Conditioning of bauxite residue with bottom ash in view of recovery of valuable metals: a sustainable approach

Hugo LUCAS[1], Gözde ALKAN[1], Buhle XAKALASHE[1], Bernd FRIEDRICH[1]

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

hlucas@ime-aachen.de, galkan@ime-aachen.de, bxakalashe@ime-aachen.de, bfriedrich@ime-aachen.de

Abstract

Bauxite residue also known as red mud is rich in iron and aluminium oxides and represents a large-scale residue with no significant industrial application. Besides being a potential source of iron, red mud contains valuable elements such as Ti or Sc representing an economical potential for this kind of waste. Recovery processes reported in literature for the recovery of Ti and Sc from bauxite residue usually mention the need for interference of iron. On the other hand, municipal solid waste incineration (MSWI) has become normal practice in Europe to reduce the volume of municipal waste. After metal recovery using mechanical separation techniques, the mineral residue, rich in aluminosilicates is in most cases landfilled. In this study, bauxite residue was mixed with different proportions of MSWI bottom ash as fluxing agent. Pyrometallurgical treatment step allowed high iron recoveries. The slags produced after the carbothermic reduction were subjected to acidic leaching using a solution of 2.5M H_2SO_4 *and 2.5M* H_2O_2 *at 75 °C. The amorphous structure of slags produced by the use of bottom ash promoted leaching efficiencies between 70% and 80% for Ti, and among 50% and 60% for Sc.*

Introduction

Each year in the European Union, 1.7 billion tonnes of mineral waste is produced and the majority of this is being landfilled.[1] Bauxite residue (BR) and municipal solid waste incineration (MSWI) bottom ash are some of the various mineral wastes that contain valuable metals and different mineralogies end up discarded.

Today, around 5-6 million tonnes of bauxite residue are generated per year in the EU.[2] Bauxite is the raw material used to produce alumina (Al_2O_3) and this mineral is refined using the Bayer process. The BR is also known as red mud due to its red colour caused by high concentration of iron oxide. This residue not only represents a promising source of iron but also once iron is extracted, it becomes a potential source of aluminium, titanium, scandium and some REEs. Among other metals, Ti and Sc have started to be classified as critical metals owing to the increasing demand.[3,4]

The extraction of Ti and Sc by acidic leaching is conceivable but due to the content of iron, the extraction yield is poor.[3-5] For this reason, extraction of Fe from BR using Electric Arc Furnace (EAF) allows for valorisation of Fe and also produces a favourable slag concentrate to extract valuable metals by hydrometallurgical methods. Due to the large content of hematite (Fe_2O_3) and alumina (Al_2O_3), BR has a high melting point, and the use of fluxing agents become essential. The use of pure raw materials such as CaO or SiO_2 as fluxing agents to reduce the slag melting point also results in some cases increased amounts of waste throughout the process. For this reason, mineral wastes could be more sustainable and economical fluxing agents than the traditional fluxing materials.

Incineration has become normal practice in Europe to reduce around 90% the volume of municipal solid waste. This technique allows for valorising of the calorific value of waste to produce electrical energy. Around 18 million tonnes of bottom ashes are produced in European incinerators every year.[6,7] These ashes, rich in aluminosilicates, contain metals such as iron, aluminium, copper, and zinc which can be extracted by mechanical separation techniques.[8] The final mineral residue is in most cases landfilled. MSWI bottom ash contains high concentration of Si and Ca which could perfectly help to reduce the melting point of BR allowing the formation of a vitrified slag after smelting.

In this study, BR was mixed with vitrified MSWI bottom ash as a fluxing agent. The slag produced after the carbothermic reduction to recover iron in an EAF, were subjected to acidic leaching. Two different slags were investigated, having different proportions of BR and bottom ash. Mixtures of H_2O_2 and H_2SO_4 were used as leaching agents, in order to provide an oxidative environment and tackle the gelation issue.[5,9] The efficiencies of the leaching samples were analysed and evaluated via ICP-OES. Slags were also analysed in terms of crystallinity by XRD, in order to understand various leaching behaviour. The behaviour 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. and MSWI bottom ash comes from the MSW incineration company AVR located in Netherland. Bottom ash was pre-processed in an EAF in order to extract metals. The mixing chemical composition of the BR analyzed by XRF and ICP-OES technique is listed in Table 1.

