Enhancement of Sc and Ti extraction rates from Fe-depleted slag by hydrogen peroxide and sulfuric acid leaching

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Abstract

Conditioning of bauxite residue for enhanced Sc and Ti leaching efficiencies was performed in this study. Acidic leaching conditions provided higher Sc and Ti leaching but also resulted in higher dissolved Fe in leachate. In order to tackle Fe interference, red mud is treated in electric arc furnace for prior Fe removal. Various conditions during smelting, such as variable cooling rate (5 °/ min. 20 °/min, quenched) and feedings with lime (CaO) and silica (SiO_2) were explored in order to obtain slags with different crystallography and chemistry. All slags were subjected to acidic leaching with 2.5 M hydrogen peroxide (H_2O_2): 2.5 M sulfuric acid (H_2SO_4) combination with a solid to liquid ratio of 1: 10 at 75 °C. Slags were analyzed in term of phase content, crystallinity and morphology by XRD and SEM analyses. Effect of various smelting conditions on leaching efficiencies and kinetics of Sc and Ti was investigated.

Introduction

Bauxite residue (BR), the residue of the Bayer process, is produced at a rate of 108.7 ~ 163.1 million tons globally, stockpiled all over the world[1], but nonetheless, considered as a candidate secondary resource owing to its promising metal (Fe, Al, Ti, Sc, and REE) content. When reduced process costs with respect to primary metal production routes are considered, valorization of BR is also favorable in terms of economic aspects. Among other metals, Ti and Sc have started to be classified as critical metals owing to the increasing demand. The extended utilization of Ti as metal, compound and alloy form, would result in decreasing availabilities and qualities of the titanium ores. Moreover, scandium, which can be used as a tuning metal in aluminum alloys, has limited primary sources and has to be extracted mainly from secondary raw materials or as a by-product of uranium, nickel-laterite or titanium pigment processing.[2,3] Complex extraction and purification routes as well as the geological scarcity, made the prices of scandium extremely high (228 $/g in metallic form).[4] Although BR is a very promising material to recover Ti and Sc by acidic leaching, high Fe content decreases the efficiency. Poor selectivity of Ti over Fe was reported in previous studies in direct leaching process. Moreover, high amount of Fe ions in solvent extraction process hinders Sc extraction and necessitates intensive purification steps.[5,6]

In this study, utilization of iron-depleted slags, which were produced after the electric arc furnace treatment of BR, were subjected to acidic leaching. Two different slags were investigated, having the same chemistry but different assempblage of crystal phases. Mixtures of H_2O_2 and H_2SO_4 were used as leaching agents, in order to provide an oxidative ambient and tackle with the gelation issue.[7,8] The efficiencies of the leaching samples were analyzed and evaluated via ICP-OES. Slags were also analyzed in terms of microstructure and crystallinity, by XRD and SEM, in order to understand various leaching behavior. The behavior of iron-depleted slag use was reported as a function of Sc and Ti leaching efficiencies.

Experimental Procedure

The BR used in this study was obtained from Aluminum of Greece S.A. The chemical composition of the BR analyzed by ICP-OES technique is listed in Table 1.

Table 1. Chemical composition of bauxite residue and EAF treated slag

wt%	Fe_2O_3	Al_2O_3	CaO	SiO_2	TiO_2	Sc (mg/kg)
Bauxite residue	43.5	24	10.2	5.5	5.6	130
Slag	1.8	38.3	43.2	7.6	7.6	170

The dried BR was subsequently mixed with lignite coke and lime containing 87 wt% fixed carbon and 95 wt% CaO, respectively. The additions of lignite coke and lime to bauxite residue were 1:10 and 1:5, respectively. Batch masses of 1.5 kg of the aforementioned recipes were fed into a 100 KVA DC electric arc furnace. The material was contained in a graphite crucible, and the smelting was undertaken at temperatures in the range between 1500-1550 °C for a holding time of one hour. At the end of each experiment the molten material was poured into one of the two containment set-ups for cooling as follows: a refractory-lined mould where the material cooled down under ambient conditions and the metal settled at the bottom of the mould, or a bucket filled with water for fast cooling of the molten material (water quenching). The cooled material was separated into slag and metal and then weighed. In the case of water-quenched cooled sample, drying was undertaken prior to weighing of the samples. The slag was then prepared for leaching where it was crushed and milled to obtain a slag fraction of <90 μm.

