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Hydrometallurgical Extraction of Scandium from Bauxite Residue based on Sulfuric Acid Process

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Abstract

In this study, scandium extraction from Bauxite residue based on sulfuric acid leaching is presented. Scandium dissolves at elevated temperatures under high acid concentration reaching recovery yields up to 90%. It was found that increasing acid concentration in the range of 3-4 mol/L at elevated temperature, increase Sc recovery whereas simultaneously overcoming silica gel issues that occur from Si dissolution obtaining fast filtration rates while working at high pulp densities. Upon H₂SO₄ leaching, the main elements present in Bauxite residue such as Fe, Ti and Al co-dissolve, resulting to a pregnant solution of several g/L and Sc concentration in the range of 10-20 mg/L. Neutralisation of leachate for Iron precipitation as well as direct solvent extraction were applied to successfully remove iron or directly extract Sc from solution.

Introduction

Rare earth element (REE) hydrometallurgical extraction from Bauxite residue (BR) has been thoroughly studied by direct mineral acid leaching.¹ Mineral acids that applied for REE leaching provide high recovery yields but in many cases impurities that co-dissolve interfere with the downstream REE purification process. Therefore many studies are mainly focused on REE selective leaching against the major elements present in Bauxite residue such as Fe, Al, and Ti.^{2,3} Particularly Sc which accounts for 95% of the total value of REE found in bauxite residue is usually the main target metal.^{4,5} Most of the hydrometallurgical studies on BR were conducted at low pulp densities indicating a limitation of Sc selectivity against Fe.^{6,7} Thus it has been realised that no more than 50% of Sc can be selectively recovered by direct leaching, mainly due to the high association of Sc with Fe mineral phases, leading to low Sc concentration in the final solution. Despite these studies, there are limited or no presentation of literature data concerning direct BR leaching and Sc recovery at high temperature of 95 °C, high acid concentration such as 3-4mol/L H₂SO₄ while working at high pulp density >10 %w/v. Additionally, silica gel formation is a major issue for consideration when BR leaching is conducted at high

pulp densities. In this study direct BR leaching with H₂SO₄ resulted to almost 90% of Sc recovery with major co-dissolution of Al, Ti and Fe while silica gel formation is hampered by increasing acid concentration and leaching temperature. Subsequently, neutralisation of the PLS results to >90% iron precipitation with Sc losses less than 8%. Alternatively direct solvent extraction of the pregnant solution without precipitation applied, where selective extraction of Sc directly from solution is achieved. The proposed process reveals a new way of Sc recovery during non-selective leaching of BR using H₂SO₄.

Experimental

Greek BR samples were obtained directly from the filter press of the alumina refinery plant in December 2016. Samples were dried and further crushed and sieved below 200 µm. H₂SO₄ and deionised water of laboratory grade were used. Chemical analysis of BR samples was performed by the fusion method with a mixture of Li₂B₄O₇/KNO₃, followed by nitric acid dissolution. Metals in solution were measured by ICP-OES and AAS. Calcium was determined with XRF. Leaching experiments conducted in glass reactors placed in heating plates with magnetic stirring, incorporated with a glass sensor for temperature controlling and a vapour condenser.

Bauxite residue characterisation

Chemical analysis of BR sample used for leaching is presented in Table 1:

Table 1. Chemical analysis of BR sample (obtained Dec. 2016) and individual REE concentration

Element		wt%	REE	ppm
SiO ₂	8.4	%	La	84.8
Al ₂ O ₃	13.3	%	Ce	306.9
Fe ₂ O ₃	44.1	%	Pr	19.1
CaO	10.8	%	Nd	88.2
MgO	0.2	%	Sm	16.8
Na ₂ O	3.8	%	Gd	17.4
TiO ₂	6.2	%	Dy	16.3
TREO	0.1	%	Er	10.9
LOI	10	%	Yb	12.1
other	2.8	%	Y	82.9
			Sc	100.3

XRD analysis identified minerals such as hematite [Fe_2O_3], gibbsite [$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$], diaspore [$\text{AlO}(\text{OH})$], cancrinite [$\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{CaCO}_3)(\text{H}_2\text{O})_2$], katoite [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$], calcite [CaCO_3], boehmite [$\text{AlO}(\text{OH})$], anatase-rutile [TiO_2] and goethite [$\text{FeO}(\text{OH})$]. The identified minerals were also observed by scanning electron analysis microscopy shown in Figure 1. The particle size distribution of BR samples revealed a $d_{50} = 2.1 \mu\text{m}$.

