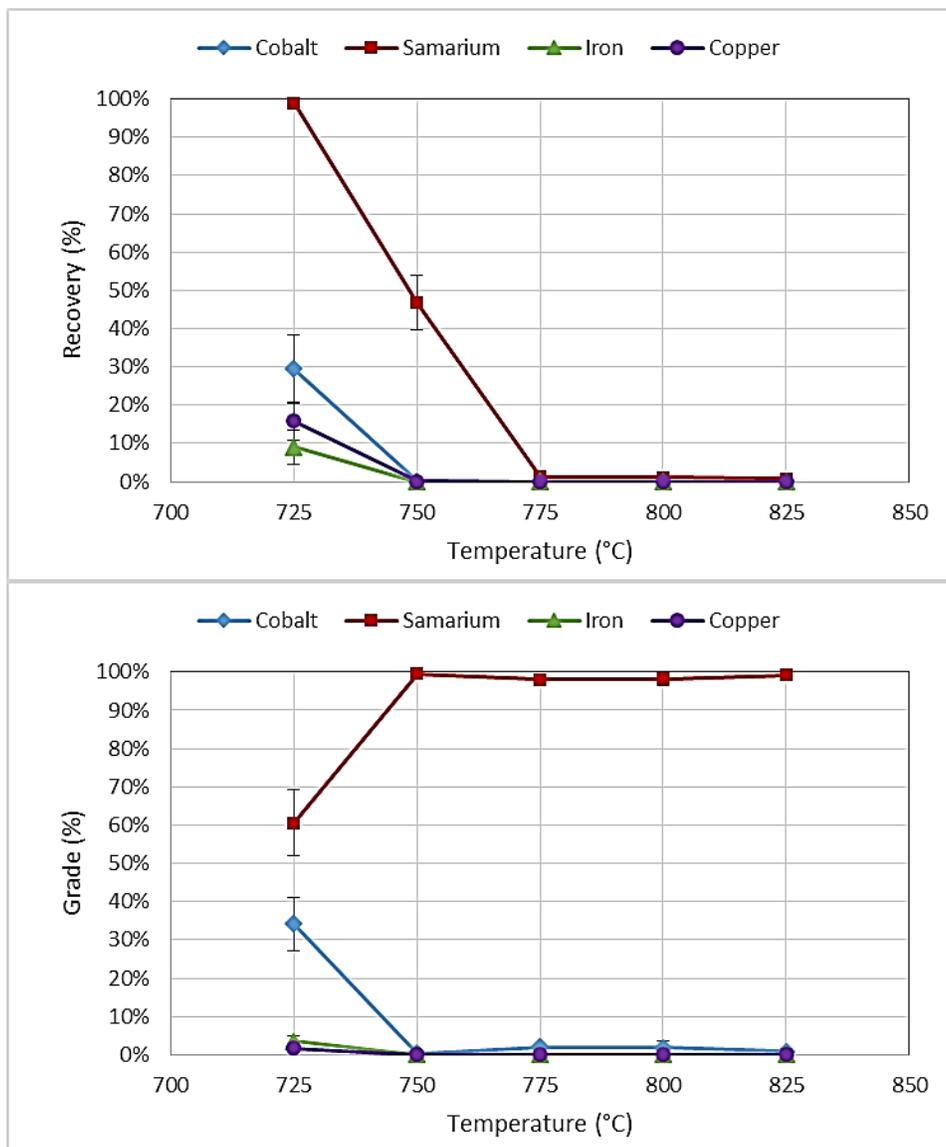
Figure 3.2: Recovery (top) and grade (bottom) of four elements in leach solutions versus temperature in muffle furnace tests.
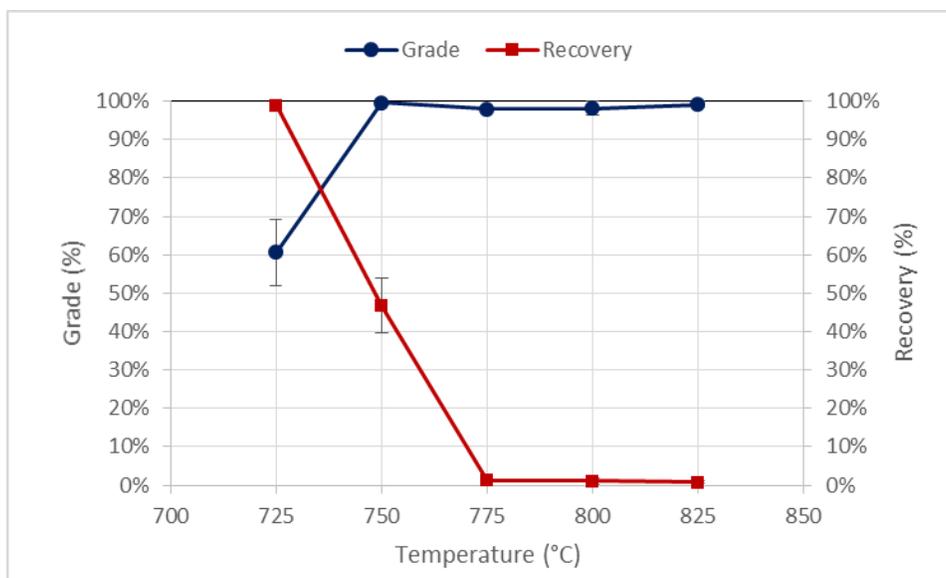
Figure 3.3: Grade (blue) and recovery (red) of muffle furnace leach solutions comparing samarium values versus temperature.

The exact decomposition temperature of samarium sulfate is not determined in these experiments. From the data shown in Figure 3.3 it appears that the decomposition point is at some point below 750°C. Decreasing temperature could result in higher recoveries but would require a much longer residence time in the reactor. It is appears possible from these experiments that decreasing the overall residence time at 750°C may result in higher samarium recoveries while maintaining an excellent grade. Meanwhile, increased acid addition may improve samarium recovery only if the conditions for complete sulfation are not met in these experiments. Future muffle furnace experiments determine the effects of acid addition and residence time on samarium grade and recovery.

3.3   Muffle Furnace – Acid Molarity

The effect of acid molarity on the grade and recovery in muffle furnace tests is shown for the four major elements in Figure 3.4. Procedures outlining the steps followed in these experiments are listed in Section 2.5.4. It was found that an acid molarity of 4.8 was sufficient for samarium recoveries between 67% to 98% and leach composition grades above 99% samarium with respect to the other four base metals. Standard error bars represent variations across at least three sample repeats.
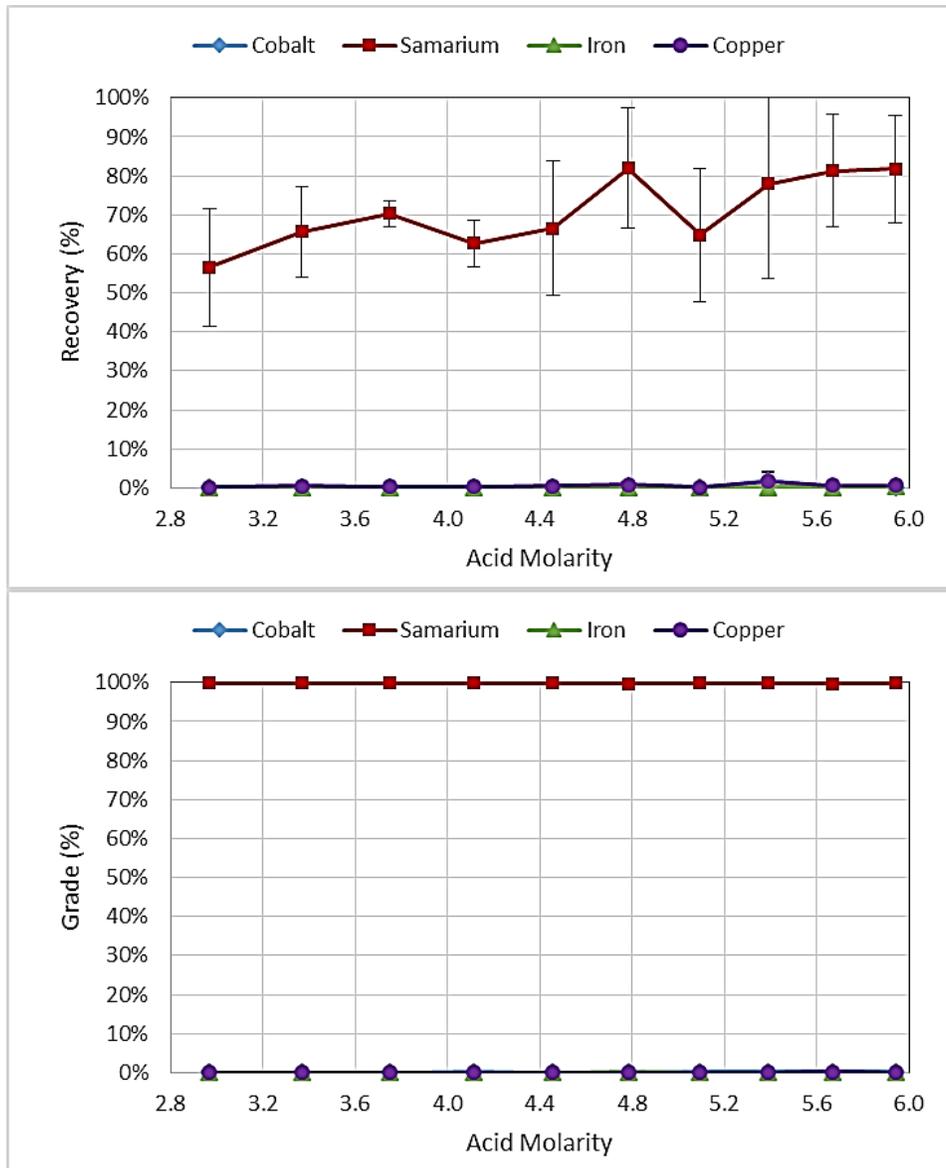
Figure 3.4: Recovery (top) and grade (bottom) of four major elements in leach solutions versus acid molarity in muffle furnace experiments.