A typical leaching test was carried out with a glass beaker, heating plate and magnetic stirrer for controlling the reaction temperature and stirring speed. Slags were fed into the reactor, containing preheated sulfuric acid and hydrogen peroxide combination. Mixtures of sulfuric acid with hydrogen peroxide should be carefully prepared by slowly adding hydrogen peroxide into sulfuric acid to control the rapid exothermic reaction. Two different acid concentrations on leaching efficiency were investigated at a set temperature of 75 °C, 250 rpm stirring speed, and S/L ratio of 1/10. The two slags were leached in identical conditions for direct comparison purposes and were vacuum filtered with a vacuum pump and fine filter paper to separate solid residue and leachate. Leachates were analyzed by ICP-OES technique. Slags were investigated by XRD and SEM analyses. XRD analyses were performed by a Bruker D8 Advanced Diffractometer, which use Bragg-Brentano Geometry and θ-θ synchronization for X-Ray tube and the detector. 10°-80° (2 θ) were scanned with a 5 °/min rate. The generator voltage was 40 kV and the current was 40 nA. BSE and SE image acquisition was done by the same system in SEM-mode using an acceleration voltage of 15 kV. For a better resolution of the images, the working distance was decreased to 11.7 µm. After reaching the most efficient leaching efficiencies, leachates were planned to be investigated in terms of recovering of Ti and Sc by precipitation. The complete process flow diagram can be seen in Figure 1.

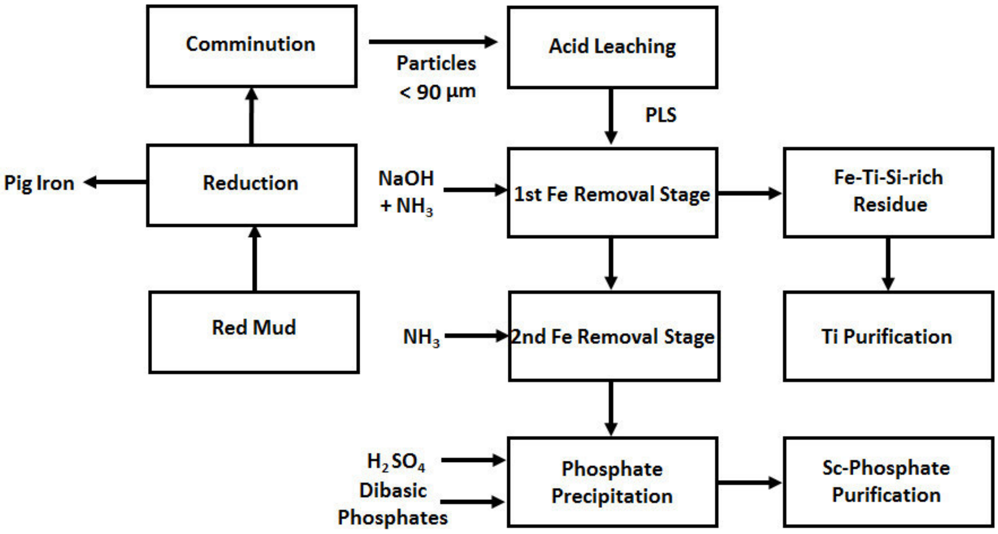

Figure 1. Process flowsheet for combined pyrometallurgical and hydrometallurgical treatment of BR to recover Fe, Ti and Sc

Results and Discussion

H_2SO_4: H_2O_2 combination was utilized as leachate to utilize oxidative nature of H_2O_2 when it is used with H_2SO_4. Moreover, this combination has been reported as Piranha solution with higher leaching efficiencies. Initially, acid molarity was examined to optimize leaching efficiencies of Ti and Sc with low acid consumptions. Figure 2 presents the dependence of Sc and Ti leaching efficiencies on acid concentration.