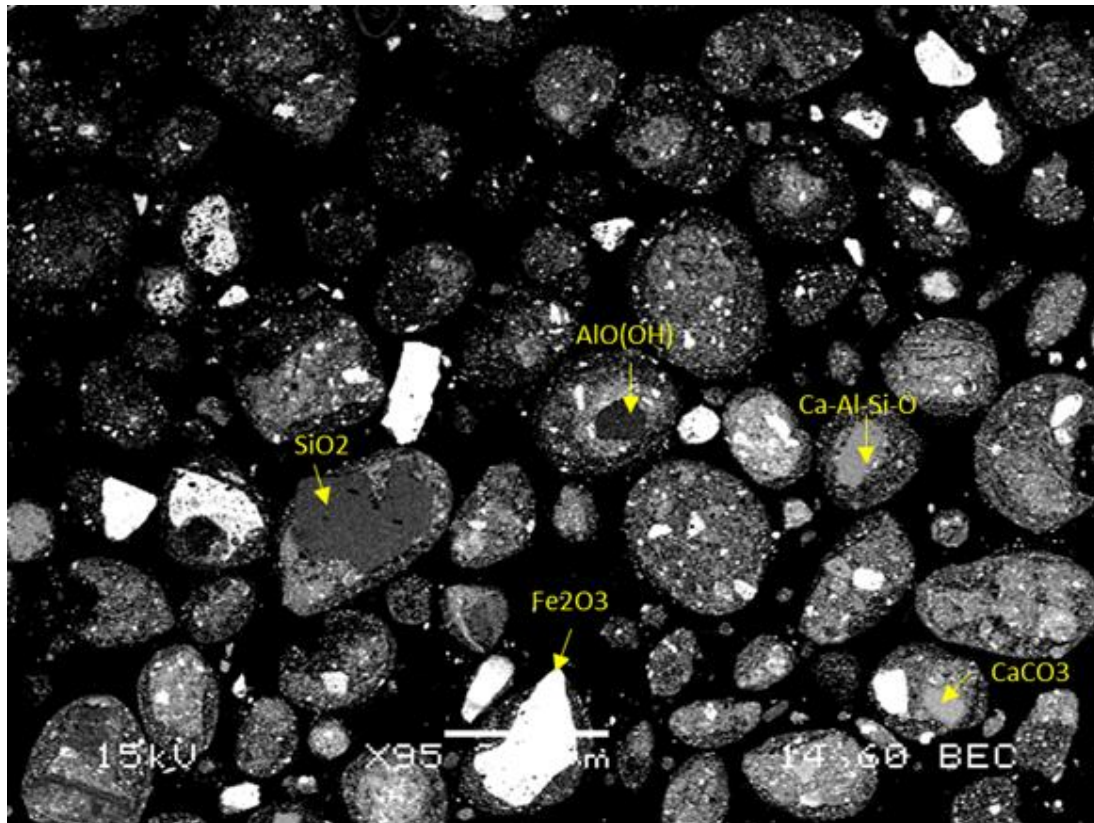


Figure 1. Backscattered electron SEM image of BR sample (scale bar 200 μm)

Results and discussions

Factors studied during direct BR leaching with H_2SO_4 were acid concentration (1-5 mol/L H_2SO_4), retention time (1-24 h), leaching temperature 30-90°C and pulp density (10-20%w/v). The effect of temperature on metal recoveries at 4M H_2SO_4 for 24 h, at intense stirring at a 10% pulp density can be seen in Figure 2.