Samarium recovery in these experiments varied from 40-99% with a general increase in recovery with higher acid content (Figure 3.5). Higher recovery values above 90% are observed at and above an acid molarity of 4.8. Leach solution grade with respect to samarium remains above 99% for all samples tested. Large variations in recovery as large as 55% were observed in these experiments. Several factors that may contribute to this error include variation in the head grade, poorly controlled gas diffusion and mixing within the samples, loss of sample due to expulsion during heating, and temperature variations within the reactor.
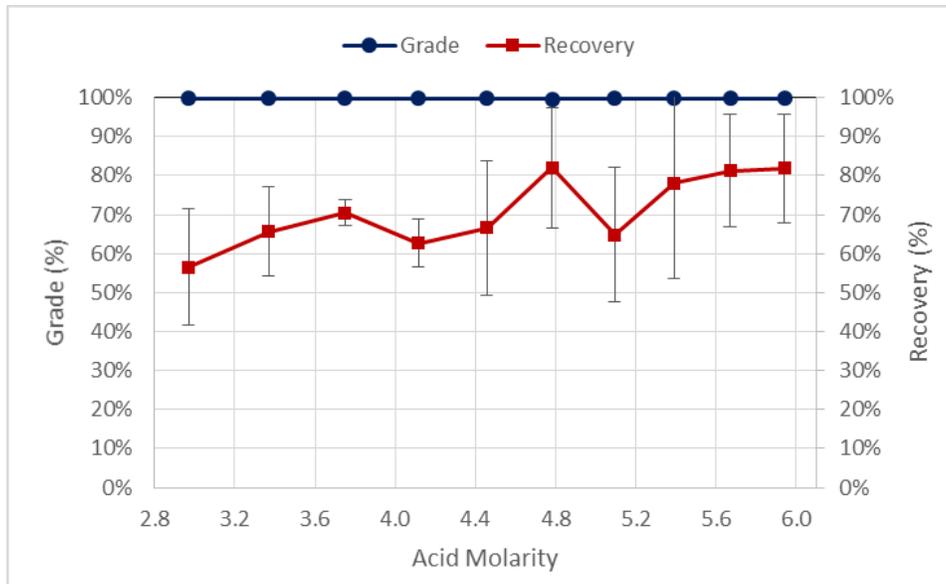
Figure 3.5: Grade (blue) and recovery (red) of muffle furnace leach solutions comparing samarium values versus acid molarity.

It may appear upon initial observation that recovery is proportional to the amount of sulfur available for reaction. While this is true on a fundamental chemical basis, the overall required acid should be much lower than what was observed in these experiments. The minimum acid-to-swarf molar ratio utilized in these tests was 5:1. Complete reaction of the starting material is theoretically possible with molar ratios of sulfur and the feed material as low as 1.5:1.

It is unclear as to the extent of temperature variation and atmosphere composition within the muffle furnace reactor. It is possible that low or high temperature pockets exist within the reactor. The same is possible with diffusion of sulfur dioxide and oxygen within the furnace. Any variations in gas composition or temperature could have an effect on the recovery of samarium in this system. High amounts of sulfur and oxygen are capable of creating a sulfation-roasting atmosphere in which sulfate samples are not converted to oxides. Lower or higher temperatures may also cause increased or decreased kinetic rates of sulfate decomposition within this system. No experiments were conducted to determine the effects of these factors in muffle furnace tests. However, temperature and gas composition are more accurately controlled in rotary kiln tests.

One of the other major challenges faced while running these experiments was ejection of material from the crucible during heat ramping of the furnace (Figure 3.6). It was found during initial

testing that placing wet or hydrated samples in the muffle furnace at pre-heated temperatures above 600°C resulted in major loss of sample due to rapid expansion and evaporation of water. Slow heating rates (<5°C/min) were applied to wet samples to allow water evaporation without sample loss. However, this still resulted in wildly erratic recovery values when the acid molarity was below 2.97. Samples with higher acid molarities appear to retain much of the original material (Figure 3.6). Sample loss due to expulsion during heating is a likely reason for the wildly erratic recoveries observed in these experiments.

Figure 3.6: Crucible samples showing the appearance of roasted samples with acid molarities of 1.62 (left) and 5.97 (right).

Apart from loss of sample from the crucible it may be possible that insufficient mixing or diffusion of sulfuric acid through the starting sample could result in lower samarium recovery. Mineralogical mapping from QEMSEM shows that some pockets of high samarium content are trapped within larger particles (Figure 3.1). It was also found that a large fraction of the starting material remains as a metallic alloy instead of segregated oxides. This material must first be oxidized before any sulfates can be formed according to the reaction sequence below:

$$Me + \frac{1}{2} O_2(g) = MeO$$

$$MeO + H_2SO_4 = MeSO_4 + H_2O$$
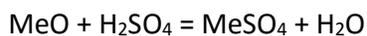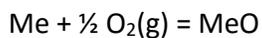
Another method of sulfation includes a reaction of sulfur trioxide with metal oxide to form sulfates. This reaction will occur within the temperature stability range of sulfur trioxide, which is dominant with respect to sulfur dioxide between 300°C to 700°C. The reaction of metal oxide with sulfur trioxide gas is shown as follows:

$$MeO + SO_3(g) = MeSO_4$$

37
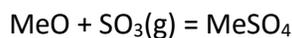
Although the recovery values obtained from the acid molarity muffle furnace experiments was highly erratic, the final grade of samarium in the leach solution was always above 99%. This indicates that an effective separation of the base metals from samarium is possible. The lowest acid molarity with the highest grade and recovery was 4.8 and this value was utilized in future residence time experiments.

3.4   Muffle Furnace – Residence Time

The residence time needed for the baking stage at 750°C was varied using fixed parameters determined in previous experiments. Procedures for these experiments are listed in Section 2.5.5. A residence time of 50 minutes produced average samarium recovery of 86.9±10.9% with a grade of 99.6±0.6% with respect to the other base metals (Figure 3.7). Longer residence times maintained a high grade of samarium but overall recovery decreased. Residence times shorter than 50 minutes produce a samarium grade of 80% or less.

It was found that complete decomposition of cobalt, iron, and copper sulfate occurred after 50 minutes. Samarium recovery steadily decreased above 50 minutes while solution grade remained above 99% (Figure 3.8). For these reasons, 50 minutes was chosen as the ideal residence time at 750°C with an acid molarity of 4.8.

The steady decrease in samarium recovery indicates that 750°C is above the decomposition temperature of samarium sulfate. However, the difference in the decomposition rate between samarium sulfate and cobalt sulfate is sufficient enough for a separation to be possible. It is unclear as to the exact decomposition point of samarium sulfate from these experiments.

Decomposition rates could be determined through a kinetic study of this process and would allow for the exact calculation of residence time within muffle furnace experiments. It would still be necessary, however, to study the kinetics of larger sample sizes. One of the major limitations of all muffle furnace tests in this study is the small sample sizes (<0.5 grams). Diffusion rates of liquids and gases through larger samples are altered by the quantity of sample being tested and mixing conditions within each experiment. Determination of the exact reaction mechanism and kinetics of this process is only possible through a better-controlled reactor set-up such as rotary kilns.
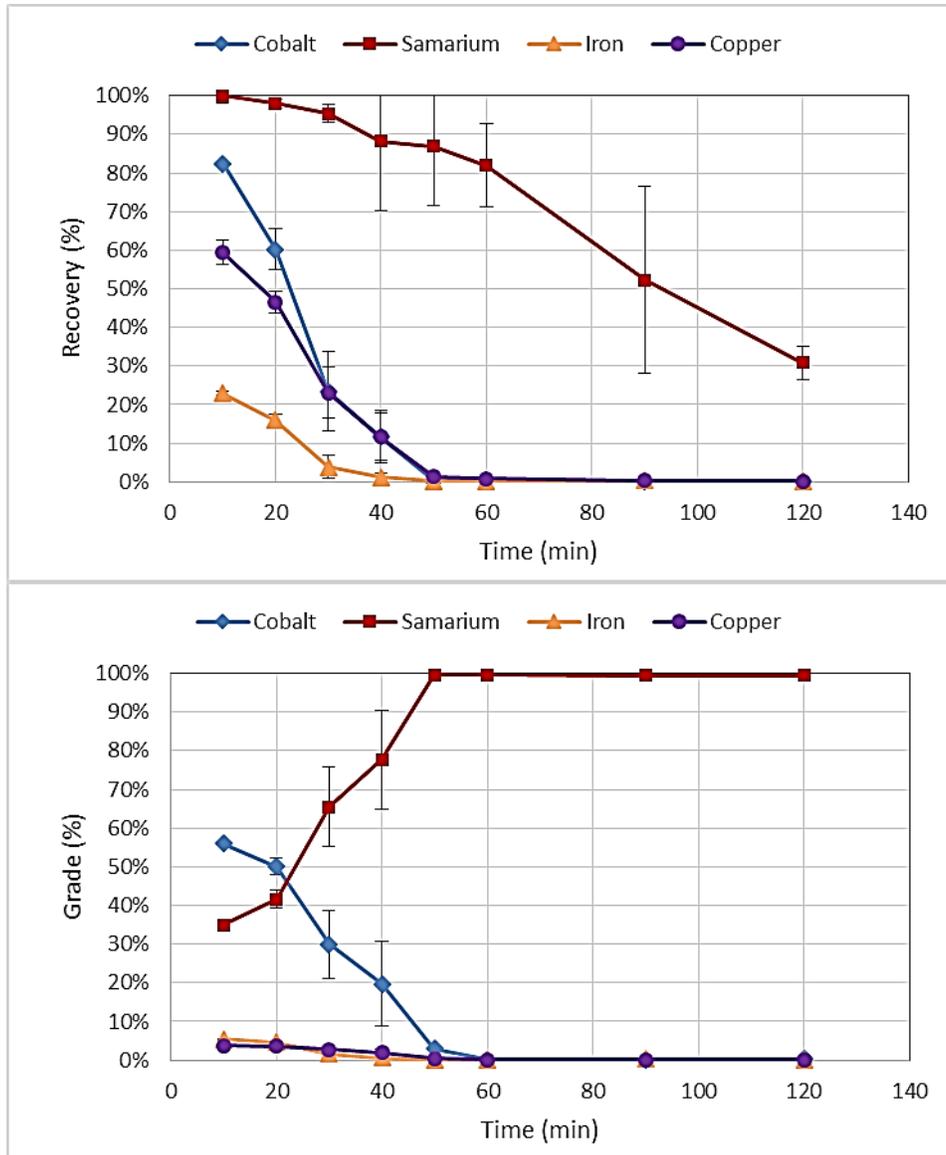
Figure 3.7: Recovery (top) and grade (bottom) of leach solution analyzing four elements versus residence time in muffle furnace experiments.
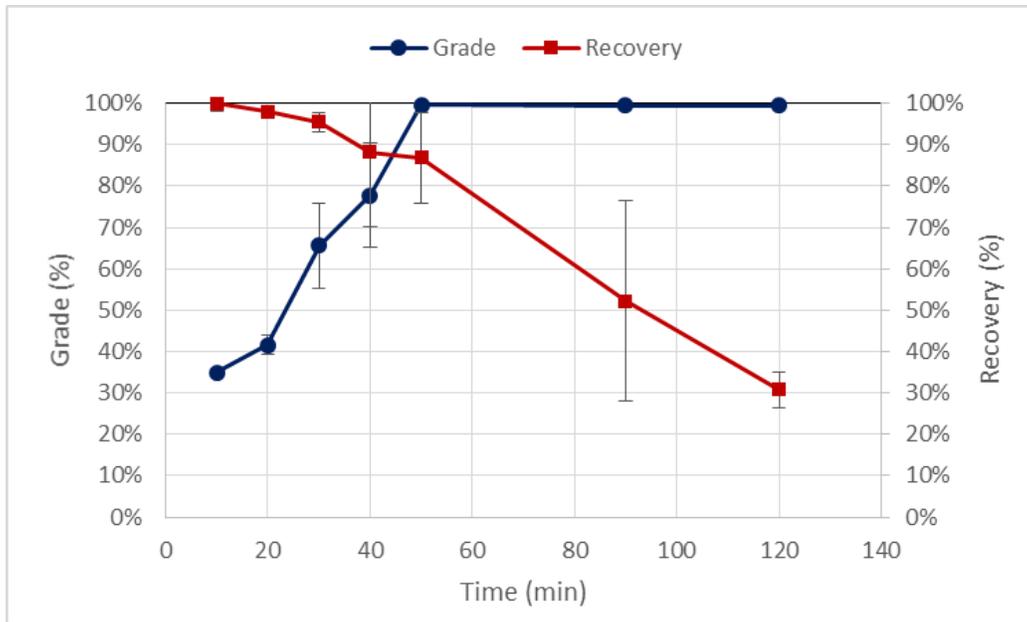
Figure 3.8: Grade (blue) and recovery (red) of muffle furnace leach solutions comparing samarium values versus residence time.