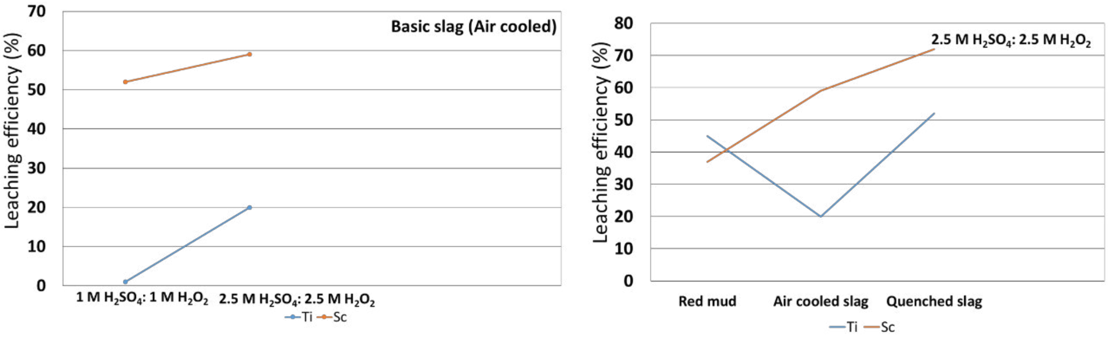

Figure 2. Sc and Ti leaching efficiencies for different acid concentrations (left) from different slags (right)

In terms of Ti leaching, very poor leaching efficiencies were achieved when 1 M acids were utilized. The Ti extraction of 1% of was increased to 20 % with an increase to 2.5 M acid. As listed in Table 1, very high amounts of Ca in slag may result in such low Ti dissolution. It is known that calcium sulfate formation is a very fast exothermic reaction, which may use major sulfate introduced to the system and suppress Ti dissolution. It is also worth to emphasize that gelation tendency in this system was high, also due to insufficient peroxide in the system.

However, when 2.5 M was used, there was no silica gelation observed and relatively higher leaching efficiencies obtained. It is also interesting that Sc exhibited almost no dependence on acid molarity, just slightly increased with an increase to 2.5 M. It was observed that when 1M of leaching solution was utilized, 50% Sc leaching efficiency was obtained and when the concentration of both H_2SO_4 and H_2O_2 increased, around 80% of the Sc was transferred to the leaching solution. Since Sc is freed from the hematite mineral with EAF treatment, it is not surprising to observe this behavior. Since most of the Sc is entrapped in hematite, after removal of it, Sc became easily achievable by leachate.

2.5 M H_2SO_4: 2.5 M H_2O_2 was used further to investigate the effect of slag crystallinity on leaching efficiencies. Figure 2 represents also leaching efficiencies of Sc and Ti from two different slags. For comparison purpose, red mud leaching efficiencies were also given when leached under the same conditions.

As it can be seen in Figure 2, use of both slags enhanced dramatically Sc leaching efficiency. Especially in quenched slag, relatively high extraction of 92% was reported. In the case of Ti leaching, despite the increased Ti concentration in the slag, extraction efficiency was suppressed in the air-cooled slag. However, it is also increased when quenched slag is used, which is expected due to the less crystalline and easily soluble nature of it.

Beyond leaching efficiencies, Ti and Sc contents in pregnant leach solutions (PLS) are given in Figure 3.