Bauxite residue and MSWI bottom ash were dried over a period of 24 hours at 100 °C. Around 2 kg of MSWI bottom ash was pre-melted in the EAF at 1400 °C, over a holding time of one hour and subsequently quenched in water to produce a vitrified slag. A metallic alloy rich in iron and copper was recovered after this experiment. The vitrified bottom ash (BA) was dried at 100 °C for 24 hours and used as a fluxing agent for BR smelting.

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

Components (wt%)	Fe_2O_3	Al_2O_3	CaO	SiO_2	TiO_2	Na_2O	Sc (mg/kg)
Bauxite residue	44.3	25.3	8.5	6.2	5.2	2.0	130
Vitrified MSWI BA	1.2	20.4	21.7	51.4	1.1	4.1	-
Slag 1 (20% BA)	13.1	34.9	15.3	23.8	6.8	3.9	127
Slag 2 (30% BA)	14.3	31.1	16.0	28.6	5.8	3.8	159
Slag 3 (16.7% lime)	1.8	38.3	43.2	7.9	7.6	2.7	170
Components (wt%)	Fe	Si	Ni	Cr	Sb	V	Yield (%)
Metal 1 (20% BA)	97.87	0.61	0.50	0.21	0.01	0.03	63.3
Metal 2 (30% BA)	99.03	0.12	0.46	0.11	0.01	0.02	54.5
Metal 3 (16.7% lime)	98.93	0.11	0.3	0.6	0.01	0.05	95.0

To recover iron by carbothermic reduction, lignite coke (87 wt% carbon content) was mixed with BR in a ratio of 1:10. Three different slags were prepared using the EAF, two with the addition of BA to BR in a ratio of 1:4 and 3:7 and one with the addition of lime to BR in a ratio of 1:5. In both cases, the furnace temperature was controlled between 1450-1550 °C and the experiments were holding for almost one hour. At the end of each experiment, the molten material was quenched in water in order to promote the formation of a vitrified slag.

Subsequently, the samples were dried again at 100 °C for 24 hours and were subjected to comminution using a labor-jaw first and then a planetary-ball-mills to obtain a grain size below 90 µm.

For better understanding of the final slag properties mixing different waste, previous the smelting process, a SiO_2-Al_2O_3-CaO-$4\%Na_2O$-$8.5\%TiO_2$ ternary diagram detailing the liquid slag phase between 1200 and 1800 °C was performed using FactSage 6.4 (see Figure 1).

Leaching experiments were carried out in a glass reactor and heating-stirring were controlled by the use of a hot plate with a magnetic stirrer. Solid materials were washed with de-ionized (DI) water and dried at 90 °C and hand milled to ease leaching. All slags were subjected to leaching using a solution of 2.5M H_2SO_4 and

2.5M H_2O_2. The mixture of sulfuric acid with hydrogen peroxide should be carefully prepared by slowly adding hydrogen peroxide into sulfuric acid to control the rapid exothermic reaction. The effect of the mixing BA/BR was investigated at a set temperature of 75 °C, 250 rpm stirring speed, and S/L ratio of 1/10.[5,10]

BR, BR:BA slags 1 and 2 and BR:CaO slag 3 were leached under identical conditions for direct comparison purposes and were subsequently vacuum filtered with a vacuum pump and fine filter paper to separate solid residue and leachate. Leachates were analyzed by ICP-OES technique. PANanalytical WDXRF spectrometer Axios was used for the chemical analysis of slags. XRD profiles were performed by a PANanalytical X'Pert³ x-ray diffractometer scanning the samples between 10°-80° (2 θ) with a 5 °/min rate. X'Pert HighScore Software was used for mineral identification.