3.5   Rotary Kiln Experiments – Determining Conditions for Complete Sulfation

Several factors were compared when determining the necessary conditions for complete sulfation of the starting swarf material. These include temperature, time, acid-to-swarf stoichiometric ratios, air flow rate, mixing of the reactor vessel, and pulp density. The goal of these experiments is to determine the optimal conditions for complete sulfation of the starting swarf material. Procedures listing the steps taken in these experiments can be found in Section 2.6.2. The low and high values for each of these factors are shown in Table 3.3 below. A partial factorial design of experiments is utilized to determine the interactions and significance of each of the tested factors. This is conducted through 17 experiments including one midpoint.

Table 3.3: High and low values tested for each factor in sulfation rotary kiln experiments

Factor	Temperature	Time	Acid:Swarf	Gas Flow Rate	Mixing	Pulp Density
Low	300°C	0 min	1.4 : 1	2 L/min	no mix	5% solid
High	400°C	60 min	2.8 : 1	9 L/min	mix	20% solid

In order to better understand the results of these experiments, the data has been analyzed according to differences in residence time. Factors such as pulp density, temperature, acid-to-swarf ratio, mixing, and gas flow rate were averaged as they had no significant effect on complete

conversion. No combination of these factors achieved complete sulfation at a residence time of zero minutes. Meanwhile, complete conversion was achieved at 60 minutes regardless of variations within the other factors.

The recovery and grade of cobalt, samarium, iron, and copper in the leach solutions are compared against roasting time in Figure 3.9. Error bars represent variation due to combined differences due to pulp density, temperature, acid-to-swarf ratios, mixing, and gas flow rate.

Figure 3.9: Leach solution recovery and grade of cobalt, samarium, iron, and copper compared with residence time and roasting temperature shown as a bar chart.

At the minimal residence time of zero minutes, the average recovery for cobalt is 85.2% ± 11.8%, samarium is 97.8% ± 0.5%, iron is 91.9% ± 6.1%, and copper is 0.2% ± 0.2%. However, the average recovery at the maximum residence time of 60 minutes is above 99.6% for each element analyzed. In every instance tested at 60 minutes there is complete dissolution of the starting material in the final leach solution with a sample loss ranging from 0.4% ± 0.1% of the starting mass. This mass loss accounts for the 99.6% recovery determined from the calculations. Further tests at 15 minutes determined that complete sulfation occurs at some point between 0-15 minutes regardless of variations within any other factor (Figure 3.10).
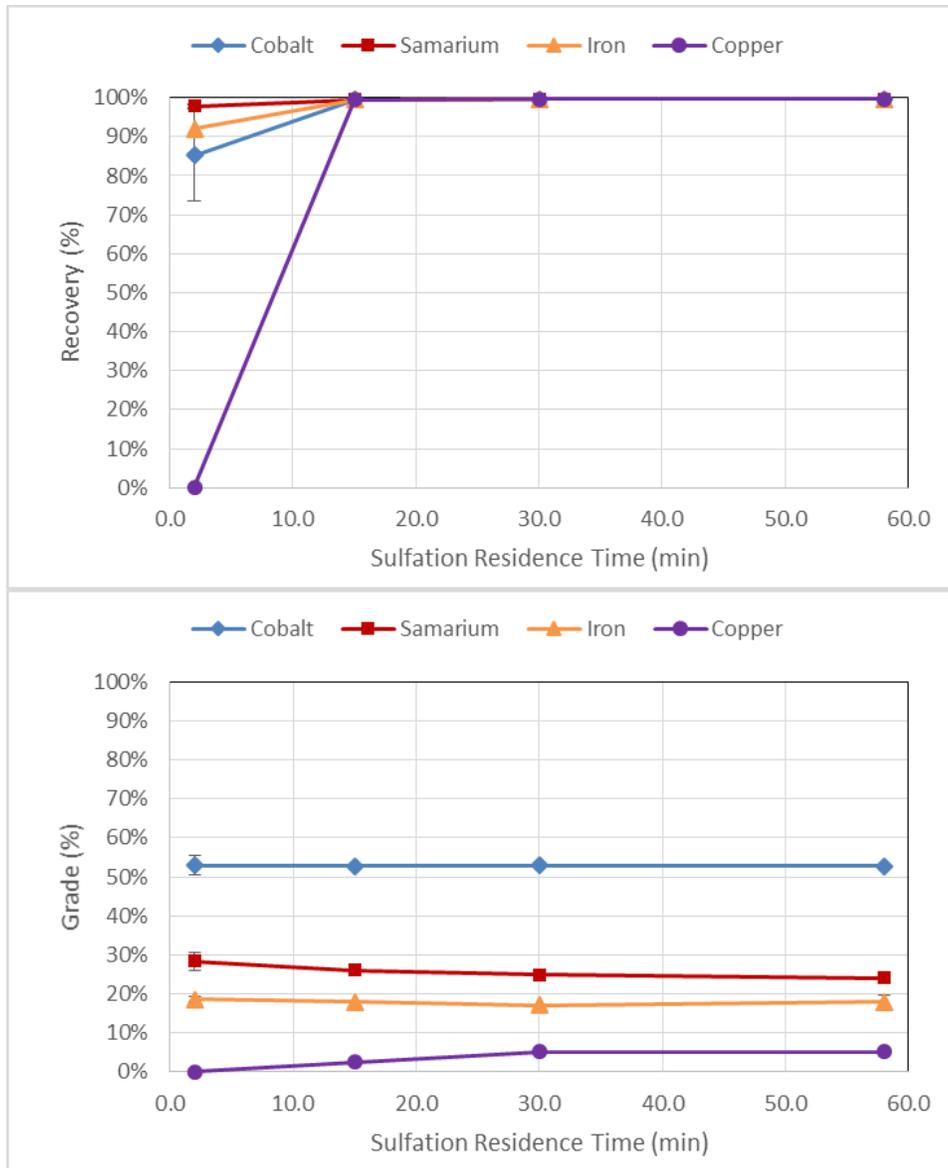
Figure 3.10: Leach solution recovery and grade of cobalt, samarium, iron, and copper compared with residence time shown as a line graph.

Optimal sulfation conditions were chosen based on convenience, minimal chemical costs, and minimal operation costs. The ideal sulfation conditions were determined to have a roasting temperature of 400°C, acid-to-swarf ratio of 1.4:1, gas flow rate of 2 liters per minute, mixing at 10 rpm, and pulp density of 5% solids. Complete sulfation occurs after 20 minutes or until anhydrous sulfate is formed. This is accompanied by a change in color from deep purple or pink to a pinkish-yellow color and the removal of any indication of moisture in the samples (Figure 3.11).

Figure 3.11: Image showing differences in appearance of swarf-acid mixture during and after sulfation.

3.6   Rotary Kiln – Gas Composition

Rotary kiln trials showing the effect of gas composition on the recovery and grade of samarium are shown in Figure 3.12 below. Procedures for these experiments can be found in Section 2.6.4. Recovery is shown as a diagonal line pattern while grade is demonstrated by small dots. There is a large difference in recovery between argon and air with a difference of <1% and 83%, respectively. Grade varies between 48-60% between argon and air.

Figure 3.12: Effects of gas composition on the recovery and grade of samarium in rotary kiln leach solutions.

It was found that utilizing an air atmosphere results in a much higher recovery of samarium than in argon. This is likely due to unoxidized metals or alloys in the feed. In order to convert reduced

metal into sulfate it must first react with oxygen to form an oxide. The first stage in any sulfation reaction is oxidation of the starting material. This should be considered in any future processing method for this material.

3.7   Rotary Kiln – Effect of Temperature and Gas Flow Rate

A series of tests have been conducted to determine the effect of roasting temperature on the grade and recovery of samarium in the final leach solution. Temperatures of 740°C, 760°C, and 780°C have been tested over one hour to determine their effects. Higher temperatures result in lower recoveries of all metals in the final leach solutions (Figure 3.13). The ideal sulfation parameters are followed for each experiment. Procedures for these experiments can be found in Section 2.6.3.

