Combining pyrometallurgical conditioning and dry acid digestion of red mud for selective Sc extraction and TiO_2 enrichment in mineral phase

Gözde ALKAN[1], Bengi YAGMURLU[1,2], Yiqian MA[1], Buhle XAKALASHE[1], Srecko STOPIC[1], Carsten DITTRICH[2], Bernd FRIEDRICH[1]

[1] RWTH Aachen University, IME Institute of Process Metallurgy and Metal Recycling, Aachen, Germany

[2] MEAB Chemie Technik GmbH, Aachen, Germany

Abstract

Conventional acidic leaching of red mud results in severe gelation problems as well as in non-selective metal mobilization. In order to increase the value of the final mineral product aiming to be used in the construction applications, it is beneficial to keep the TiO_2 undissolved. Nevertheless, in the case of high Sc containing bauxite leach residues, it is worth investigating the possibilities to remove Sc before it goes to the mineral products. The scientific approach of the present experimental study is the transformation of leachable anatase/rutile into insoluble perovskite via reductive smelting in electric submerged arc furnaces (EAF) and controlled crystallization. This process also allows for concentration of Sc as most of the iron has been recovered as metal. Due to the high Si content of the resulting slag, the gelation problem is magnified during following the hydrothermal process. In order to tackle the gelation issue by keeping higher Sc extraction rates and ensure the formation of a table Ti-oxide, this study focuses on the dry digestion method, invented at IME for Rare Earth element containing ores. Two slags with different chemistry and red mud were exposed to dry digestion and direct leaching methods in a comparative manner. ICP-MS was used to determine chemical content of leach liquors and XRF and XRD was used to perform chemical and phase analyses of solid residues. Various ratios of acid to red mud and to slags (20 mL, 15 mL, 10 mL and 5 mL per 15 g) were examined to evaluate the optimum acid requirement for decomposition and complete wetting of various solid materials.

Introduction

Recovery of metals by hydrometallurgical and pyrometallurgical methods from bauxite residue has been intensively studied in last decades.[1,2] Owing to increasing demand due to various application areas of Ti and Sc, the utilization of red mud as a secondary resource for those metals is promising.[3] Although Sc should be removed before it goes to the mineral products, it is beneficial to keep the TiO_2 undissolved in order to increase the value of the final mineral product aiming to use it in the construction applications.[4,5] There are direct acidic leaching routes previously reported with common drawbacks such as poor selectivity over Fe and complex solvent extraction process that necessitates intensive purification steps.[6] A combined pyrometallurgical and hydrometallurgical processing of bauxite residue concentrate production through carbothermic reduction of bauxite residue may be promising to produce a slag concentrate and to apply leaching and precipitation conditions to the produced slag concentrate for recovery of Ti and Sc.[7] However, standard acidic leaching of minerals enriched in terms of Si results in severe gelation problems as well as in non-selective metal mobilization. Red mud with a Si content around 5 wt. %, as reported earlier, has a tendency to gelation during acidic leaching treatment.[7] An electric arc furnace (EAF) slag with enriched Si content may experience even more emphasized gelation problem.

A novel leaching method has been reported against gelation problem, so-called dry digestion, which utilizes the addition of highly concentrated acid to starting material to form a pasty mass followed by water leaching.[8] In a previous study, the addition of an acidic solution to eudialyte concentrate heated at boiling temperatures, and the subsequent water leaching of the treated concentrate, could result to a high recovery of REE while avoiding silica gel formation.[9]

In this study, red mud and two slags with different silica content were exposed to dry digestion and the behavior of Sc, Ti and Si were evaluated in a comparative manner. The best condition for high Sc leaching rates with a TiO_2 enriched residue without any gelation problem was suggested.

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. Ignition losses were due to water-losses during the drying of samples for ICP-OES analysis.

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
Basic Slag	1.8	38.3	43.2	7.6	7.6	170
Acidic Slag	1.4	36.8	15.3	38	7.3	170

BR is subsequently mixed with lignite coke and lime containing 87 wt% fixed carbon and 95 wt% CaO respectively. The additions of lignite coke to bauxite residue 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 one hour. At the conclusion of the experiment, the molten material was poured into a refractory lined mold where the material cooled down and the metal settled at the bottom of the mold. The cooled material was separated into slag and metal and then weighed. The slag was prepared for leaching where it was crushed and milled to obtain a slag fraction of -90 µm.