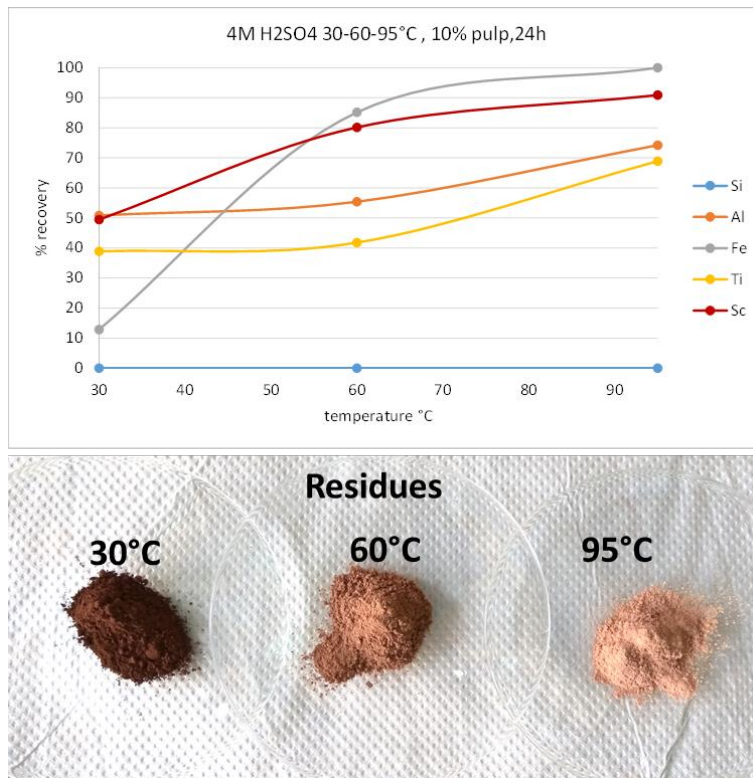


Figure 2. % metal recoveries during BR leaching with H_2SO_4 and their subsequent dry residues (below). Conditions used: 4M H_2SO_4 , 10% pulp density, 24h at 30-60-95 °C.

For a steady pulp density of 10% w/v, using 4M H_2SO_4 and 24h of retention time the following results obtained at 30°C: Sc 50% with 12% Fe recovery, while at 60°C: Sc 80% with 85% Fe recovery and at 95°C: Sc 90% with 99%Fe. The results indicate that in order to achieve 90% Sc efficiency, temperature must increase up to 95°C, at high acid concentration where almost all of Fe co-dissolves while Al and Ti recoveries are about 70% with no Si dissolution. The respective residue obtained at 95 °C consist of diaspore, quartz and anhydrite (Figure 3).

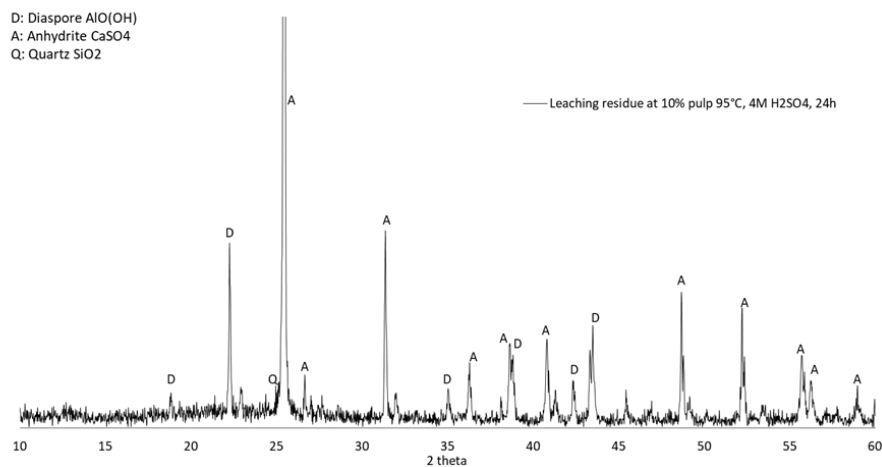


Figure 3. XRD of leaching residue after 4M H_2SO_4 leaching at 95°C for 24h.

A series of experiments were conducted using 1-5M H₂SO₄ at retention time 1-2-4-24 h keeping constant 95°C at 20% pulp density. The results of metal recoveries of Sc, Fe and Si are presented in Figure 4.