The effect of gas flow rate at various roasting temperatures is found to have a significant impact on the overall grade and recovery of samarium in the leach solution. This can be observed in Figure 3.13 below. A significant decrease in cobalt recovery from 73.0% to 22.2% is observed after one hour from 740°C to 780°C, respectively, after one hour. Final cobalt grade in the leach solution dropped from 53.3% at 740°C down to 30.0% at 780°C. The recovery of samarium was 97.8% at 740°C versus 89.3% at 780°C over the same time.

A similar set of experiments testing higher gas flow rates of 9 L/min were conducted over the same temperature range of 740-780°C. The conversion rates of sulfates to oxides is much faster with higher gas flow rates through the system. Results from these experiments can be seen in Figure 3.14 below. The recovery of cobalt dropped from 37.9% to 0.9% between 740°C and 780°C. Similar trends were observed for iron and copper with decreased recoveries from 11.2% to 0.0% and 24.2% to 0.3%, respectively. Samarium recovery decreased from 99.1% to 20.7% at temperatures from 740°C to 780°C.

The gas flow rate is believed to have a direct effect on the atmospheric composition of the reactor vessel by influencing the rate of gas evolution from the system. Higher gas flow rates result in a deficiency of sulfur dioxide in the system thereby shifting the sulfate stability region to that of oxide (Figure 3.15). The stability region of samarium sulfate could not be estimated through HSC due to the fact that multiple phases of samarium sulfate and oxysulfate are not available. It can be assumed from this information that higher gas flow rates will increase the rate of sulfate decomposition in this system.

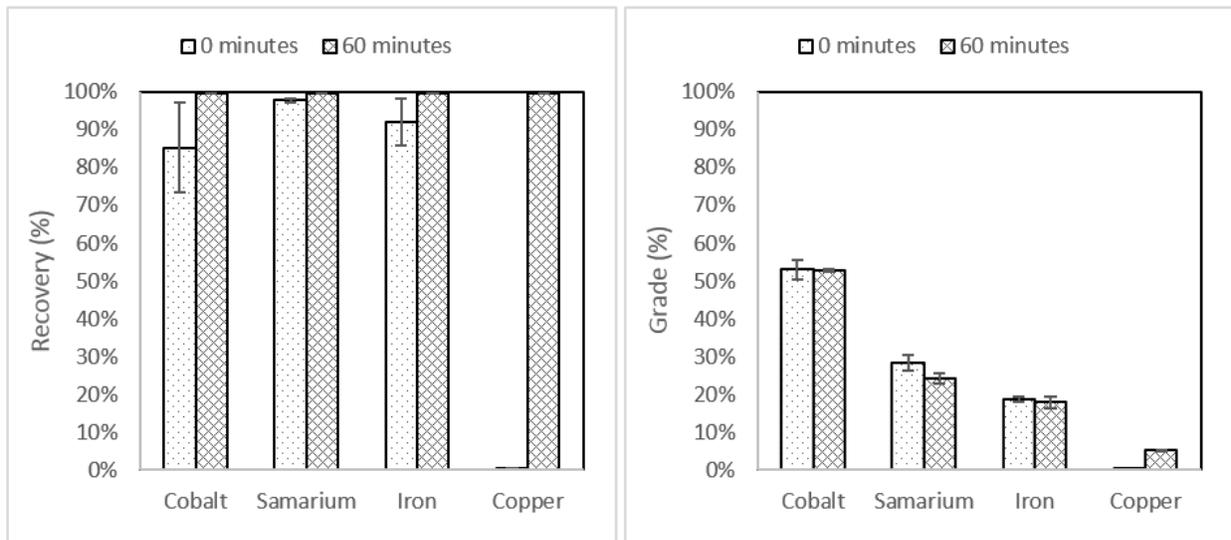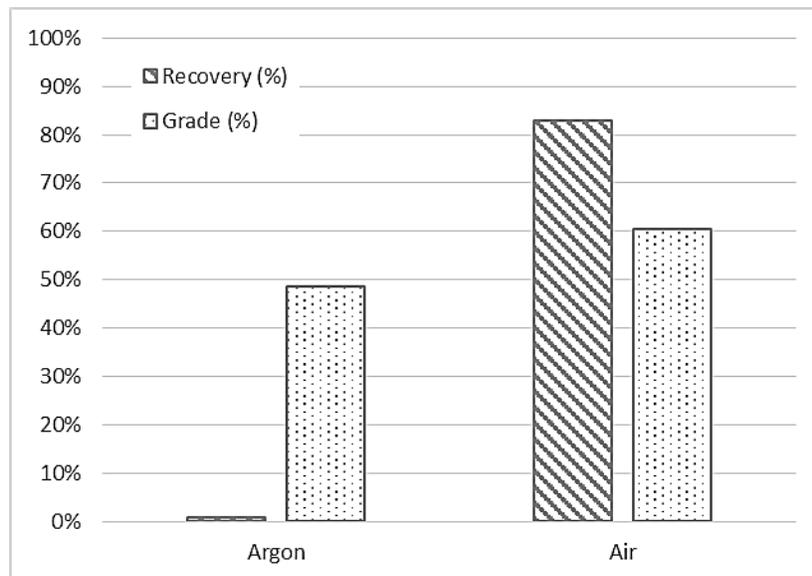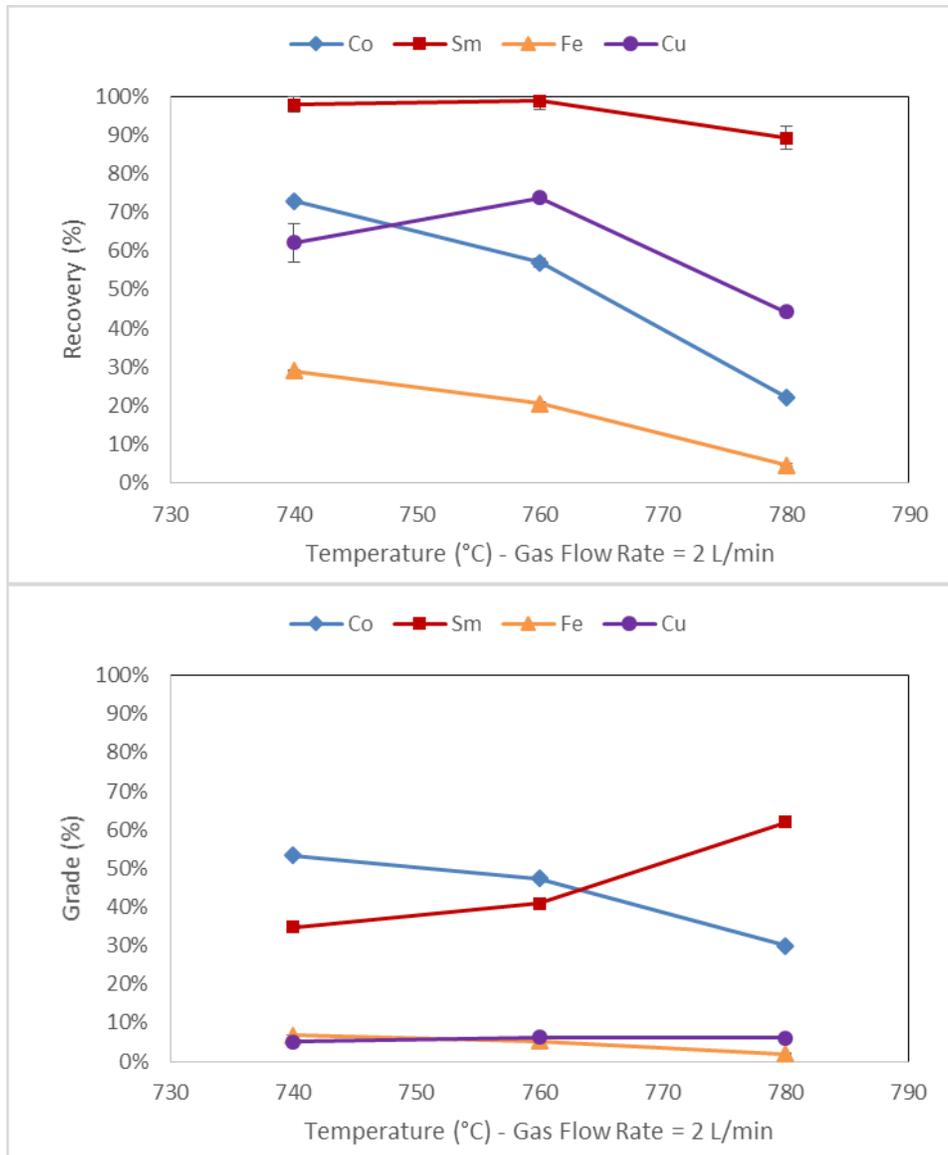Figure 3.13: Leach solution recovery (top) and grade (bottom) of four elements compared with roasting temperature and gas flow rate.
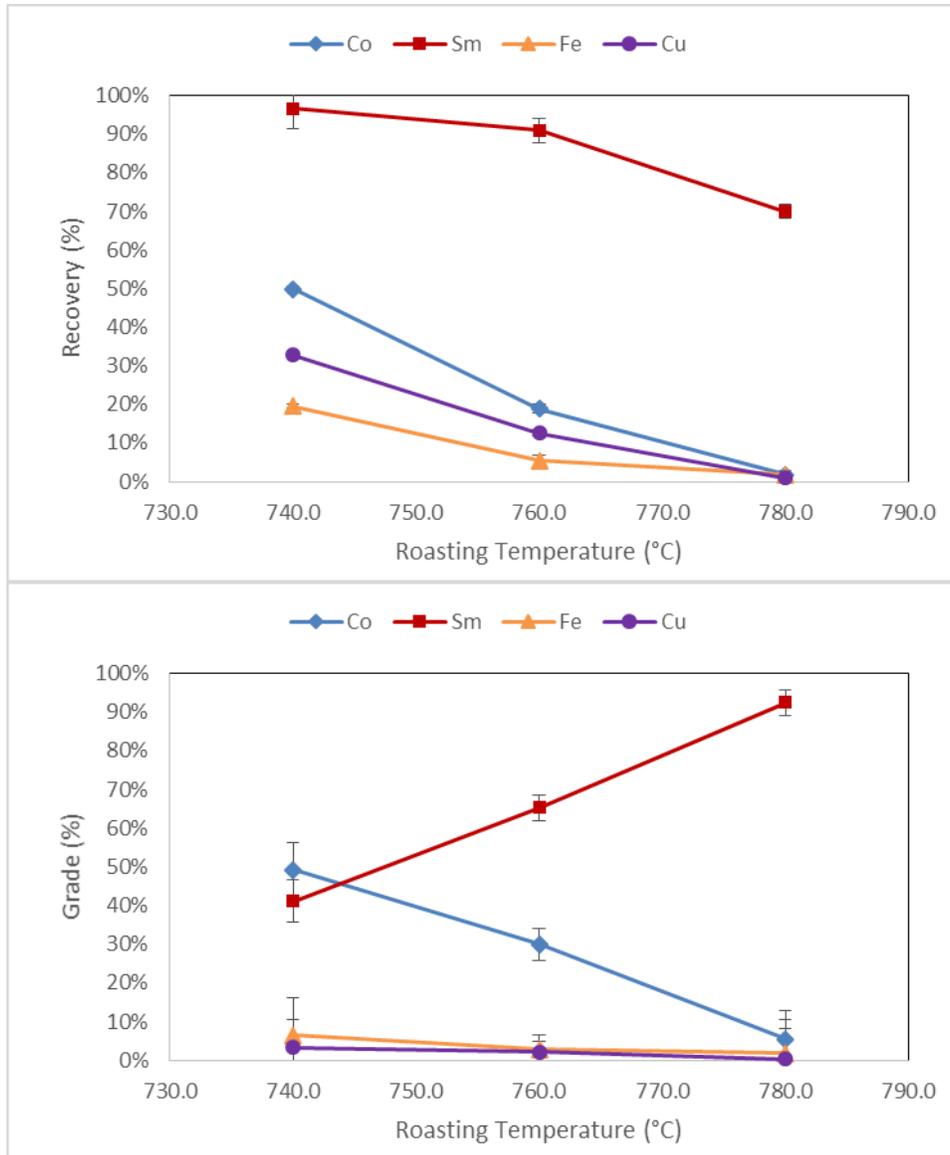
Figure 3.14: Leach solution recovery and grade of cobalt, samarium, iron, and copper compared with roasting temperature. Residence time fixed at one hour.
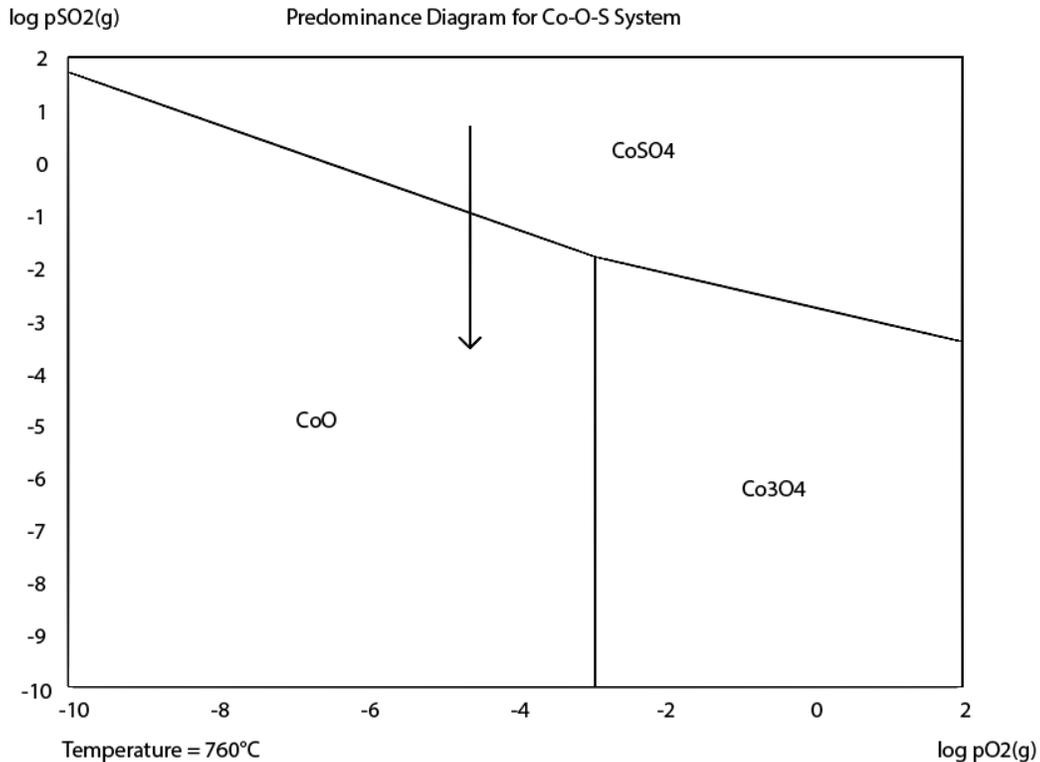
Figure 3.15: Predominance diagram for the Co-O-S system showing the sulfate stability region for cobalt. Diagram created through HSC 7.