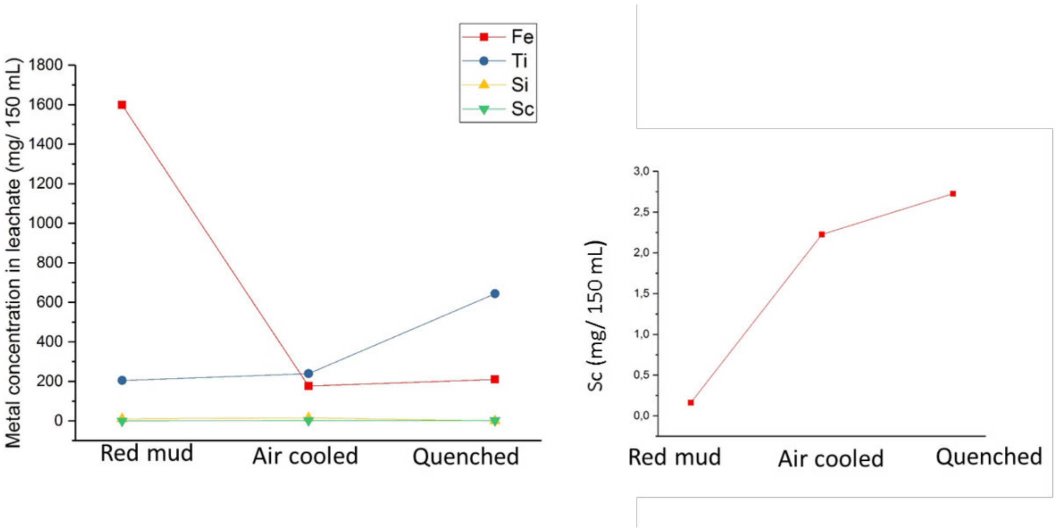

Figure 3. Metal concentration in PLS for Fe, Ti and Si (left) and detailed shown for Sc (right)

Metal concentration of PLS highlights an almost 3 and 5 fold increase in Ti and Sc, respectively, when compared with BR PLS. Moreover, a 10 fold decrease of Fe in leachate indicates selectivity of the process.

These results highlight that for Sc recovery, slag utilization is highly promising. Since Sc is mainly incorporated in Fe including phases,[9] after recovery of Fe around 99 %, most of the Sc may be present relatively free in the slag. This may increase the extraction efficiency. However, in the case of Ti, the enhancement was not as high as expected. Especially, in the case of the air-cooled slag, lower efficiencies were obtained. This is attributed to the formation of crystals during cooling, which probably surround or incorporate the targeted elements, and result in lower leaching rates. In order to improve these values, a better understanding of slags' microstructure is required. For this purpose, both air-cooled and quenched samples were investigated in terms of crystallinity. Figure 4 reveals XRD diffractograms of both slags.

Contrary to the well-defined and narrow peaks in air cooled slag, quenched slag exhibited poor crystallinity with amorphous nature, as expected. While quenched samples exhibited only the gehlenite ($2CaO.Al_2O_3.SiO_2$) and perovskite (calcium titanite) phase, in the air-cooled sample formation of various calcium silicate and aluminate compounds was observed. SEM micrographs of the same samples with chemical analyses are provided in Figure 4.

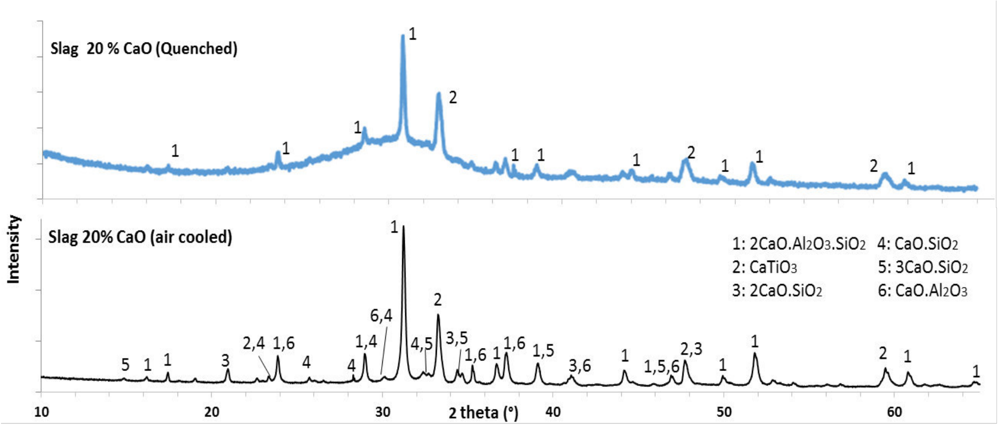

Figure 4. XRD patterns of air cooled and quenched slags

In Figure 5, the regions labeled as "liquid" correspond to amorphous content. In parallel with XRD findings, highly amorphous content of quenched slag is observed where perovskite phase is entrapped. However, in air-cooled slag, better-crystallized matrix and calcium silicate surrounding perovskite were detected.

