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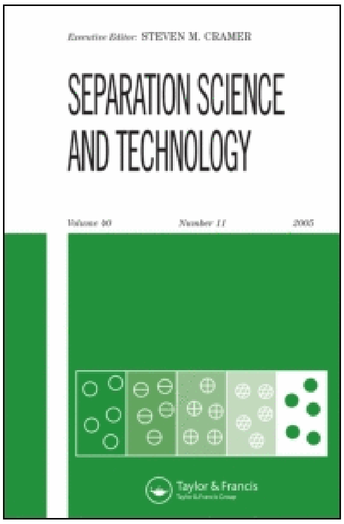

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A ROAST-LEACH PROCESS FOR EXTRACTION OF RARE EARTHS FROM COMPLEX MONAZITE-XENOTIME CONCENTRATES

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ABSTRACT

The proposed process approaches the problem of solubilizing rare-earth phosphates (monazite and xenotime) found at the Pea Ridge iron mine in Sullivan, MO, from both a pyrometallurgical and hydrometallurgical point of view. It utilizes a roasting operation that converts the rare-earth phosphates to rare-earth oxides (REOs), which eliminates some costly and hazardous processing steps currently in practice. Different combinations of roasting temperatures and acid concentrations have been investigated to selectively extract the rare-earth values. Cerium is selectively solubilized by roasting at 427°C and leaching with a sulfuric acid concentration of 265 g/L. After the cerium is removed, the neodymium and lanthanum can be solubilized at a roasting temperature of 500°C and a sulfuric acid concentration of 88 g/L. Finally, neodymium, praseodymium, and yttrium are solubilized at a roasting temperature of 871°C and a sulfuric acid concentration of 265 g/L. Alternative leaching media, such as thiourea, sulfuric acid-doped thiourea mixtures, ammonium thiosulfate, nitric acid, and hydrochloric acid have also been investigated along with the addition of ultrasonic agitation. Using ultrasonics in addition to mechanical agitation, hydrochloric acid proved to be the best leaching medium. The best roasting temperatures for selective solubilization remained the same, but all of the leaching steps were conducted at 64 g/L hydrochloric acid.

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INTRODUCTION

With the recent advances in superconductivity and laser applications, which involve the use of rare earth-compounds, the rare-earth elements are attracting added attention

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and have taken on some added importance. At present, technology for solubilizing rare-earth concentrates involves a relatively high-temperature leach (>200°C) using highly concentrated, corrosive leachants (i.e., 1700 g/L H_2SO_4) and prolonged leaching times (24 h). A roast-leach process for solubilizing monazite-xenotime ores allows the leaching stage of the processing to become more productive and less corrosive. Acid concentrations never need to be >400 g/L, and the leaching can be conducted at room temperature with leaching times of about 4 h.

Currently, all rare-earth recovery from monazite is being conducted in a hydrometallurgical fashion. Two major hydrometallurgical processes exist, one using sulfuric acid (the most common), and the other using sodium hydroxide. The sulfuric acid method requires minus 100-mesh monazite concentrate to be slurried with 98% H_2SO_4 and then agitated in cast-iron pots at a temperature of 200 to 220°C for 24 h. The result of this leaching procedure is a thick, acidic, grey mud that must then be processed (1,2). The processing of this mud requires specialized equipment with linings that are inert to the rare-earth solution produced during subsequent leaching. The caustic process is very similar to the sulfuric acid process. In the caustic process, minus 300-mesh monazite concentrate is slurried with 70% NaOH and agitated for 4 h at 140°C. This process is unattractive, however, because of higher reagent costs and problems encountered during the filtration of the slurry when the concentrate contains <70 pct rare-earth oxides (REOs)(2).

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Roasting of monazite concentrates has been examined previously with limited success (3). The optimized procedure utilized a 6-h sodium carbonate plus sodium fluoride roast, followed by a hydrochloric acid leach that extracted 95% of the cerium and thorium from the concentrate. The problems with this process are the introduction of fluorine into the chemical scheme, the long roasting time needed for the conversion reaction to occur, and the amount of thorium leached into the final liquor.

The ultimate goal of the research was selective extraction of the rare-earth values. Selectively leaching the rare earths would eliminate the need for additional separation operations and allow for increased production.