3.8   Rotary Kiln – Effect of Residence Time

The decomposition rate of the four major elements has been determined through an experiment where multiple samples were tested in 15-minute time intervals at 780°C. Results from these tests can be seen in Figure 3.16 below. Samarium recovery was approximately 70% after 60 minutes with a grade of 92.4±3.4%. A steady increase in grade is observed with a comparable decrease in recovery over time at 780°C.

There was no mixing at this temperature with a gas flow rate of 9 liters per minute compressed air. For these reasons, the decomposition rate is believed to be slower than it could be. It has been shown from previous experiments that the gas flow rate has a direct impact on the decomposition rate. This is believed to be due to a sulfation atmosphere that is created during roasting and the gradual evolution of sulfur dioxide from the system. It is possible that the sulfur dioxide composition of the input gas could be controlled to preferentially drive base metals to oxides while maintaining samarium in its sulfate form. Likewise, mixing in the system could increase the reaction rate by limiting the formation of a fluid film around sulfate particles above the

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decomposition temperature threshold. These hypothesis could be tested in future experiments in a continuous rotary kiln system but are unable to be tested with the current apparatus due to technical limitations.

Further testing of residence time beyond one hour of roasting at 780°C produced an interesting trend in the behavior of samarium sulfate in this system. Overall samarium recovery in 5-gram sample tests remained high as long as cobalt recovery remained above 20% (Figure 3.16). In contrast to this, 10-gram sample tests revealed that overall samarium recovery remained high until cobalt recovery dropped below 10%. These larger samples are shown in Figure 3.17 below, where sulfate conversion in grams (top) and elemental recovery (bottom) are compared with time. Gram values were calculated by subtracting leach solution recovery from the total amount of each element in each test.

There is a linear correlation between the onset of samarium sulfate to oxide conversion and the mass of cobalt sulfate in the system. In the 5-gram sample tests, the samarium recovery remained above 95% while cobalt recovery was above 20%. The same mass of cobalt is represented by 10% recovery in the 10-gram samples. Likewise, the partial pressure of sulfur dioxide drops below 0.01 atmospheres after 2 hours and is simultaneously correlated by a sharp decrease in samarium recovery.

