Investigations into Optimized Industrial Pilot Scale BR Leaching for Sc Extraction

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Abstract

Scandium is a critical metal with increasing demand in modern technologies, like solid oxide fuel cells and light-weight Al-Sc alloys. Sc is present at considerably high concentrations in various metallurgical by-products, including the bauxite residue (BR). Scandium extraction from the Greek bauxite residue (BR) that contains 70–100 mg/kg Sc has been demonstrated at an industrial pilot plant at MYTILINEOS. BR has been treated with sulfuric acid at conditions that allow for low acid consumption. In such conditions, high Sc leaching selectivity is achieved over Fe and Ti, which are the main impurities for the further purification of the leachate through the ion-exchange technique. This paper reports on the recent investigations on the effect of pH control during the leaching process, which can lead to optimized results. Moreover, the treatment of the produced leachate solution is also studied, in order to further refine it, prior to the ion-exchange.

Keywords

Red mud • Bauxite residue • Scandium • Recovery of scandium

Introduction

The primary production of aluminium requires approximately 2 tons of metallurgical grade alumina (Al_2O_3) for each ton of metal produced through molten salt electrolysis. To produce 2 tons of such alumina, alumina refineries need to process approximately 4 tons of bauxite ore through the Bayer process. The latter relies on the use of a caustic soda to selectively dissolve the aluminium content of the bauxite ore, which contains 40–60% aluminium oxides. The remaining ore, forms the solid by-product of the Bayer process which is termed *bauxite residue (BR).* BR contains various undissolved metal oxides and hydroxides of Fe, Al, Ti and Si from the original bauxite ore as well as complex Al-Si-Na-Ca phases formed during the Bayer processing. Furthermore, BR contains in trace amounts metal oxides like V, Ga, REE/Sc and others, the concentration of which has practically doubled from the respective concentrations in the bauxite ore.

The acidic leaching of Sc from the BR faces two major challenges: (i) selectivity of leaching Sc against Fe and Ti which are both found in much greater concentrations in the BR and both tend to be co-extracted with Sc during ion exchange and (ii) acid consumption, as BR is naturally an alkaline material with a varying amount of Na, depending on the initial bauxite ore, processing conditions and process upsets in the alumina plant.

The selective leaching of Sc from Greek BR utilizing sulfuric acid to produce a suitable Sc containing solution for ion-exchange Sc extraction has been established in the previous work of the authors [1].

In the present paper, a method for automated control of the process based on the desired pulp pH is presented. Such a process should be able to optimize acid consumption and allow for the regulation of changes in the BR feed sodium chemical composition.

In addition, a lab scale study at the National Technical University of Athens (NTUA) of the produced PLS

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(pregnant liquid solution) is presented aiming at elucidating PLS composition and pre-treatment steps needed prior to ion-exchange.

Experimental

MYTILINEOS: The MYTILINEOS acid-leaching pilot plant consists of three polypropylene reactor tanks of up to 800 L capacity, with mechanical steering and heating/cooling through immersed coils for circulating steam and cooling water, respectively. Filter-pressed BR produced at MYTILINEOS alumina refinery is mixed with industrial water in the first reactor (100-TK-10) to produce pulp of specific density measured through an inline Coriolis Mass Flow Meter. The pulp is pumped to the second reactor (100-TK-30), where is heated and contacted with concentrated sulfuric acid. The pulp exiting the 100-TK-30 is driven to the cooling tank (200-TK-40), where it is cooled to 60 C and is subsequently passed to the filter press circuit. The filter press separates solids from liquid, generating the final PLS (Pregnant Liquid Solution) and the neutralized bauxite residue. The filter press used consists of 25 frames of 470 × 470 mm with 11 chamber plates and 12 membrane plates and a total filter area of 6.6 m^2. Inlet slurry is drawn via a diaphragm pump with a maximum working pressure of 15 bar. The filter cake washing was conducted directly on the filter press with fresh water inserted through the inlet slurry and directed to the washate-receiving tank. Cake squeezing and cake air blowing were also applied in the filter press.