The process currently being investigated approaches the problem of solubilizing rare-earth phosphates from a combined pyrometallurgical and hydrometallurgical point of view. It utilizes a roasting operation that converts the rare-earth phosphates to easily solubilized REOs. This eliminates the need for extensive caustic and acidic leaches for long periods of time at elevated temperatures and is capable of increasing the speed of recovery of rare earths in systems currently using the acid process. A single stage roast/leach operation could allow for a decrease of as much as 50% of current processing costs and allow pregnant liquors to be prepared in 1/8 the time currently required.

EXPERIMENTAL

When experimentation on the roast/leach process for extracting rare earths began, it was decided that a rare earth concentrate would be used as feed material. The concentrate used in this test work was prepared in-house from raw ore obtained from the Pea Ridge Iron Mine, Sullivan, MO using characterization data acquired from earlier USBM involvement with the mine (4). The raw ore was ground wet in a ball mill to 100-200% mesh, and the solids removed from the grinding fluid by conventional filtration. The solids were then mixed with water to obtain a slurry containing 25% solids. The pH of the slurry was adjusted to 5 with sulfuric acid, and treated with potassium amyl xanthate (sulfide collector) and methyl isobutyl carbonyl (frother) and the pyrite contained in the ore was removed by conventional flotation. The tail from the flotation test was then passed over a vanner, and a rare earth concentrate containing 60-65% REO was obtained.

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Since several parameters needed to be examined, roasting tests were the first component of the process to be investigated. The parameters studied included reagent type, roasting temperature, roasting time, and quantity of carbonate added (based on stoichiometric calculations).

Roasting was investigated with the addition of calcium carbonate, sodium carbonate, or sodium bicarbonate. Monazite concentrate (minus 200 mesh) was mixed with a stoichiometric excess of carbonate in a vibratory mill to form a simple solid mixture. The mixture was then placed in a tube furnace being held at a temperature of 650—815°C for 30—90 min. The mixture was then removed from the furnace, cooled, and lightly reground in a mortar and pestle to eliminate the sintering effect of the roasting operation. The resulting powder was then leached in the appropriate solvent. After roasting, the powder was slurried with either a sulfuric or hydrochloric acid solution (3%

solids) and was stirred using either mechanical, ultrasonic, or a combination of mechanical and ultrasonic agitation. Various acid concentrations were used.

Roasting temperatures and times and leaching acid concentrations and times were varied to determine the parameters that favored the solubilization of the individual species.

Analyses of test products were carried out using a scanning electron microscope equipped with a wavelength-dispersive spectrometer (WDS) and an energy-dispersive spectrometer (EDS), an automated powder diffractometer equipped with an X-ray generator, an emission spectrometer, an atomic adsorption unit, an ICP, and an X-ray fluorescence unit (calibrated with standards analyzed on AA and ICP mentioned above). Basic microscopic analysis of the test products was performed using a standard binocular light microscope.

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RESULTS AND DISCUSSION

The success of the roasting operation depended on the ability to find a chemical capable of converting the rare-earth phosphates into REOs. Calcium carbonate was initially used as the reagent for the chemical conversion during roasting but was abandoned because the desired reaction was either too slow or nonexistent. This prompted the use of sodium carbonate. The first test using sodium carbonate showed an exceptional weight loss after a 2-h 88-g/L sulfuric acid leach of the roasted material, which pointed to an increased solubility of the rare-earth compounds. Analysis of the reaction products showed that the leach solution contained appreciable amounts of cerium, yttrium, lanthanum, praseodymium, neodymium, and samarium. Because sodium carbonate performed better than the calcium carbonate, sodium bicarbonate was examined as a reagent. Results of the testing showed that the overall extraction of rare earths, using the same test parameters, increased 4-10% when using sodium bicarbonate instead of sodium carbonate. It was determined during this series of tests that the best chemical conversion during roasting was achieved using a roasting temperature of 760-816°C, a 1-h roasting time, and a 25% stoichiometric excess of sodium bicarbonate. Because sodium bicarbonate provided better results than sodium carbonate, it was utilized in the remainder of the tests.