One possible reason for this correlation is that the availability of sulfur dioxide is directly linked to the stability of samarium sulfate. This would be reasonable as the stability range of samarium sulfate to samarium oxysulfate is directly linked to the availability of oxygen and sulfur dioxide at this temperature range. Unfortunately, no previous research has studied the stability of samarium sulfate in sulfur-oxygen systems in a controlled environment. It is therefore impossible to correlate these suggestions with any previous work. From the results of this study it appears that samarium sulfate is stable at sulfur dioxide partial pressures above 0.01 atmospheres. This partial pressure would be an essential design characteristic of a roasting reactor for this system.
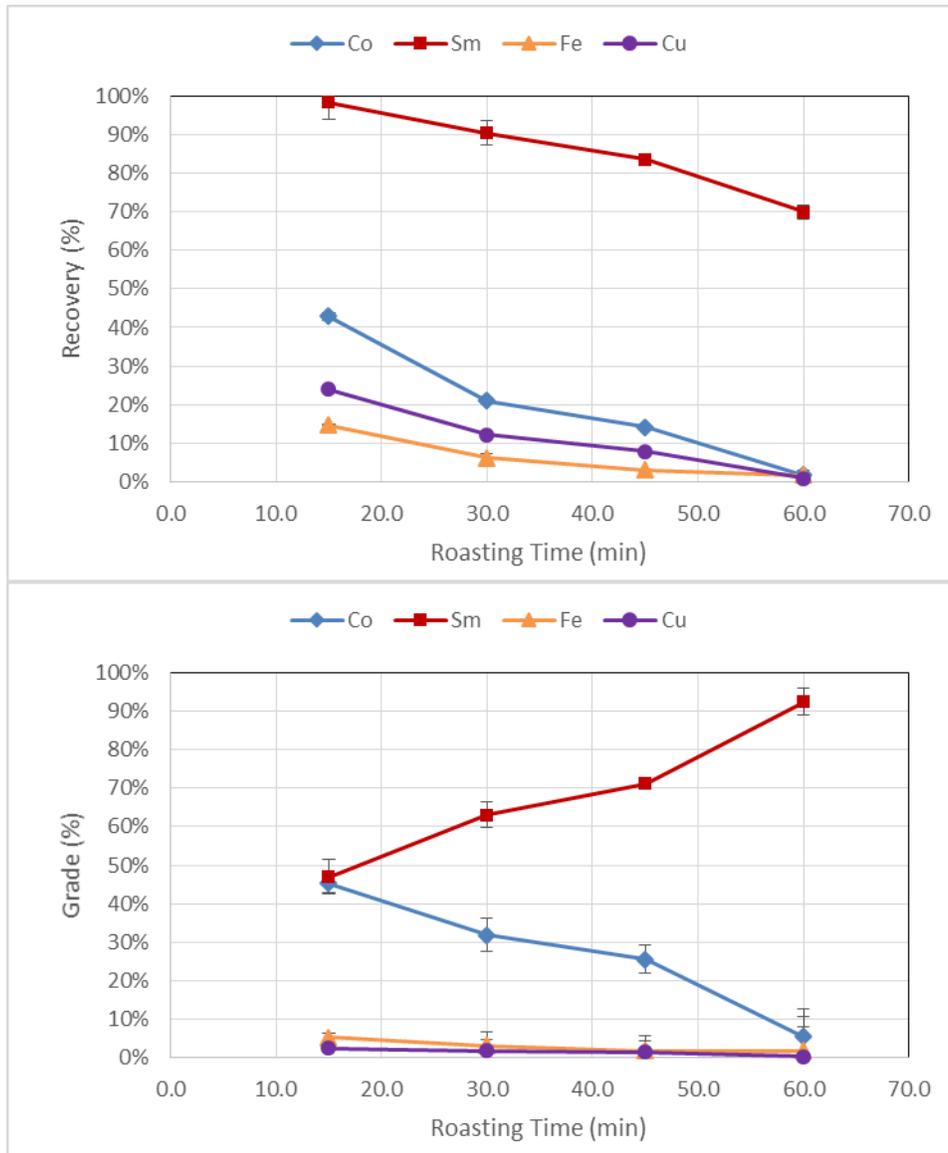
Figure 3.16: Recovery (top) and grade (bottom) of cobalt, samarium, iron, and copper in leach solutions versus residence time in rotary kiln experiments.
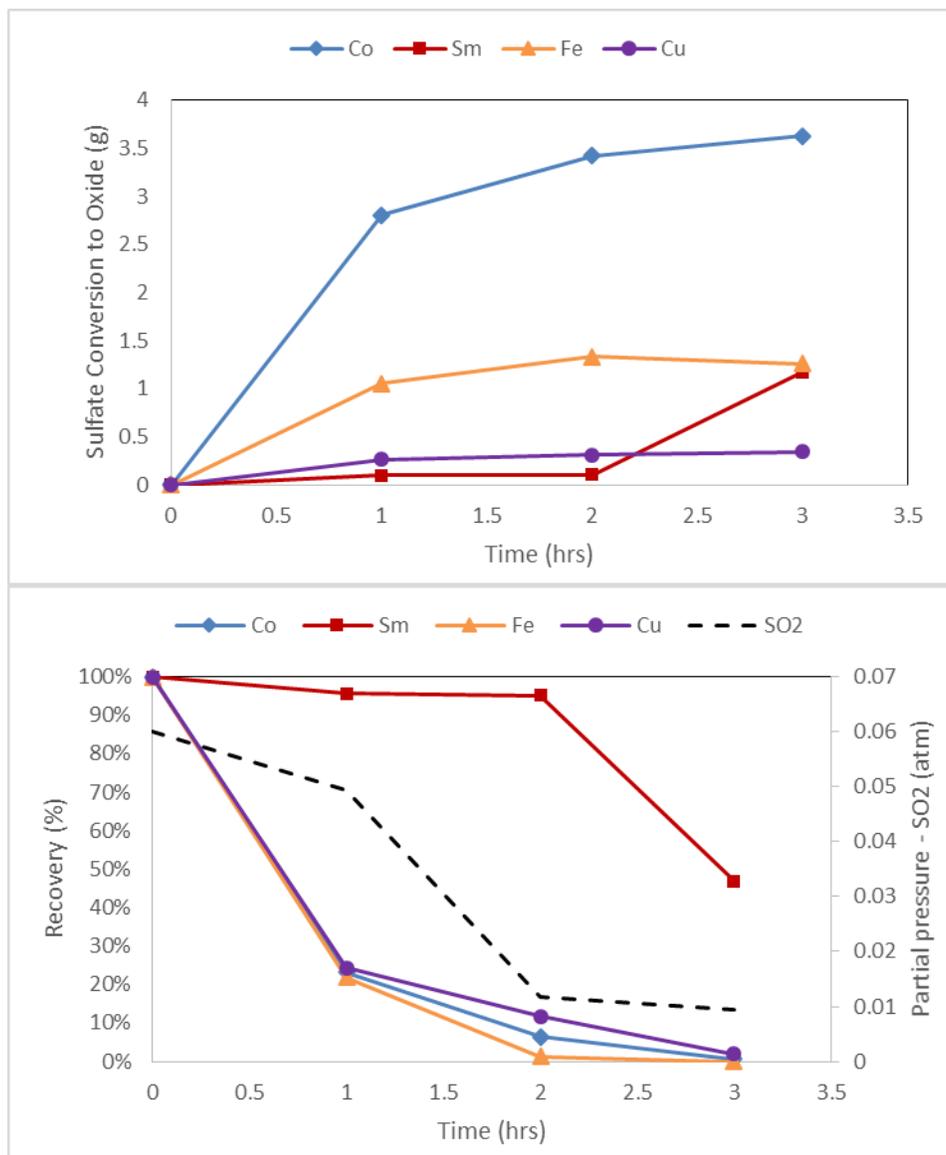
Figure 3.17: Sulfate decomposition in grams versus time (top) and recovery of cobalt, samarium, iron, and copper in leach solutions versus time (bottom) at 780°C.

CHAPTER 4

ECONOMICS

Ideal roasting conditions were chosen based on samarium recovery and grade in the final leach solution. A two-stage process is proposed as a method for treating samarium-cobalt magnet swarf (Figure 4.1). This would include two continuous rotary kiln reactors operated at 740°C and 780°C. The initial feed would be inserted into the rotary kiln heated to 780°C in the presence of sulfuric acid, oxygen, and water. A countercurrent flow of off-gases would drive feed in the input to convert to sulfates while the output is a mixture of samarium sulfate and base metal oxides. System operating parameters in the first roasting stage would be designed to maximize samarium recovery while removing most of the base metals by controlling the roasting atmosphere. Solid residue is leached before vacuum distillation and insertion of the sulfate precipitate into a secondary roasting reactor operated at 740°C. In this stage, conditions are optimized to promote samarium grade while removing remaining base metals at a slower rate. The residue is leached with demineralized water and filtered to produce a pure samarium leach solution. Oxalic acid addition is utilized to precipitate samarium oxalate which is then calcined to provide a pure samarium oxide product. Cobalt-rich residue is also recovered from the waste streams, which can be sold to cobalt refining operations or further enriched through the same system to remove iron.

Economic analysis is based on complete recovery of cobalt from the system which is priced as scrap metal for cobalt refineries at $2 per kilogram. Samarium recovery is assumed to be 70% with a grade above 99%. Samarium oxide at this purity level can be sold at market for $1.8 per kilogram. If purity can be increased to 99.9%, the price of samarium oxide is $12 per kilogram. Economic estimates are based on the conservative value of $1.8 per kilogram. Sulfuric acid is priced at $0.8 per kilogram with a 97% recovery in the acid plant. Oxalic acid prices are estimated at $1 per kilogram with no recycling.

Two cases are presented to compare the net present value (NPV) after 5 years in processes with and without an acid plant. Costs are based on a feed input of 1000 metric tonnes per year samarium-cobalt swarf material with a sulfuric and oxalic acid consumption of 1500 metric tonnes

and 200 metric tonnes per year, respectively. Adjusted cash flow is estimated with a 5% interest rate. Product price estimates are made with conservative values for both samarium and cobalt.

It appears possible to achieve a NPV of $2.2 million over a five year period with a payback period of just under 2 years if this process is coupled with an existing acid plant operation. Cost estimates for the purchase of a new sulfuric acid plant are not included in this process because annual processing rates are too low to warrant its construction. This process is not economically feasible if a pre-existing acid plant is unavailable.

An overview of capital expenditures can be found in are shown in Figure . These include estimates based on equipment, installation, instrumentation, auxiliary and engineering expenditures, and a 20% contingent plan. The total capital costs for construction of a plant processing 1000 metric tonnes of feed material per year is estimated at approximately $1.48 million. Chemical and energy costs are estimated at $355,000 per year while revenue is projected at approximately $1.99 million per annum.
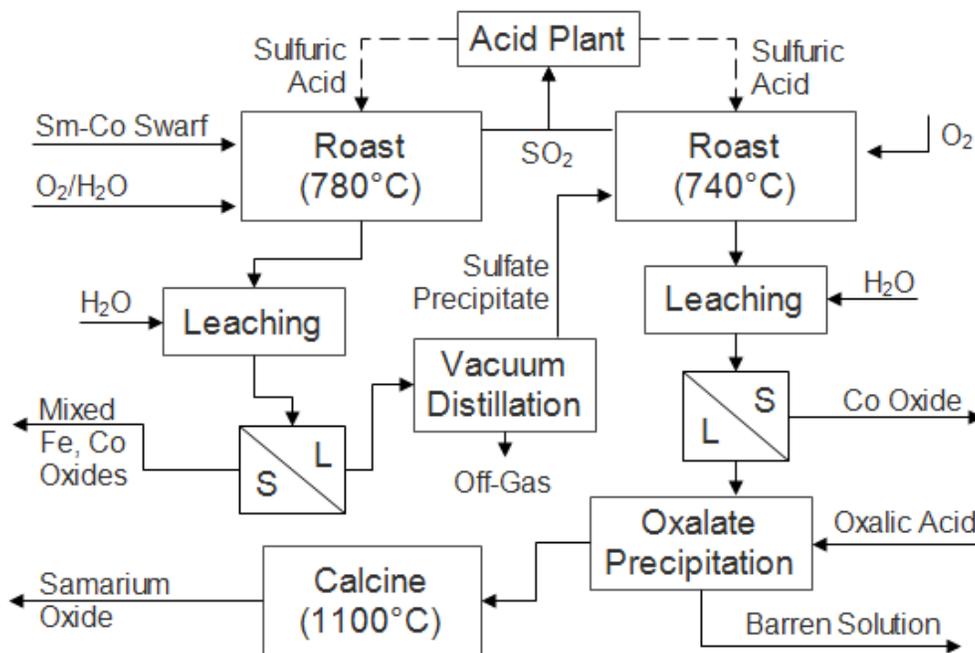

Figure 4.1: Proposed process flow diagram for a two-stage roasting process followed by leaching, cementation, and calcination

CHAPTER 5

CONCLUSIONS

A series of parameters were tested to determine their effect on the grade and recovery of four major elements from samarium-cobalt magnet swarf through an acid-bake-leaching process. These experiments were first carried out in muffle furnace experiments to fine-tune parameters such as temperature, residence time, and acid addition. Meanwhile, rotary kiln experiments demonstrated the ability of scaling up this process to treat a larger amount of material. Parameters tested in rotary kiln experiments included temperature, residence time, acid addition, pulp density, gas composition, and gas flow rate.