To achieve better control of the leaching process, automation control was applied, utilizing a pH meter (Ceraliquid CPS41D, Endress and Hauser) in 100-TK-30 linked to the pilot's SCADA controlling the sulfuric acid peristaltic pump (Qdos, Watson-Marlow). The system was set to maintain the pH of the pulp at a value of 2.3 by controlling the flow of concentrated sulfuric acid in the 100-TK-30 reactor. Likewise, the temperature was controlled by automatically regulating the flow of pressurized steam in the heat exchange coils of the 100-TK-30 reactor, to achieve and maintain a temperature of 85 °C. The retention time of the BR pulp in the 100-TK-30 reactor was 30 min, and approximately 230 kg of dry BR was processed in this way per day. Two PLS samples were taken daily directly from the filtrate of the filterpress and analysed by ICP-OES (Avio 220, PerkinElmer) for their Sc, Fe, and Ti concentrations at MYTILINEOS. The PLS produced daily was homogenized in 5m3 tanks and samples were provided to NTUA for further analysis by ICP-OES and study.

NTUA: Chemical analysis—To analyze the chemical composition of the BR, alkaline fusion and wet chemical analysis using the inductively coupled plasma–optical emission spectrometry (ICP-OES) Optima 8000 by Perlin Elmer (Waltham, MA, USA) and Atomic Absorption Spectroscopy (AAS), (PinAAcle 900 T, Perkin Elmer, Waltham, MA, USA). Calibration standard solutions were prepared from commercially available ICP, standards obtained from Merck (Darmstadt, Germany). The standard solutions were prepared in a suitable concentration and diluted further with 1% v/v analytical grade nitric acid (65% wt.) as required for working standards. High-purity deionized water (18.2 MW/cm) and argon of special purity (99.999%) were used.

Measurements—The pH was measured by a Metrohm mobile pH meter 826 with an Ecotrode Plus electrode. The Oxidation/Reduction potential was measured by a Hach HQ40D Portable Multi Meter with a digital oxidation-reduction potential (ORP/Redox) probe IntelliCAL® MTC101. The results were transferred to the Eh using the equation $Eh = E_{m\ (redox)} + E_{ref}$, where the E_{ref} was 207 mV, according to the probe used.

Physicochemical characterization—The X-ray diffraction analysis XRD pattern was recorded on a Rigaku Miniflex 600 benchtop diffractometer (Rigaku, Tokyo, Japan), with CuKa radiation (λ = 1.5405 Å) operating at 40 kV and 15 mA (the diffraction pattern was recorded between 3° and 75° (2θ), in 0.02° (2θ) steps with a scanning speed of 5° (2θ/min)).

Modeling of the PLS—The HSC software by Outotech (version 10.0.6.7) was utilized to model the PLS using both the Aqua and the Eh–pH modules. On the Eh–pH analysis, only aqueous and neutral species were considered. Also, the only S species that were considered were the SO_4^{-2} ones. Some iron species ($HFeO^-$, $HFeO_2^-$) were also not considered.

Results

Pilot Plant Leaching Campaign

The chemical composition of the BR used can be seen in Table 1. In total 9.8 t of BR were processed in the pilot over the course of 43 tests, producing 13.4 t of PLS. The pH control of the process proved effective as overall the pH values varied around 2.3 with ± 0.1 in each trial. Indicative variations of the pH during leaching are presented in Fig. 1, for two different trials, at conditions where a steady flow in reactor 100-TK-30 has been achieved. The BR pulp in the reactor tends to act as a buffer solution, neutralizing the incoming acidity; as a result the system constantly fluctuates the flow rate of the concentrated sulfuric acid stream. Depending on the variations in the initial pH levels in the BR pulp and the overall system response, differences in the total acid consumption are noted in each trial.