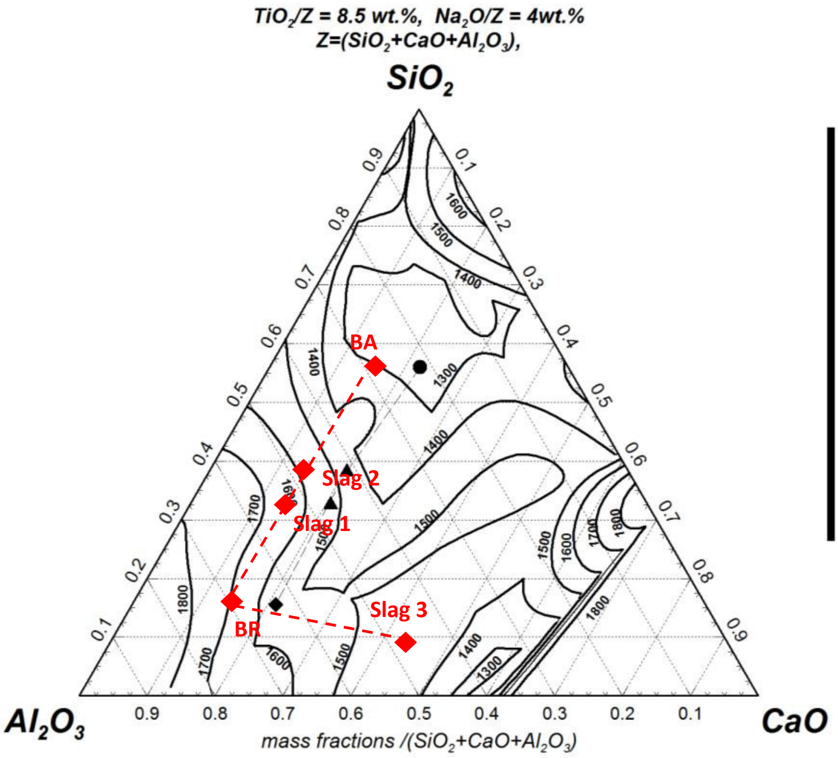

Figure 1. Ternary phase diagram as predicted by FactSage 6.4 for SiO_2-Al_2O_3-CaO-4%Na_2O-8.5%TiO_2 detailing the liquid slag phase for different temperatures

Results and Discussion

Ideally, a complete reduction of iron oxide from bauxite residue allows not only to recover iron but also to concentrate titanium and scandium in the final slag. As shown in Figure 1, bauxite residue without iron would contain the same amount of CaO as MSWI bottom ash (BA) this means that any mixing of BA and BR would only change the proportion of silica and alumina. BA is an acidic slag due to the high SiO_2 content. Silicates tend to form networks which favour the formation of glass, and the XRD profile of BA confirms this (see Figure 2).

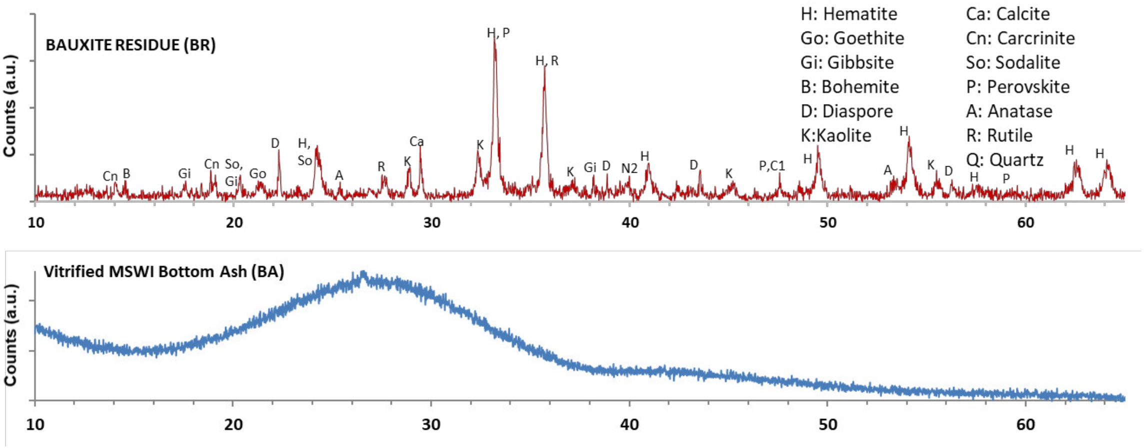

Figure 2. XRD patterns of bauxite residue and MSWI bottom ash

The phase diagram in Figure 1 shows that mixing of BR with BA allows for lowering of the melting point of slag by almost 100 °C for slag 1 (80 wt% BR+20 wt% BA) and 200 °C for slag 2 (70 wt% BR+30 wt% BA). During the smelting, this model was confirmed.