In the direct leaching tests, a glass beaker, a heating plate and a magnetic stirrer were used for controlling the reaction temperature and stirring speed. Red mud and slags were fed into the reactor, containing the preheated sulfuric acid solution. Leaching efficiency was investigated at a set temperature of 75 °C, 250 rpm stirring speed, and S/L ratio of 1/10.

Dry digestion process was performed with high concentrated 97% (v/v) sulfuric acid. Concentrated sulfuric acid (H_2SO_4) is introduced to red mud and slags to form a paste and ensure silica precipitation. The absence of free water results in an extreme ionic strength avoiding chain formation of a gel. Starting materials were mixed with various amounts of acid (5, 10, 15, 20 mL), mixed 5 minutes. After that slurries were kept constant at 75 C oven for 1 hour. As a second step, the paste is washed with water to collect recovered metals.

Results and Discussion

Figure 1 represents the leaching efficiencies of Ti, Sc, and Si from red mud by means of sulfuric acid. Direct leaching, dry digestion with the same acid amount with direct leaching condition and three more acid concentrations are included in a comparative manner**.**

50% of Ti leaching has been dramatically suppressed with the application of the dry digestion technique. All acid amounts in the case of dry digestion ended up very poor in Ti leaching, i.e. around 20-30%, implying a leach residue relatively enriched in terms of TiO_2. In contrast, with an optimum acid amount, Sc leaching was improved to 50% by dry digestion. The highest 20 mL and lowest 5 mL acid utilization affected all elements adversely, implying an optimum acid concentration. However, it is important to note that dry digestion suppressed silica solubility, which would result in gelation, for all acid concentrations. These investigations on red mud reveal that the application of dry digestion with an optimum acid amount ends up to improved Sc leaching without any gelation problem and a leach residue in terms of TiO_2.

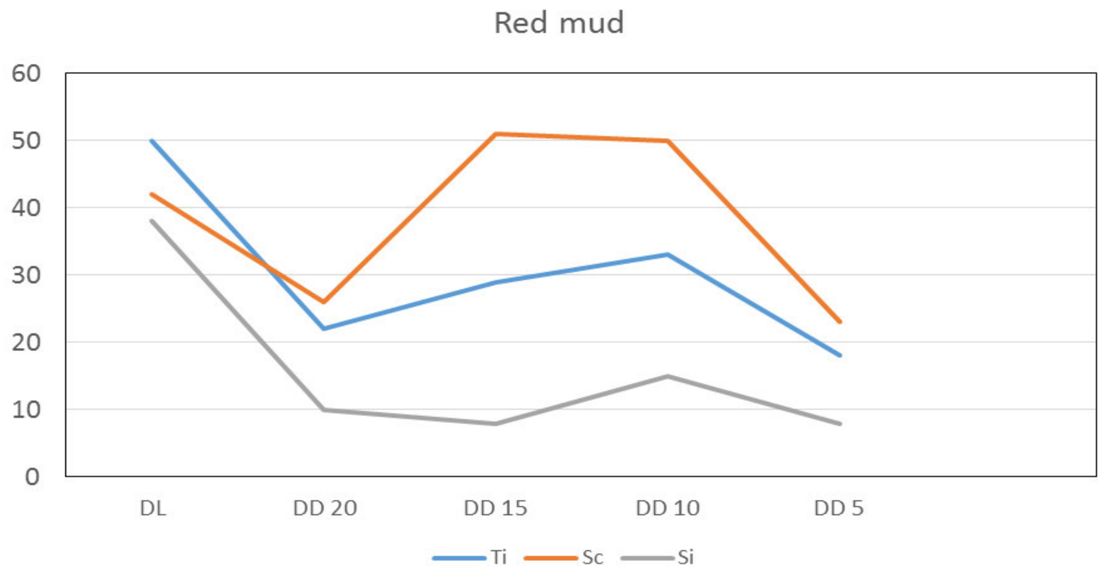

Figure 1. Extraction efficiencies of Ti, Sc, Si from red mud where DL. Direct leaching, DD: Dry digestion

In order to understand the limits of dry digestion and to suppress gelation, two different EAF treated slags were leached at same conditions with red mud. Also, forming a more stable Ti compound such as perovskite may favor enrichment of residue in terms of Ti oxide and improve selectivity of Sc leaching. Figure 2 shows the first slag treated with SiO_2 in EAF, enriched in terms of Si content.

