Hydrometallurgical recovery of yttrium from waste crucible materials

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Abstract

Yttrium compounds find interesting applications in many industrial fields (superconductors, catalysis, crucible, oxygen sensor). The feasibility of using yttrium oxide as a crucible material or coating respectively for induction melting of titanium is widely used in metallurgy. During the production of crucibles based on yttrium oxide as well as through the melting/casting operations significant waste materials were formed. In this study the recovery of yttrium from various waste crucible materials by chlorination, leaching and a subsequent precipitation was investigated. The solubility of available yttrium oxide in waste materials is a function of concentration, type of the used chlorinating/leaching reagent as well as other process parameters. Chlorination and carbochlorination process were investigated in order to obtain yttrium chloride from waste crucible materials using ammonium chloride (NH_4Cl), and calcium chloride ($CaCl_2$) as chlorinating agents and added sucrose. Tests were conducted in a muffle furnace to 400°C and 600°C and at different times 15, 30 and 60 min. Selective dissolution of yttrium was investigated in solutions with $(NH_4)_2CO_3$, HCl, H_2SO_4 and HNO_3 under atmospheric and high pressure conditions aiming the process efficiency and the feasibility for an industrial application.

1 Introduction

The rare earth elements are chemically similar to one another, and invariably occur together in the source minerals and behave as a single chemical entity. The separation of each element is mainly based on three methods: the reduction of the anhydrous chloride, the reduction of the oxide, and the electrolysis of the fused salt. So it is very important to study the synthesis and kinetics of formation of the rare earth chlorides. The high reactivity of chlorine towards various compounds at moderate temperatures makes chlorine technology a competitive alternative for the extraction and recovery of several valuable metals. The chlorination process is a potential dry method of production of the rare earth chlorides as precursors, which allow the separation of metals from ores and concentrates, refining metals and recovering metals form slags, besides having application in advanced ceramic areas. However the use of chlorine gas creates problems for the producers, as storage of chlorine gas is costly and dangerous, besides the conventional processes produce waste acid, alkali or discharge gas to pollute the environment, making it necessary to find other chlorinating agents to carry out the chlorination process.

Chlorinating RE of bastnaesite with NH_4Cl was invented by Tsinghua University. In this process, RE in the ore is chlorinated by HCl which is decomposed from NH_4Cl. The recovery of RE elements reaches 85% under the optimum conditions. Generally rare earth ore should be firstly defluorinated with Na_2CO_3 roasting, then the fluorine (NaF) is washed away with hot water before chlorinating RE with NH_4Cl. Actually the proposed process would also pollute the environment for containing fluorine wasting water. It should be further studied if the chlorinating process is suitable for the recovery of RE from the Baotou rare earth concentrate. To avoid generating containing fluorine wastewater, MgO is selected to fix the fluorine of the rare earth concentrate in the calcine. After fixing-fluorine treatment, chlorinating RE with NH_4Cl roasting is further applied to concentrate. The condition of fixing-fluorine and chlorination with NH_4Cl is determined in this investigation. The process of chlorination with NH_4Cl roasting has good selectivity to Fe, Al, Si and Th and it simplifies the fluorine treatment of rare earth ore [1].

The selective chlorination would decrease the dissolution of impurities such as Fe, Al, Si and Th, so it would simplify the purification process of recovering rare earth elements. Using ammonium chloride (NH_4Cl) as chlorinating agent, the effects of chlorination temperature, chlorinating time and NH_4Cl dosage on chlorination of La_2O_3 and CeO_2 and the thermal decomposition of $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$ were investigated. The results show that 80% of both La_2O_3 and CeO_2 can be chlorinated at 300°C for 90 min, and have an advantage to chlorination of lanthanum and cerium oxides at higher temperature [2].

The chlorination kinetics of Y_2O_3 with chlorine to produce YOCl was studied by thermogravimetrical analysis over a temperature range 575°C to 975°C [3]. The influence of connective mass transfer into the boundary layer surrounding the sample, gaseous diffusion into the sample pores, partial pressure of chlorine, and temperature on the reaction rate were analyzed in order to determine the rate controlling step. The results showed that the process follows a model of nucleation and growth and the process is chemically controlled for temperatures lower than 800°C, with activation energy of 187± 3kJ/mol. In the 850°C to 975°C range the reaction rate was affected by diffusion of Cl_2 through the gas film surrounding the sample, with apparent energy of 105 ± 11 kJ/mol [3].

