Thermodynamic Analysis of Rare Earth Chlorination and Bromination Processes

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Thermodynamic Analysis

Thermodynamic analyses were performed on four arbitrarily chosen reagent grade rare earth oxides: holmium, neodymium, samarium, and ytterbium oxides. The free energy minimization algorithm in HSC Chemistry 7.0 was used to predict stable phases that form under various process conditions, and equilibrium compositions were determined as a function of temperature as illustrated in Figures 3-10. These data were used to delineate the temperature and REE oxide to halogenating agent molar ratios used in subsequent laboratory scoping experiments.

Optimization and Statistical Validation

After the scoping evaluation results showed ytterbium oxide was the most recalcitrant of the four REE oxides, it was selected for more extensive optimization experimentation. A three-variable Response Surface matrix was created using Design Expert Version 9.01 (Stat Ease) to examine the effects of varying roasting time (1 to 4 h), temperature (150 to 400°C), and halogenation agent to REE oxide mole ratio (6 to 24) on halogenation conversion efficiency. The results of the parametric optimization experiments for chlorination and bromination are illustrated on the response surface diagrams in Figures 1 and 2, respectively.

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Research funded by the Army Research Laboratory (ARL), the Metallurgical and Materials Engineering Department at Montana Tech investigated various methods of extracting and refining rare earth elements (REEs) from mineral ores and concentrates. Extensive thermodynamic, thermogravimetric, and differential thermal analyses were performed to evaluate the relative stabilities of various REE compounds in order to assess potential methods for selective separation and recovery of specific REEs. Conversion of rare earth oxides (REO) to rare earth chlorides or bromides is a possible initial step in pyrometallurgical and hydrometallurgical processing of REEs. REO can be converted to chlorides or bromides by roasting in the presence of a chloridizing or bromidizing reactant. (e.g. NH₄Cl and NH₄Br).

Confidence

The statistical analysis identified parameters leading to maximum conversion of rare earth oxides to their respective chlorides and bromides. Confirmatory experiments were performed to further validate the selection of optimal windows of operating parameters and the high (greater than 90%) conversion efficiencies. The results of the confirmatory experiments are summarized in Tables 1 and 2.

Ore and Concentrate Samples

REE ore and concentrate samples were roasted under the optimal halogenation conditions established with ytterbium oxide. The sample assays ranged from four to fifteen percent total rare earth oxide. The four most prevalent REE in the samples are cerium, dysprosium, gadolinium, and lanthanum. Application of the optimal halogenation conditions yielded high conversion efficiencies for each of these REEs as depicted in Tables 3 and 4.

Vaporization

Vaporization of REE halides represents a possible extraction method. Preliminary studies were performed using thermogravimetric and differential thermal analysis (TGA/DTA). The purpose of this study was to evaluate the relative stabilities of various REE compounds in order to evaluate potential methods for selective separation of specific rare earth elements. Comparison of the thermograms in Figures 11 and 12 illustrate the potential for selective vaporization of samarium chloride versus europium chloride.