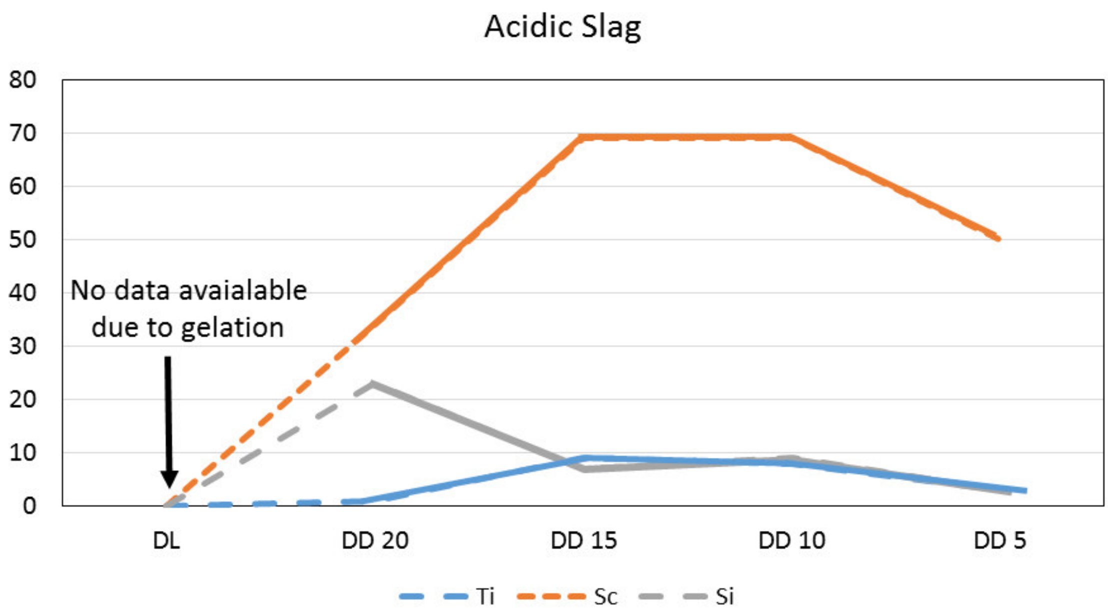

Figure 2. Sc, Ti, Si leaching efficiencies of acidic slag where DL: Direct leaching, DD: Dry digestion

Firstly, direct leaching of this slag resulted in rapid gelation, which is problematic for the handling of leachate and analyses. Introducing the dry digestion method at all acid concentrations inhibited Si dissolution rates and therefore the gelation. Similar to the red mud, dry digestion of slags exhibited also very promising Sc leaching efficiencies around 70%. It is known that Sc is found incorporated in hematite matrix in red mud. Removal of Fe may end up in the formation of free Sc surfaces and hence increase leaching rates importantly with respect to red mud (as presented already in Figure 1). However, all dry digestion conditions ended in very low Ti extraction, lower than 10%. When compared with red mud, these lower Ti leaching values are due to stable perovskite formation as represented in XRD analyses in Figure 3.