After one hour of smelting, the chemical results listed in Table 1 reveal the presence of a high content of iron oxides in both slags. The reduction of iron occurs as detailed in equation 2 and 3 in two-steps; firstly, the hematite is reduced to wüstite and then to iron which collects on the bottom of the crucible.

$$Fe_2O_3 + C \rightarrow 2FeO + CO \tag{1}$$

$$FeO + CO \rightarrow Fe + CO_2 \tag{2}$$

However, the presence of a high content of silicates favours the formation of other complex compounds such as fayalite (see equation 3), which reduces the activity of iron oxide and, therefore, a complete reduction becomes more difficult.

$$2FeO + SiO_2 \rightarrow Fe_2SiO_4 \tag{3}$$

The XRD patterns hereinafter show clearly that the BR undergoes a transformation during the smelting process. The use of MSWI bottom ash as a fluxing agent was not only effective to reduce the slag melting point but also prevented the formation of crystalline compounds containing titanium which is one of the keys to increase the recovery yield of Ti by hydrometallurgical treatment. The use of lime as a fluxing agent also reduced the melting point of BR, producing a basic slag. However, even if this slag was quite amorphous, it did not prevent the precipitation of perovskite.

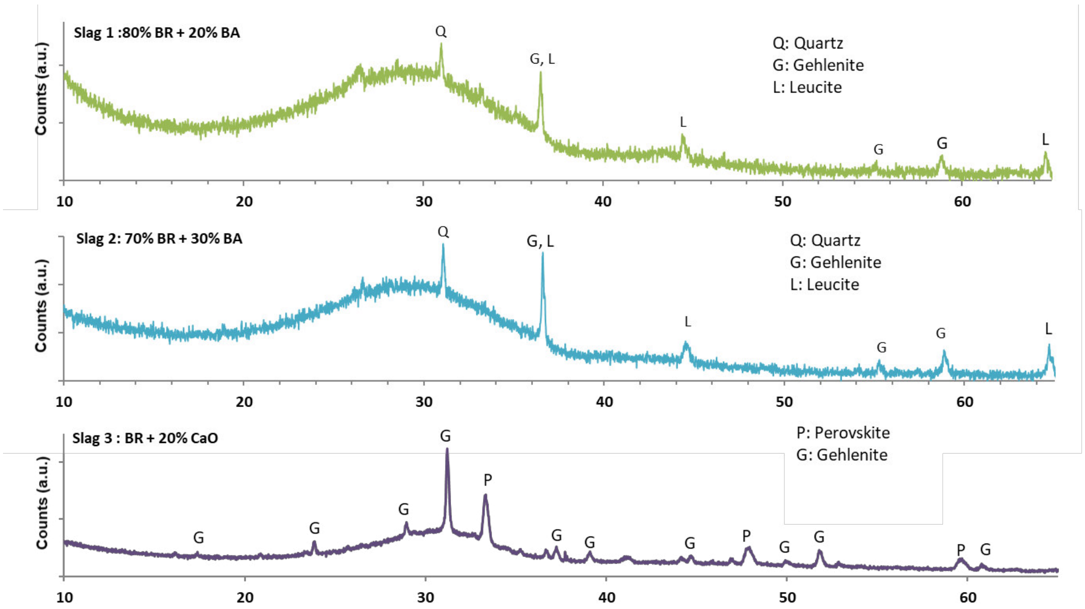

Figure 3: XRD patterns of produced quenched slags

The main limitation about direct leaching of bauxite residue is the high content of iron oxide which affects negatively both the recovery rates and the leaching conditions.[1] Several studies reveal that during the smelting process it is possible to recover pig iron while titanium and scandium concentrate in the slag.[5,10] In this case, the yield of iron recovery for both BR:BA slags was between 50 and 60%. On the other hand, iron recovery was almost complete for the BR:CaO slag due to the low SiO_2 content (see Table 1).