Table 1 Chemical composition of the BR from MYTILINEOS measured at NTUA

wt.%						ppm
Fe_2O_3	CaO	Al_2O_3	SiO_2	TiO_2	Na_2O	Sc
38.15	8.37	23.28	7.82	4.67	3.15	79.20

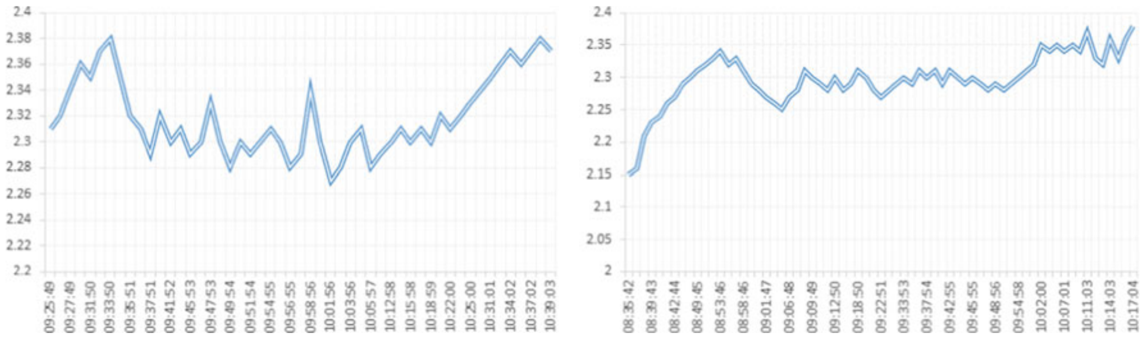

Fig. 1 Indicative pH profiles during leaching in two separate leaching tests

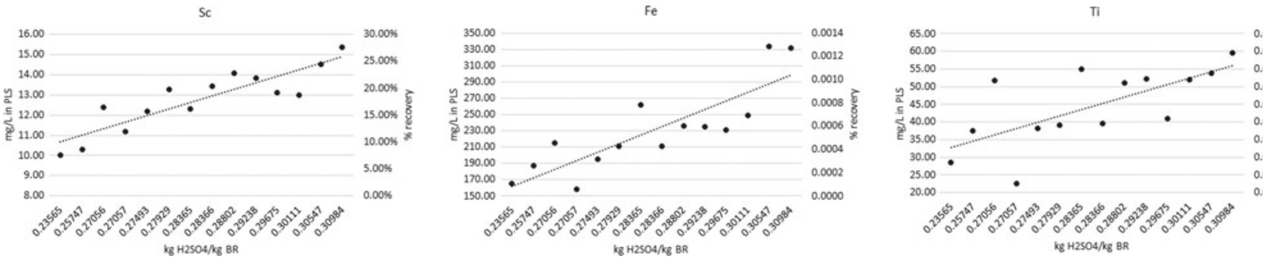

Fig. 2 Indicative Sc, Fe and Ti concentrations in the PLS at various kg H_2SO_4 /kg BR

Indicative results in terms of Sc, Fe and Ti extraction are presented in Fig. 2 as a function of the mass of concentrated sulfuric acid consumed per mass of BR treated. Dissolved Sc in the PLS ranged between 10–15 mg/L while Fe and Ti impurities were between 150–300 and 20–60 mg/L respectively.

From the results, a clear trend is confirmed between increasing the specific acid consumption and the recovery of Sc, Ti and Fe. This becomes more apparent when the specific acid consumption (kg acid/g Sc leached) is compared to the specific Sc leaching (gr Sc leached/ t BR), in Fig. 3. The potential for further optimization of the process can be seen if one moves towards the bottom right of the specific graph to achieve leaching of more than 20 g of Sc per t of BR with less than 15 kg of sulfuric acid per g of Sc.

The comparison of the homogenized PLS produced from this pH-driven campaign is presented in Table 2 and compared to the results achieved with the flowmeter campaign, where the pilot automation controlled the flow rate of the sulfuric acid pump at a set ratio with the BR pulp flow rate form 100-TK-10 [1]. The comparison of the two campaigns indicates a significant decrease in impurities levels as expressed by the dissolved Ti/Sc ratio in the PLS, for the pH-driven campaign.