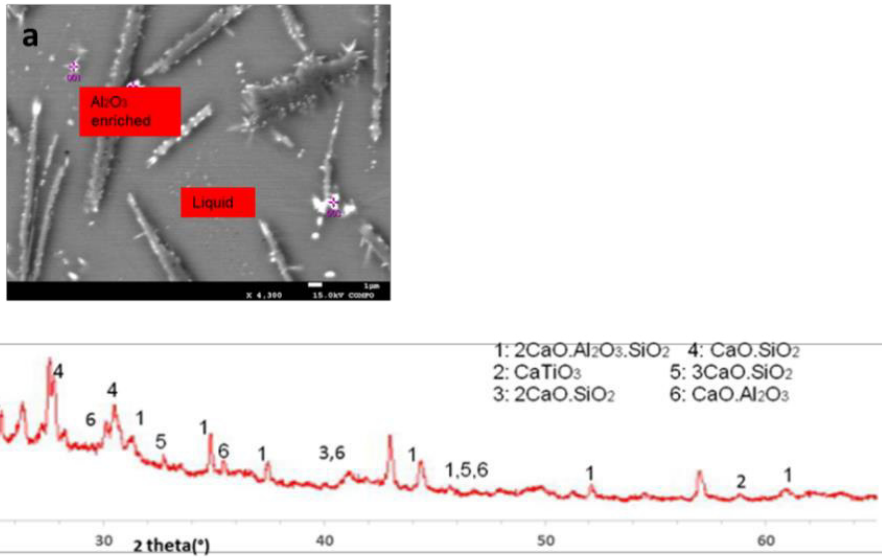

Figure 3. SEM (a) and XRD (b) analyses of acidic slag

Application of dry digestion on SiO_2 enriched slag (~40 wt%) prevented silica gelation and proved the efficiency of the method against gelation problem. Moreover, utilization of slags improved dramatically Sc leaching rates and TiO_2 enrichment in the leach residue.

Leaching efficiencies for basic slag (CaO fed) are given in Figure 4. Firstly, it is worth to highlight that 94% Sc leaching efficiency was achieved by direct leaching of that slag. However, within a few hours all PLS is gelated, which necessitates utilization of dry digestion. Introducing concentrated sulfuric acid decreased the Si dissolution up to almost 0%. When compared with direct leaching, Sc leaching efficiency decreases with dry digestion. However, a reasonable amount was still achieved (>70%). Moreover, suppressed dissolution with respect to red mud but relatively higher extraction of Ti with respect to acidic sag was achieved in this slag.

The formation of perovskite revealed in the XRD analyses (Figure 3 and 5) is the reason behind the lower dissolution rates.

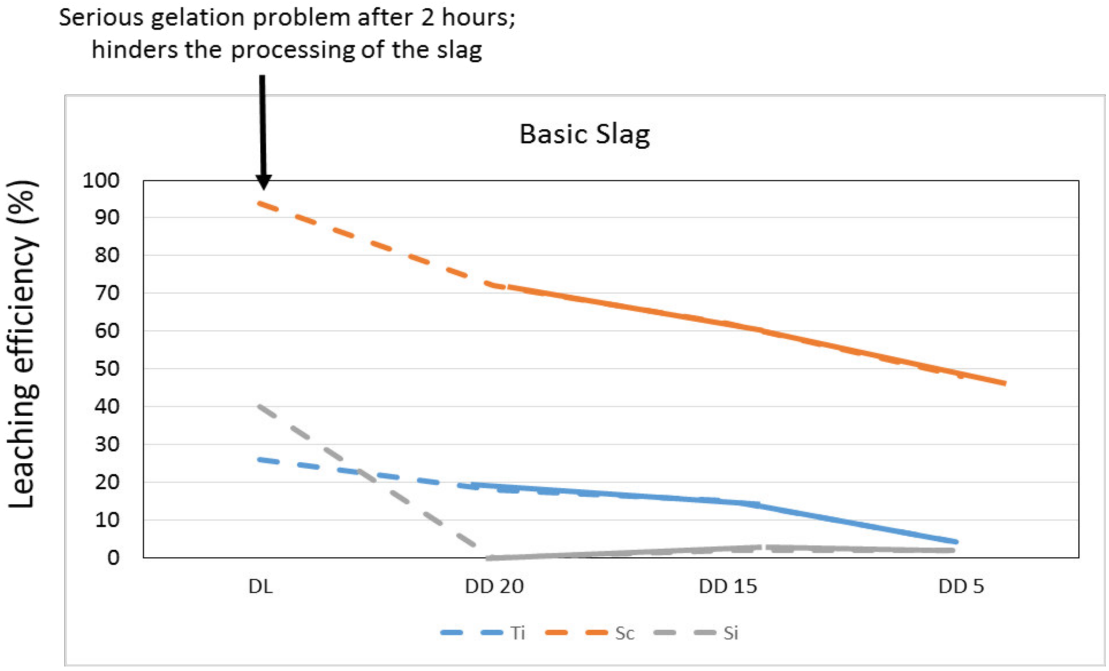

Figure 4. Sc, Ti, Si leaching efficiencies of basic slag where DL: Direct leaching, DD: Dry digestion