Using chemical analysis obtained for the roasted material, two basic schemes of chemical reactions were proposed for the roasting process, one set using sodium carbonate, and another using sodium bicarbonate. The first set of reactions that may occur, using sodium carbonate, are as follows:

$$2\ REPO_4 + 3\ Na_2CO_3 \rightarrow RE_2(CO_3)_3 + 2\ Na_3PO_4$$

$$RE_2(CO_3)_3 \rightarrow RE_2O_3 + 3\ CO_2\ (gas)\ .$$

The second set of reactions that may occur, using sodium bicarbonate, are as follows:

$$2\ REPO_4 + 6\ NaHCO_3 \rightarrow RE_2O_3 + 2\ Na_3PO_4 + 3\ H_2O\ (gas) + 6\ CO_2\ (gas)$$

$$RE_2(CO_3)_3 \rightarrow RE_2O_3 + 3\ CO_2\ (gas)\ .$$

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X-ray diffraction analysis of roasted material substantiated the presence of sodium phosphate, REOs, and small amounts of sodium rare-earth phosphates. The reaction between sodium bicarbonate and the rare earth phosphates that results in the production of sodium rare-earth compounds and rare earth oxides most likely proceeds according to the following equation:

$$6\ NaHCO_3 + 4\ REPO_4 + O_2 \rightarrow 2\ Na_3RE(PO_4)_2 + 2\ REO_2$$

$$+ 3\ H_2O\ (gas) + 6\ CO_2\ (gas)\ .$$

Material balances conducted on the roasted material revealed that about 72% of the CO_2 present in the starting material evolved as a gas, which pointed to the formation of stable rare-earth oxides, rather than stable rare earth carbonates, during the roasting operation. Analysis of the roasted material using EDS and WDS revealed considerable amounts of REOs with no appreciable trace of rare-earth carbonates, although their presence is still possible.

In the leaching operation, agitation was very important. Initially, mechanical agitation was utilized using either a magnetic stirrer or overhead stirrer. Both mechanical agitation methods worked equally well. Next, ultrasonic agitation was checked. When employed exclusively, results similar to mechanically-agitated tests were obtained. It was noted, however, that the material tended to collect on the bottom of the container during the test, which reduced the interaction of the particles with the leaching medium. To eliminate this problem, an overhead stirrer was used in conjunction with the ultrasonic agitation. This combination increased the extraction by as much as 450% over mechanical or ultrasonic agitation alone. Results of the agitation series are shown in Table 1 with the extraction percentages given in total percent rare earths extracted from a concentrate initially containing 65% REO.

Several leaching media were investigated to determine the best solvent for the rare earth oxides. These media included ammonium thiosulfate, thiourea, sulfuric acid doped thiourea, nitric acid, sulfuric acid, and hydrochloric acid. Sulfuric and hydrochloric acid produced the best results, with the remaining media displaying limited success. For instance, a 96 hour leach of roasted concentrate using a 100 g/L ammonium thiosulfate solution at 3% solids produced a liquor containing $< .01$ g/L total rare earths. Similarly, a 96 hour leach of roasted concentrate using a 100 g/L thiourea solution at 3% solids produced a liquor containing .09 g/L total rare earths. A 96 hour leach of roasted concentrate using a 100 g/L thiourea + 50 g/L sulfuric acid solution at 3% solids produced a liquor containing .27 g/L total rare earths, and a 24 hour leach of roasted concentrate using a 350 g/L nitric acid solution at 3% solids produced a liquor containing .57 g/L total rare earths.

The leaching took place at room temperature and atmospheric pressure, using hydrochloric acid and leaching times of 1 to 12 h were investigated. Results of the leaching time series are shown in Table 2, with extraction percentages given in total percent rare earths extracted from a starting material containing 65% REO.

The concentration of rare-earths increased rapidly up to 4 h, continued to increase appreciably from 4 to 6 h, and showed virtually no increase from 6 to 12 h.

The leaching kinetics were also dependent on the acid concentration. The largest concentrations of rare earths were obtained at a sulfuric acid concentration of 265 g/L and a hydrochloric acid concentration of 64 g/L. Leaching tests were performed using sulfuric acid concentrations of 88 to 440 g/L (3% solids) and hydrochloric acid concentrations of 21 to 106 g/L (3% solids). Results of the acid concentration series are shown in Table 3. Additional testing is continuing in an effort to increase the overall recovery of the rare earths into aqueous solution or to maintain the current level of extraction while decreasing the roasting and leaching times.