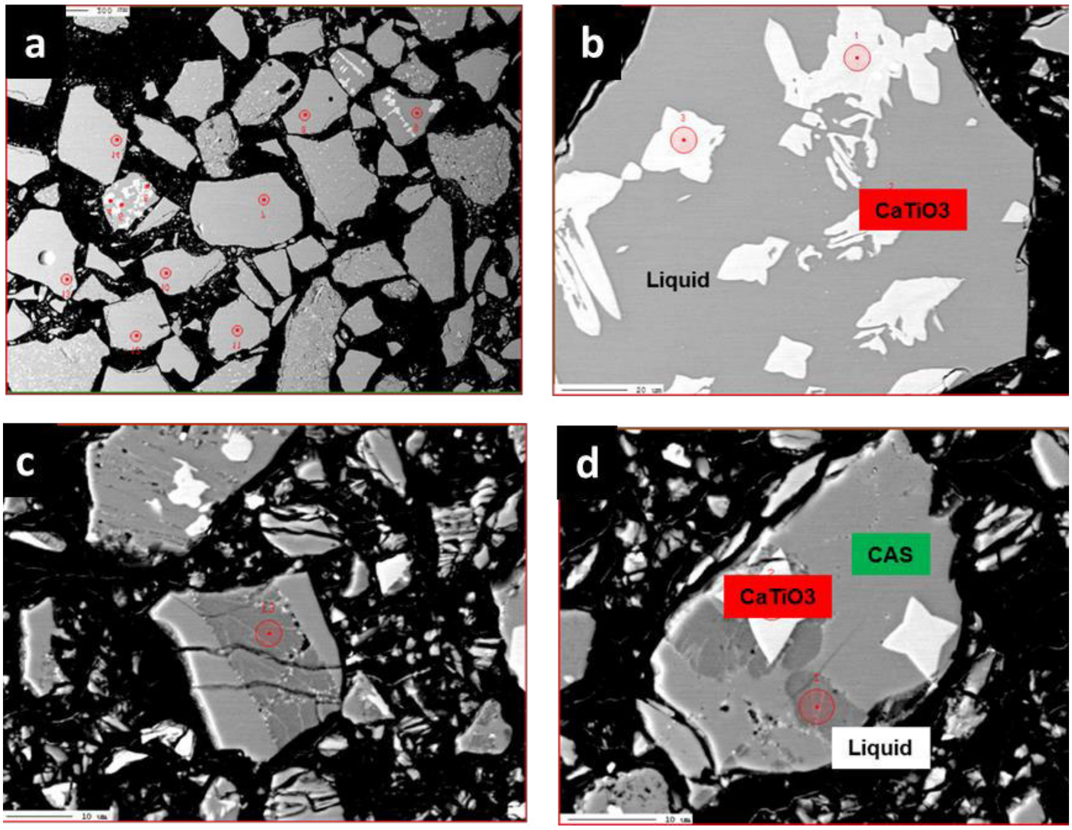

Figure 5. SEM images of the two investigated slag samples: quenched (a,b), air-cooled (c, d)

This explains the poor leaching efficiencies of Ti in air-cooled slag. Since solubility of the amorphous phase is thermodynamically more favorable, leachate may reach to the Ti-containing phase easier. However, in air-cooled slag, stable calcium silicate acts as a barrier between leachate and Ti-containing phase.

Conclusions

Removal of Fe before the acidic leaching step improved significantly the efficiency of Sc leaching. Around 90% recovery has been reported for CaO-fed EAF treated and quenched slag followed by H_2SO_4: H_2O_2 leaching. Scandium (Sc), can then be further treated with purification operations to synthesize a Sc concentrate.[10-12] In the case of titanium, there has been decrease in terms of efficiency, owing to the formation of stable perovskite. However, the quenched sample with poor crystallinity exhibited enrichment in PLS in terms of Ti. These preliminary results indicate that EAF treatment is promising when followed by H_2SO_4: H_2O_2 leaching. More detailed studies will be conducted to understand leaching mechanisms and kinetics.

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