The primary goal of this research was to selectively recover samarium from the starting swarf material. Parameters in this process were optimized to selectively remove samarium while cobalt and iron were removed as insoluble residue. This residue is later recycled through this process to enrich the cobalt value at slightly lower temperatures. Final product is obtained through oxalate precipitation and calcination.

It was found that complete sulfation of this material is possible with 40% excess sulfuric acid after a period of 15-20 minutes at 400°C. This is believed to be due to the formation of a sulfur-trioxide rich atmosphere that is responsible for the conversion of metal oxides to sulfates. Samples are then heated to temperatures above 700°C in which base metal sulfates are preferentially decomposed into oxides while samarium remains as a sulfate. Two roasting conditions are proposed as a result of the data obtained from the experiments conducted in this study. The first roasting stage will be set at 780°C with a sample residence time of 20-40 minutes which will be followed by leaching in demineralized water, filtration, and vacuum distillation of the leachate to form a relatively pure mixed metal sulfate with a samarium grade above 90%. The second roasting stage will include the mixed metal sulfate powder from the first stage set at 740°C with a residence time of 60-90 minutes. Exact roasting conditions will need to be optimized in future experiments in continuous rotary kiln reactors based on the results of batch experiments conducted in this study. The mixed sulfate-oxide product from the second roasting stage is leached again in demineralized water, filtered, and the

leachate is mixed with oxalic acid to produce samarium oxalate precipitate. This cemented powder is then filtered and calcined in a third roasting stage at 1100°C to produce samarium oxide product.

Results from the experiments conducted in this study suggest that a samarium recovery above 80% with final samarium oxide purity above 99% is possible with a sulfation roast and leaching process as proposed above. The samarium recovery estimate is a conservative value based on the results from this study. However, this process is only possible if the sulfur dioxide off-gas produced during roasting can be recycled in an acid plant. A net present value of approximately $2.2 million is possible after 5 years if an acid plant is available. The process is not economically viable without an acid plant.

5.1   Future Experiments and Recommendations

Several experiments should be conducted to better estimate cost, recovery, and product quality estimates proposed in this study. Rotary kiln experiments determined that gas flow rate in the reactor during roasting has a large effect on the sulfate decomposition rate. The highest gas flow rate tested was 9 liters per minute compressed air. Higher gas flow rates may increase the rate of sulfate decomposition and decrease necessary residence time in the reactor. In addition, mixing at high temperatures was not conducted due to technical complications with the reactor and risks associated with sample loss. Future experiments utilizing continuous rotary kiln reactors should consider increasing gas flow rates and test the effect of mixing during high-temperature roasting.

It is unclear from the results of these experiments of the phase stability of anhydrous samarium sulfate or the various samarium oxy-sulfates proposed in the literature (Poston et al., 2003; Wilfong et al., 1964). A more accurate understanding of the phase stability of the various samarium sulfate and oxy-sulfate phases may enable a more selective separation of samarium from the base metals at higher temperatures and decrease residence time. From several experiments it appears that samarium sulfate is stable as long as a sufficient amount of cobalt sulfate remains in the system. This suggests that the evolution of sulfur dioxide from decomposing cobalt sulfate may create a partial pressure of sulfur dioxide sufficient to maintain samarium sulfate at temperatures well above its decomposition point. It is well known that the rare earth sulfate temperature stability region is higher than the base metals. Future experiments should consider varying the availability of sulfur dioxide in the reaction vessel during roasting. From these tests it may be possible to maintain

samarium sulfate at 780°C while converting all other metals to oxide and greatly improving the grade of the final product. It may even be possible to increase the samarium oxide grade above 99.9%, which would result in a price increase of nearly $10 per kilogram. This would result in an annual revenue increase of nearly $2.1 million with lower residence time and fewer capital costs.

Several major factors that were not tested in these experiments were the effect of leaching conditions, the amount of oxalic acid necessary for precipitation, and the behavior of this process on a pilot-scale. Leaching of samarium sulfate is nearly instantaneous in dilute demineralized water. However, the pulp density of the leach solution was not tested. The cost of water is not included in this study and could pose major operational expenditures in both supply and waste disposal depending on the location of the plant. Future experiments should investigate the minimum pulp density required to leach samarium sulfate as well as filtering behavior on various types of filtration equipment.

Another set of experiments should determine the necessary amount of oxalic acid that is required for samarium oxalate precipitation. These experiments would be fairly simple. The first step would be to obtain a samarium sulfate saturated leachate and slowly titrate oxalic acid into the solution until no more precipitate is formed. In this manner, it is possible to estimate the necessary oxalic acid require for complete cementation. These tests would need to be further updated after pilot-scale studies to determine the amount of oxalic acid required for continuous precipitation systems.

The majority of the influential factors in sulfation roasting and leaching have been determined through the experiments conducted in this study. These include residence time, acid addition, and temperature for complete sulfation, roasting temperature and residence time, and some estimation of roasting gas composition. Future experiments could improve these results for continuous and pilot-scale equipment. Final grade and recovery of the samarium oxide product could also be upgraded although the process is already determined to be economically feasible. Any future experiments will only add to the profit proposed in this project.

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ACID DISSOLUTION TESTS

A series of tests were initially conducted to determine which acid was most suitable for treating Sm-Co magnet swarf. These were done using nitric, sulfuric, and hydrochloric acid and were tested against acid molarity, leaching temperature, mixing speed. Leaching residence time was fixed at one hour. Samples at 0.5 grams were mixed with 36 mL of the chosen acid while temperature and mixing speed were varied. Results from these experiments are shown in Figure A.3A.3. Recovery and grade are shown to vary only slightly with changes in temperature and mixing speed. Acid molarity appears to be the largest contributing factor. Nitric acid functions slightly better than sulfuric acid in both grade and recovery. However, due to higher costs of nitric acid, sulfuric acid was chosen as the solvent for future experiments.
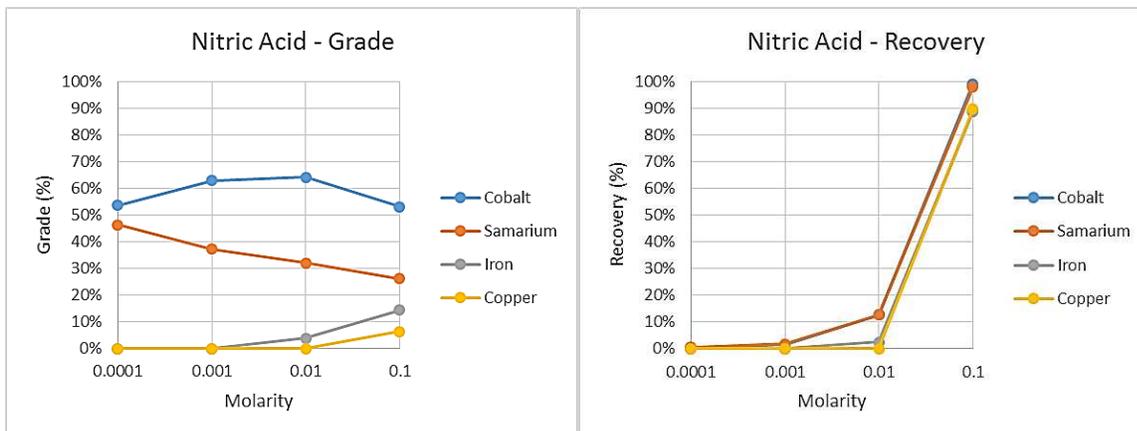

Figure A.1: Grade and recovery curves for four elements versus nitric acid molarity
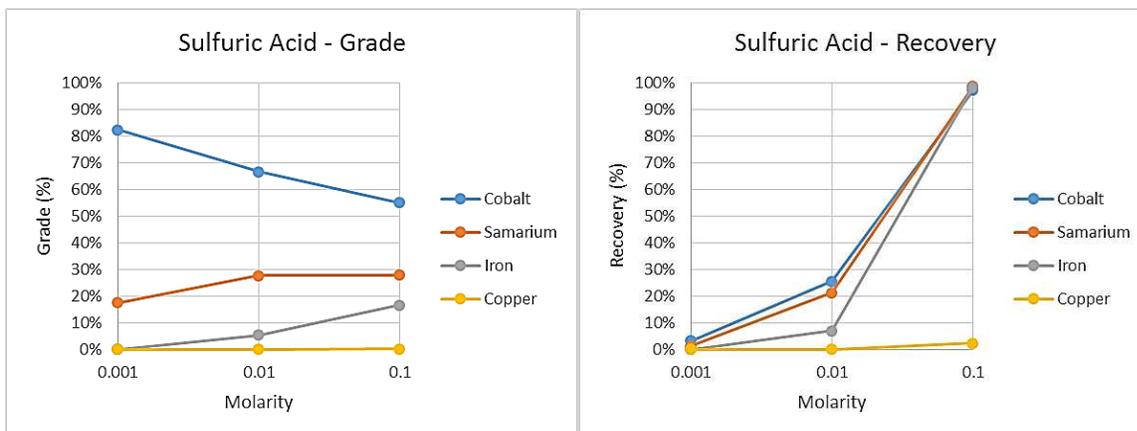

Figure A.2: Grade and recovery curves for four elements versus sulfuric acid molarity
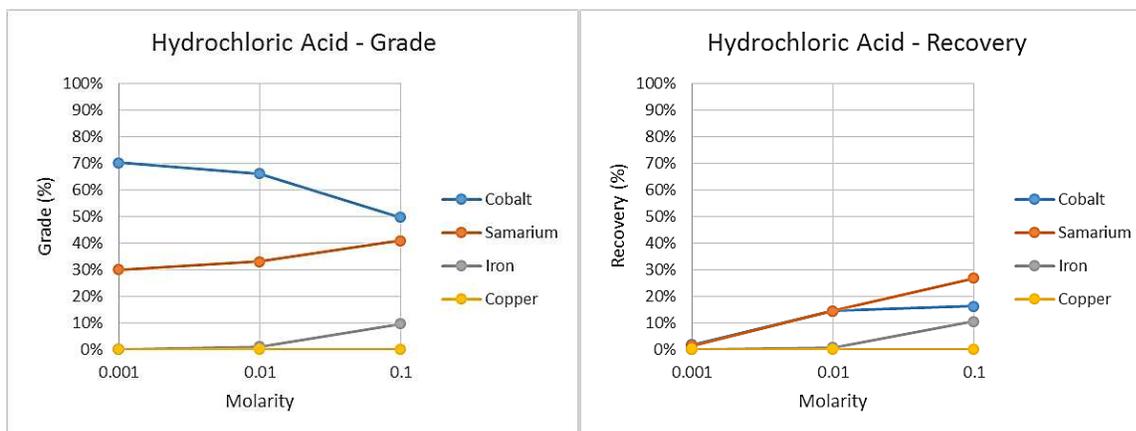
Figure A.3: Grade and recovery curves for four elements versus hydrochloric acid molarity