Regarding to the leaching process of lanthanides several diluted conventional acids such as HCl, HNO_3, HF and H_2SO_4 were usually investigated in order to selective dissolve the rare earth elements. A hydrometallurgical process for extraction of lanthanum, yttrium and gadolinium from spent optical glass (43.12 % La_2O_3, 9.37 % Y_2O_3, 4.67 % Gd_2O_3) was reported by Jiang et al. [4]. The process contain the initial conversion of rare earth elements from a borosilicate phase to the hydroxide compound followed by hydrochloric acid leaching of the residual solids from conversion. The pretreatment of glass with aqueous NaOH is essential to the dramatic improvement of the RE dissolution in hydrochloric acid. Compared with RE borosilicates, the converted RE hydroxides easily react with hydrochloric acid.

$$RE(OH)_3 + 3\ HCl = ReCl_3\ (aq) + 3\ H_2O \qquad (1)$$

The optimal conditions for leaching the RE hydroxides were reported at 95°C with 6 M hydrochloric acid using a liquid-to-solid ratio of 4 for 30 min. The obtained solution was contained 7.38 g/l Yttrium with 100 % leaching efficiency. The proposed procedure can be used for recycling such secondary RE resources as spent ophthalmic glass and spent optical fiber, besides spent optical glass.

A systematic study of the selective extraction of yttrium by different leaching agents from the red mud samples, coming from the Greek Alumina Production, was carried out by M. Ochsenkühn-Petropulu et al. [5]. After the previous treatment (sieving, magnetic separation and roasting) the effect of most important parameter such as a type of acid, the concentration of the leaching agent, reaction time and temperature was investigated. Among all these agents diluted HNO_3 showed the best recoveries and best selectivity, especially for Y and Sc. Diluted HCl showed similar leaching efficiencies with nitric acid, but it is not selective regarding to increased percent of iron dissolved. The using of nitric acid facilitates the purification step via the subsequent solvent extraction.

Yttrium solubility with ammonium carbonate from the chemical treatment of monazite sand by NUCLEMON in São Paulo was investigated [6]. Their solubility is function of the carbonate concentration and the kind of carbonate as sodium, potassium and ammonium. Vasconcellos et al. [6, 7] have investigated the REE concentrate containing (%): 2.4 Y_2O_3, 0.6 Dy_2O_3, 2.7 Gd_2O_3, 2.5 CeO_2, 33.2 Nd_2O_3, 40.3 La_2O_3, 4.1 Sm_2O_3 and 7.5 Pr_6O_{11} with 200 g L^{-1} ammonium carbonate during 10 and 30 min at room temperature. Single leaching operation was sufficient to get a rich yttrium solution with about 60.3% Y_2O_3. In a second step, this yttrium solution was treated with an excess of hydrogen peroxide (130 volumes), cerium, praseodymium and neodymium peroxides being completely precipitated and separated from yttrium. Yttrium was recovered from the carbonate solution as the oxalate and finally as oxide. The final product is an 81 % Y_2O_3.

In this study, the chlorination/carbochlorination using NH_4Cl and $CaCl_2$ was applied to the recovery of yttrium from waste crucible materials at different temperatures, amounts and times using a muffle furnace. The main aim was to establish optimal leaching parameter under an atmospheric and high pressure using different leaching agents $NH_4)_2CO_3$, HCl, H_2SO_4 and HNO_3.

2 Experimental Procedure und Results

During the production of crucibles based on yttrium oxide (ceramic shell) as well as through the melting/casting operations significant waste materials were formed. After the casting operation and separation of ceramics from the casting parts the waste powder was formed in TITAL GmbH, Bestwig. This fine powder after milling and sieving had one particle size <75µm and contains maximal 10% Y_2O_3. Besides yttrium this powder contains some compounds approx. (in mass percent): 5 Fe_2O_3**;** 29 Al_2O_3**,** 43 SiO_2.

Chlorination/Carbochlorination

The influence of different experimental parameters such us roasting temperature, time, and amounts of the added chlorinating agents (NH_4Cl or $CaCl_2$) were investigated. The mass of samples of 3, 5, 10 and 20 g were mixed with some amounts of NH_4Cl or $CaCl_2$ like chlorination agent and 5 g of sugar in each experiment. The mixture was then roasted in muffle furnace at the designed temperature. The resulting solid product was leached with hot water. By analyzing the concentration of the leaching solution, the recovery of Y, Al, Fe and Si could be calculated. The results showed that at 400°C is more effective to recover of yttrium than at 600°C, maybe because the reaction between the sample and ammonium chloride start at 387°C and at 600°C the ammonium chloride evaporated. The best chlorinating results were obtained using NH_4Cl at 400°C in 15 min (chlorinating yield about 62 %). At the same conditions using 5 g of sucrose the chlorination of yttrium amounts 46 %.The next chemical reactions were considered:

$$Y_2O_{3(s)} + 6NH_4Cl_{(s)} = 2\,YCl_{3(s)} + 6NH_{3(g)} + 3H_2O_{(g)} \quad (2)$$
$$Fe_2O_{3(s)} + 6\,NH_4Cl_{(s)} = FeCl_{3(s)} + 6\,NH_{3(g)} + 3\,H_2O_{(g)} \quad (3)$$
$$Al_2O_{3(s)} + 6\,NH_4Cl_{(s)} = 2AlCl_{3(g)} + 6\,NH_{3(g)} + 3\,H_2O_{(g)} \quad (4)$$
$$SiO_{2(s)} + 4\,NH_4Cl_{(s)} = SiCl_{4(g)} + 4\,NH_{3(g)} + 2H_2O_{(g)} \quad (5)$$

Yttrium recovery is higher with shorter residence time at a lower temperature. It’s important to continue with the research to find the optimal chlorination conditions (temperature, amounts, times for the chlorination process using NH_4Cl, $CaCl_2$ and sucrose).