Previous work demonstrates that a leaching solution of sulfuric acid and peroxides was useful to recover titanium and scandium.[3,5,9] Nevertheless, the precipitation of perovskite in an EAF treated bauxite residue has an effect on the subsequent recovery yield of titanium via leaching.[5,10] Leaching efficiencies of BR, BR:CaO and two BR&BA slags for the recovery of Ti and Sc are represented in Figure 4.

Figure 4 indicates that BR:BA slags are promising for enhanced Ti leaching. As represented in Figure 3, addition of BA to BR promotes non-crystallinity of the produced slags. Although the slag of BR after EAF treatment followed by quenching has also exhibited amorphous characteristics, there has been the stable perovskite formation which suppresses Ti leaching. Apparently, the absence of Ti under crystalline form has a strong positive influence on the leaching efficiency of Ti. However, for Sc there has not been a significant enhancement observed with

BA incorporation. It may be due to relatively higher amounts of iron oxide remaining in the slag, which is known to entrap Sc.

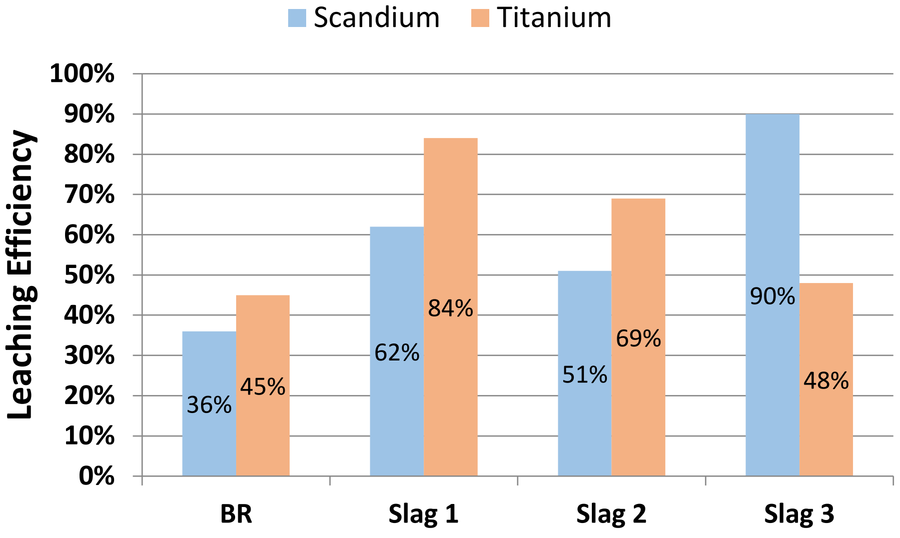

Figure 4. Scandium and titanium leaching efficiencies. Leaching solution 2.5M H_2SO_4 and 2.5M H_2O_2, s/l ratio 1:10, temperature 75 °C

Conclusions

Using MSWI bottom ash as fluxing agent not only demonstrated to be beneficial to reduce the melting point of slag but also has great advantages from the economic and ecological point of view. Indeed, this waste can be found in almost all of Europe, is generally landfilled, and its use can reduce the consumption of natural raw materials such as SiO_2 and CaO. The special characteristics of this material in terms of composition and morphology favour the production of amorphous slags when it is mixed with bauxite residue during smelting.

The conditions needed for complete recovery of iron to the metal need to be investigated further. The presence of iron seems to have a significant effect on Sc recovery, however, in this case there were no negative effects as reported in other publications on Ti recovery because the leaching efficiency was high. On the contrary, Ti recovery is directly related to its crystalline form. When the formation of perovskite is avoided the leaching efficiency increases.

A pyrometallurgical treatment of bauxite residue followed by 2.5M H_2SO_4: 2.5M H_2O_2 leaching solution at 75 °C, was effective to extract titanium and scandium. The results indicate unprecedented high efficiencies for titanium recovery from slags made with bauxite residue and MSWI bottom ash. A more detailed investigation will be carried out for an in depth understanding of the microstructure, the leaching mechanisms, and kinetics.

Acknowledgments

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