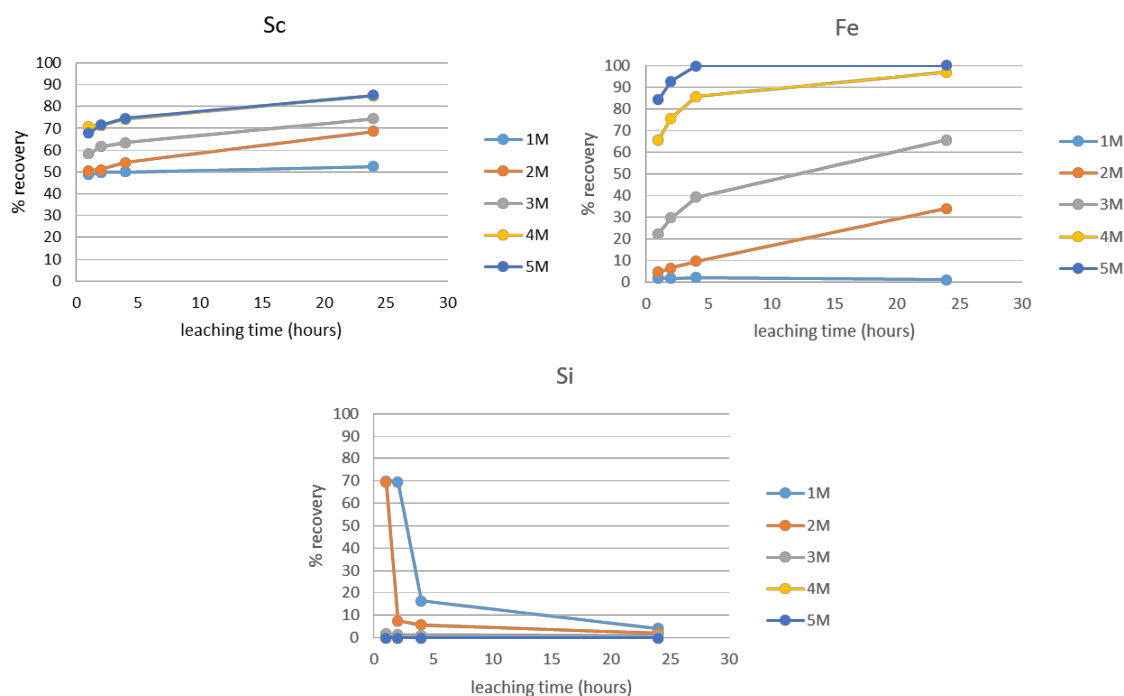


Figure 4. % recoveries of Sc, Fe and Si at 20% pulp density, 95 °C for 1-2-3-4-5M H₂SO₄ retention time of 1-2-4-24 h.

During leaching at 1-2M H₂SO₄ and 95 °C, Sc recovery remains steady at 50% providing high selectivity against Fe with no significant change after 4h of leaching yet there is large co-dissolution of Si leading to silica gel and hampering filtration. Increasing acid concentration from 3M to 4M H₂SO₄ resulted to significant increase of Sc recovery at 60-70% after 1 h with large co-dissolution of Fe while silica gel is suppressed obtaining fast filtration rates of the slurry. Increasing more acid concentration to 5M provide similar Sc recoveries and almost total dissolution of Fe with no silica gel. Si behaviour during leaching indicates that silica gel is suppressed by increasing temperature-retention time and more important by increasing acid concentration (Figure 4).

Based on these results, BR leaching with 4M H₂SO₄ at 95 °C at 20% pulp density for 2h resulted to a pregnant leaching solution (PLS) having 7g/l Al, 5 g/L Ti, 42 g/L Fe and 15 mg/l of Sc. Neutralization of the produced PLS at a pH of 3 resulted to 93% of Fe precipitation with Sc losses of 8%, yet poor filtration rate of the resulting slurry is obtained. As an alternative, direct solvent extraction to the PLS using a

mixture of DEHPA (Di-(2-ethylhexyl)phosphoric acid) and TBP (tributyl phosphate) resulted to selective extraction of Sc (87%) against Fe, Ti and Al after one step at aqueous to organic ratio 1:1. This results to Sc extraction from these challenging leachates with 70% Sc overall efficiency.

Conclusions

Selective recovery of Sc against Fe by direct BR leaching with H₂SO₄ is limited in selectivity at 50%. Leaching with H₂SO₄ at 95 °C and 10% pulp density for 24h resulted to 90% Sc recovery with total dissolution of Fe and high co-dissolution of Ti, Al. Similarly working at 20% pulp density for 2h resulted to more than 70% Sc recovery and large co-dissolution of the rest metals avoiding silica gel issues. The resulting PLS can be treated directly with solvent extraction to extract Sc selectively against the other co-dissolved metals, resulting to the development of a process that provides high efficiency of Sc extraction transcending metal interferences of other co-dissolved metals, and avoiding silica gel formation.

Acknowledgements

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