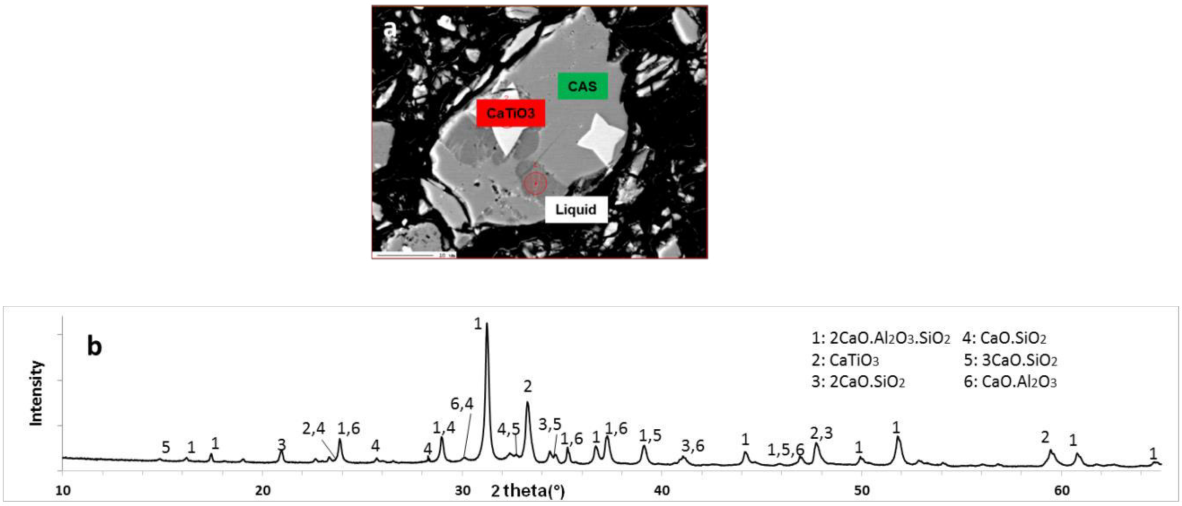

Figure 5. SEM (a) and XRD (b) analyses of basic slag

The difference between acidic and basic slag can be explained by the surrounding phase change of perovskite. In the case of acidic slag, Si enriched mineral covers perovskite as can be seen in Figure 3. Application of dry digestion, due to increased ionic strengths, results in precipitation of SiO_2 and therefore acid cannot reach Ti efficiently and ends up in the lowest dissolution. All leachates' gelation tendency can be found in Table 2, revealing the efficiency of dry digestion method.

Table 2. Gelation behavior of leaching systems

Material	Treatment	Gelation behaviour
Red mud	Direct Leaching	2-3 days
Red mud	Dry Digestion (5 mL)	No gelation
Red mud	Dry Digestion (10 mL)	No gelation
Red mud	Dry Digestion (15 mL)	No gelation
Red mud	Dry Digestion (20 mL)	No gelation
Acidic Slag	Direct Leaching	Rapid gelation
Acidic Slag	Dry Digestion (5 mL)	No gelation
Acidic Slag	Dry Digestion (10 mL	No gelation
Acidic Slag	Dry Digestion (15 mL	No gelation
Acidic Slag	Dry Digestion (20 mL)	No gelation
Basic Slag	Direct Leaching	2-3 hours
Basic Slag	Dry Digestion (5 mL)	No gelation
Basic Slag	Dry Digestion (15 mL	No gelation
Basic Slag	Dry Digestion (20 mL)	No gelation

Conclusions

A very promising hydrometallurgical route, allowing selective Sc leaching and TiO_2 enriched mineral phase formation without silica gelation issue, was designed. The dry digestion method has been applied in a comparative manner to red mud and two Fe depleted EAF slags. Application of EAF treatment resulted in the formation of a stable Ti oxide phase and suppressed the dissolution of Ti by forming a highly TiO_2-enriched mineral. After removal of Fe, which entraps a certain amount of Sc, there has been a great improvement of Sc recovery, up to 80%. Although direct leaching yields in the highest extraction efficiency, in order to suppress the gelation problem, dry digestion technique is highly efficient with high and selective Sc extraction and an enriched TiO_2 mineral phase to be used in advanced ceramic applications.

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