Leaching

Leaching tests were performed in a 1 L reactor under a) an atmospheric (glass) and b) high pressure (autoclave) using different leaching agents: H_2SO_4, HNO_3, $(NH_4)_2CO_3$, and HCl. Temperature was controlled within ± 1 ^oC by a temperature control system, manipulating both a water cooling system (see Figure 1). Agitation was provided by an impeller that is motor driven. A certain amount of waste dust was mixed with a pre-calculated amount of deionised water. The slurry is then heated up to a predeterminated temperature under continuous agitation. Upon temperature stabilisation, a certain amount of investigated leaching agent corresponding to different acid-to-ore ratios, was injected into the reactor under atmospheric and high pressure.

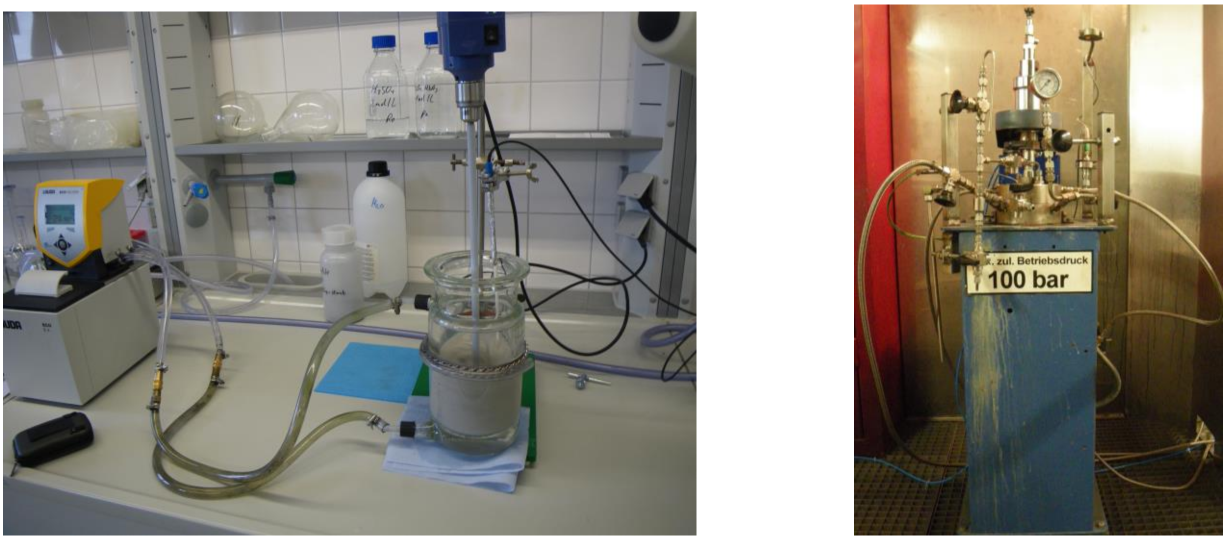

Figure 1: Leaching experiments under a) atmospheric pressure b) high pressure

Using the sampling system 20 ml of liquid was periodically withdrawn through a dip tube and then rapidly cooled. After the end of experiments, solutions aliquots were filtered and analysed aiming Y, Si, Fe, Al by an inductively coupled plasma ICP spectrophotometry. Insufficient leaching efficiency was obtained using ammonium carbonate under an atmospheric pressure, what is opposite reported results in [6, 7]. An increase of temperature up to 150°C reaches the leaching efficiency up to 25 %. The maximal leaching efficiency above 95 % was obtained using a mixture of 1 M H_2SO_4 und 1M HNO_3 under an atmospheric pressure for one hour at 80 °C. An increase of temperature from 25 °C to 150°C with 2M H_2SO_4 increases the leaching efficiency of yttrium, but also the iron concentration in solution was increased. The obtained solution under optimal conditions at 80°C was treated with oxalic acid at room temperature and thermal decomposed at higher temperature in order to produce Y_2O_3. The final product contained 67 % Y_2O_3.

3 Summary

Chlorination and carbo-chlorination process of yttrium Oxide from waste crucible materials with NH_4Cl and $CaCl_2$ have shown an advantage of used ammonium chloride. The best chlorinating results were obtained using NH_4Cl at 400°C in 15 min (chlorinating yield 62 %). The best leaching results were obtained at temperature 80°C, mixture of 1 M H_2SO_4) and 1 M HNO_3 for one hour. The full paper will be published immediately after the conference in World of Metallurgy as peer reviewed paper. The next investigations will be performed in order to improve precipitation efficiency aiming to scale up of hydrometallurgical recovery of yttrium from waste crucible materials.

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