The effect of oxidizing agents on the leaching kinetics (in the absence of ultrasonic agitation, using hydrochloric acid) was examined. Hydrogen peroxide was used as the

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Table 1. Agitation test series
(815°C, 1-h roast, 4-h leach)

Acid	Agitation	Extraction, %, total rare earth
265 g/L H_2SO_4	Mechanical	26.3
Do	Mechanical + ultrasonic	33.7
64 g/L HCl	Mechanical	16.7
Do	Mechanical + ultrasonic	93.0

Table 2. Leaching time test series
(815°C, 1-h roast, mechanical + ultrasonic agitation)

Time, h	Extraction, %
1	20.3
2	31.9
3	72.7
4	93.0
6	93.5
8	94.6
12	95.2

Table 3. Acid concentration test series
(815°C roast, 1-h, 4-h leach)

Mechanical plus ultrasonic agitation, H_2SO_4		Mechanical plus ultrasonic agitation, HCl	
Acid concentration, g/L	Extraction, %, total rare earths	Acid concentration, g/L	Extraction, %, total rare earths
88	8.8	21	33.4
166	28.0	42	45.6
265	33.7	64	93.0
353	30.6	85	80.6
440	22.2	105	78.7

oxidizing agent, and was added in two different schemes: (1) all of the oxidant was added at the beginning of the test, and (2) the oxidant was added in volumetrically-equal aliquots every half hour for the duration of the test. In both instances, the same net volume of peroxide was used. No increase in extraction was observed when hydrogen peroxide was added to the leach liquor. Testing will continue to examine the effects of hydrogen peroxide on leaching in the presence of ultrasonic agitation, and leaching during oxidation with permanganate, ferric iron, and ozone will also be investigated.

As stated in the Abstract, it was desirable to selectively solubilize the rare-earth values present in the concentrate so that a final separation process like ion exchange or solvent extraction could be avoided, but the chemistry of the rare earths are very similar. Test work conducted on this aspect of processing has shown some promise, but is still far from acceptable. Using a 1-h roast at 427°C followed by a 4-h 64 g/L leach, 65% of the cerium was extracted while only 5% total neodymium, praseodymium, lanthanum, and yttrium was extracted. The residue was then subjected to a 1-h roast at 500°C followed by a 4-h 64 g/L leach which extracted 75% of the lanthanum and only 4% total neodymium, praseodymium, cerium and yttrium. The residue was then subjected to a roast at 871°C, followed by a 4-h 64 g/L HCl leach, 80% of the neodymium, praseodymium, and yttrium was extracted with only 8% total cerium and lanthanum. Neodymium, praseodymium, and yttrium always seem to leach together, and the process parameters investigated do not allow for their selective solubilization. The difference in extraction rates is not great enough to avoid additional aqueous processing of the leach liquor. Test work is continuing to try to improve the selectivity of the leaching operation.

Some preliminary work has been completed on direct conversion roasting of the rare-earth phosphates using sodium sulfate and sodium chloride as conversion reagents. The roasting operation increased the solubility of the concentrate, but results are far from satisfactory. Some additional testing in this area is planned to determine the feasibility of utilizing alternate salts for conversion of the phosphate species.

CONCLUSION

By taking advantage of the synergistic leaching enhancement achieved by combining mechanical and ultrasonic agitation techniques, the time required for non-selective

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solubilization of all rare earth values present in the concentrate can be reduced and higher extraction percentages can be achieved. Overall, the best results obtained to date utilize a 1-h sodium bicarbonate roast at 815°C followed by a 4-h hydrochloric acid (64 g/L) leach using both mechanical and ultrasonic agitation. This test leached 93% of the available rare-earth values from the roasted concentrate. Hydrochloric acid appears to be a better leaching medium for the rare earths than the sulfuric acid. Under similar conditions, the best sulfuric acid test (265 g/L H_2SO_4) only yielded a 33.7% recovery of the total rare-earth values present in the roasted concentrate.

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