Table A.1: Recovery and grade calculations shown for each experimental condition in the acid leaching experiments. The description shown on the left describes upon what conditions each experiment was conducted while recovery and grade percentages for each element are shown on the right

Description	Recovery (%)				Grade (%)			
	Cobalt	Samarium	Iron	Copper	Cobalt	Samarium	Iron	Copper
0.1M HNO3, 1 hr, 400 rpm, 25°C	99.16%	98.03%	88.94%	89.67%	53.08%	26.24%	14.28%	6.40%
0.01M HNO3, 1 hr, 400 rpm, 25°C	12.73%	12.75%	2.53%	0.00%	64.08%	32.10%	3.82%	0.00%
0.001M HNO3, 1 hr, 400 rpm, 25°C	1.50%	1.77%	0.00%	0.00%	62.82%	37.18%	0.00%	0.00%
0.0001M HNO3, 1 hr, 400 rpm, 25°C	0.26%	0.45%	0.00%	0.00%	53.64%	46.36%	0.00%	0.00%
0.01M HNO3, 1 hr, 0 rpm, 25°C	13.09%	13.09%	1.87%	0.37%	64.65%	32.33%	2.77%	0.24%
0.01M HNO3, 1 hr, 400 rpm, 70°C	13.77%	11.99%	0.00%	0.00%	69.66%	30.34%	0.00%	0.00%
0.1M H2SO4, 1 hr, 400 rpm, 25°C	97.08%	98.55%	98.49%	2.39%	55.09%	27.96%	16.77%	0.18%
0.01M H2SO4, 1 hr, 400 rpm, 25°C	25.64%	21.36%	7.06%	0.00%	66.70%	27.78%	5.51%	0.00%
0.001M H2SO4, 1 hr, 400 rpm, 25°C	3.24%	1.38%	0.00%	0.00%	82.43%	17.57%	0.00%	0.00%
0.01M H2SO4, 1 hr, 0 rpm, 25°C	21.05%	23.70%	14.61%	0.90%	56.28%	31.68%	11.72%	0.32%
0.01M H2SO4, 1 hr, 400 rpm, 70°C	23.28%	17.62%	0.00%	0.00%	72.54%	27.46%	0.00%	0.00%
0.1M HCl, 1 hr, 400 rpm, 25°C	16.22%	26.78%	10.51%	0.00%	49.51%	40.86%	9.62%	0.00%
0.01M HCl, 1 hr, 400 rpm, 25°C	14.46%	14.42%	0.76%	0.00%	66.03%	32.93%	1.04%	0.00%
0.001M HCl, 1 hr, 400 rpm, 25°C	1.69%	1.45%	0.00%	0.00%	70.05%	29.95%	0.00%	0.00%
0.01M HCl, 1 hr, 0 rpm, 25°C	8.17%	8.92%	0.00%	0.00%	64.71%	35.29%	0.00%	0.00%
0.01M HCl, 1 hr, 400 rpm, 70°C	0.02%	0.02%	0.00%	0.00%	70.06%	29.94%	0.00%	0.00%

APPENDIX B

SWARF COMPOSITION CALCULATIONS

In the first series of experiments utilizing the muffle furnace, there were five samples that were completely converted to sulfate and dissolved in water. This was accomplished through a two-step process of heating 0.1 grams of swarf with acid and water to 250°C for 1 hour before heating to 350°C for another hour. Samples were removed and dissolved in 50 mL water. Analysis with ICP-MS gave an average mass of elemental cobalt, samarium, iron, copper, and other minor constituents. Equal-molar ratios of copper and cobalt with oxygen and a 3/2 ratio of oxygen to samarium and iron were assumed for the following calculations. Moles of elemental oxygen were calculated using the known weights and molar masses of measured values. The averaged mass of the five samples was 102.12 mg while the calculated mass of the four major elements and oxygen was found to be 101.54 mg (Table B.). This indicates that the four major elements account for 99.43% of the starting material.

Table B.1: Calculations of the mass of the swarf material assuming cobalt(II), samarium (III), iron(III), and copper(II) are all oxides.

Description	Mass (mg)	MW (g/mol)	Element (mol)	Oxygen (mol)
Cobalt	41.1	58.933	0.000697	0.000697
Samarium	20.9	150.36	0.000139	0.000208
Iron	14.1	55.845	0.000252	0.000379
Copper	3.9	63.546	0.000061	0.000061

Calculated Mass	101.54 mg		Total Oxygen (mol)	0.001346
Actual Mass	102.12 mg		Total Oxygen (mg)	21.536023
Percent of Total	99.43%			

MUFFLE FURNACE PREBAKING STAGE CALCULATIONS

One of the initial experiments ran in the muffle furnace was a study on the effect of pre-baking time on the overall recovery and grade of the leach solutions. As mentioned in the experimental methods, a pre-baking stage was determined to be necessary to prevent rapid boiling and expulsion of sample from the crucibles. A pre-baking time of 5-25 minutes in 5 minute intervals was compared against grade and recovery of four major elements: cobalt, samarium, iron, and copper (Figure C.1). These elements account for 99.4% of the starting material in magnet swarf (see Appendix B). A recovery of 86.55%±1.44% was achieved with a grade of 97.72%±0.49% within 20 minutes on account of samarium and the three other major elements (Table C.1).

Table C.1: Grade and recovery data for a pre-baking study in a muffle furnace. Four major elements are compared.

Description	Grade (%)				Recovery (%)			
Time at 250°C (fixed: 750°C for 1 hr, 30 min leach at 900 rpm)	Cobalt	Samarium	Iron	Copper	Cobalt	Samarium	Iron	Copper
5 min	0.11%	87.07%	2.75%	0.55%	0.25%	97.64%	2.00%	0.11%
10 min	0.18%	84.92%	2.46%	2.01%	0.40%	97.27%	1.90%	0.43%
20 min	0.12%	87.65%	1.76%	0.82%	0.27%	98.24%	1.32%	0.17%
25 min	4.45%	87.34%	2.17%	9.66%	7.75%	89.22%	1.42%	1.60%
	Average	86.55%			Average	97.72%		
	Std Dev	1.44%			Std Dev	0.49%		

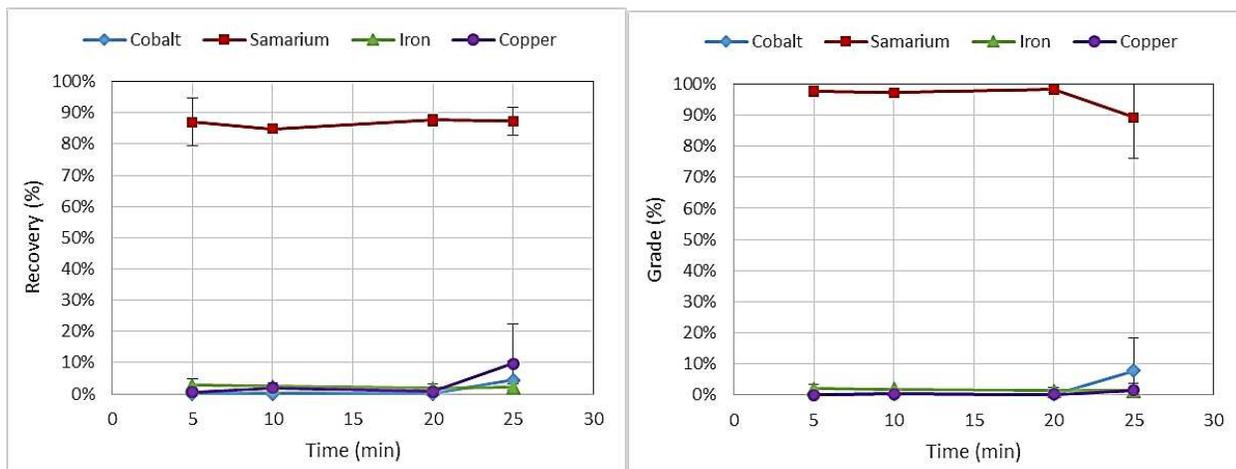

Figure C.1: Recovery (top) and grade (bottom) shown for pre-baking stage versus residence time.

CAPITAL COST CALCULATIONS

AREA	#	Equipment	Equip #	Description	Number	Price FOB	Total
Roasting	1	Loader	L-001	Skid Steer Loader	1	33,500	33,500
$575,600	2	Concrete Storage Bin	B-001	Residue Storage Bin	1	18,000	18,000
	3	Screens	C-001	Inlcined Screen	1	28,500	28,500
	4	Feed System	CN-001/002	2 Conveyor, Misc	2	10,300	20,600
	5	Kiln	T-001/002	Indirect Fire	3	90,600	271,800
	6	Heat Exchanger	P-001/002	Shell and Tube	2	101,600	203,200
Cementation	1	Agitator	AG-001/002	Closed Tank	3	21,400	64,200
$113,180	2	Pump	P-001/002	Rotary	2	10,200	20,400
	3	Filter	B-001	Plate and Frame	2	14,290	28,580
							688,780

AREA		Equipment	Installation	Piping, Instrumentation	Auxiliaries	Engineering	Sub Total	Contingent
			40%	30%	7.5%	15%		20%
Roasting		$575,600	$230,240	$241,752	$60,438	$166,205	$1,032,483	$206,497
Cementation		$113,180	$45,272	$47,536	$11,884	$32,681	$203,017	$40,603
Building (29%)		$199,746					$199,746	
Column Totals		$688,780	$275,512	$289,288	$72,322	$198,885	$1,235,499	$247,100

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TOTAL CAPITAL COSTS:	**$1,482,599**
TOTAL CHEMICAL COSTS	**$234,723**
TOTAL ENERGY COSTS	**$120,356**
PROJECTED REVENUE	**$2,344,162**

Figure D.1: Overview of capital expenditures for a two-stage sulfation roast and leaching process