PLS Treatment

A PLS sample produced from a single test in the pilot plant of MYTILINEOS was provided to NTUA for testing. The PLS sample was supersaturated, and thus, before the chemical analysis, solid to liquid separation had to be performed. The precipitate that was obtained from the solid to liquid separation was dissolved/measured by different chemical analysis methods as can be seen in Table 3.

The mineralogical composition of the solid precipitate was investigated through X-ray diffraction (XRD) analysis. The XRD profile of the solid precipitate (Fig. 4) exhibits four broad bands centered at 9.1 Å (9.7° 2θ), 3.4 Å (26.2° 2θ), 2.2 Å (40.7° 2θ) and 1.4 Å (66.7° 2θ), while it resembles that of allophane [2]. Besides the dominant occurrence of this poorly crystalline aluminosilicate, the sample also contains trace amounts of hematite, as it was possible to identify its two major peaks centered at 2.7 Å (33.1° 2θ) and 2.5 Å (35.7° 2θ), respectively.

The chemical analysis of the filtered PLS is seen in Table 4. The pH of the solution was measured at 25 °C and was found to be 3.36. In order to recover the Sc from this solution, an ion-exchange process will be used for

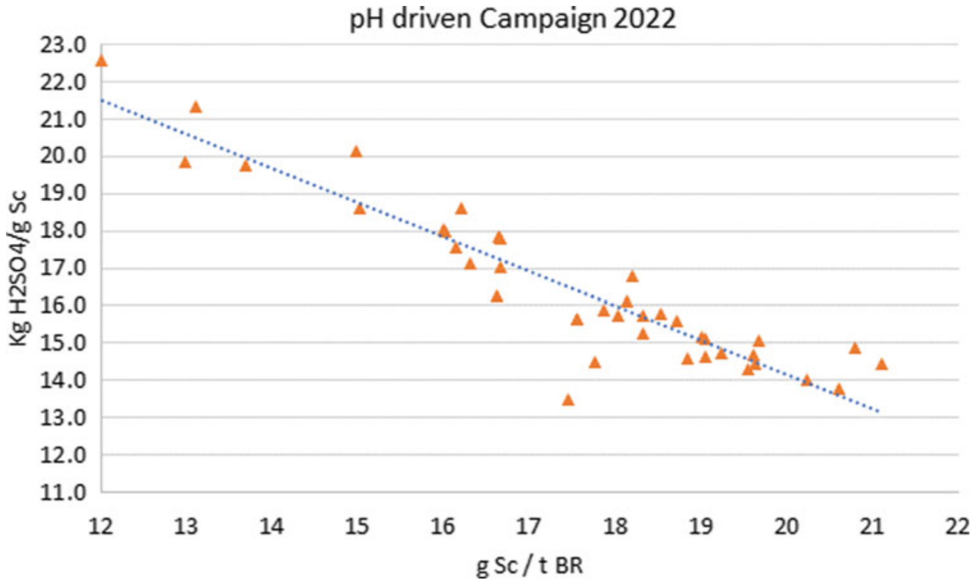

Fig. 3 Specific acid consumption versus specific Sc leaching

Table 2 Homogenized PLS results measured at MYTILINEOS

	t H_2SO_4/ t BR	Acid (kg)/ Sc (g)	g Sc/t BR	Sc	Ti	Fe	Ti/Sc ratio < 5
2012 pH-driven campaign	0.28	16.80	17.48	13.04	35.2	210.6	2.69
2011 Flowmeter-driven campaign	0.27	16.19	17.15	13.25	55.3	289.7	4.1

Table 3 Chemical analysis of the obtained precipitate

Chemical analysis	Fe_2O_3	Al_2O_3	TiO_2	SiO_2	CaO	Na_2O	Sc
XRF wt%	1.52	31.73	1.49	17.78	0.2	6.12	–
Fusion wt%	1.93	46.66	1.6	21.89	0.39	4.46	<0.05

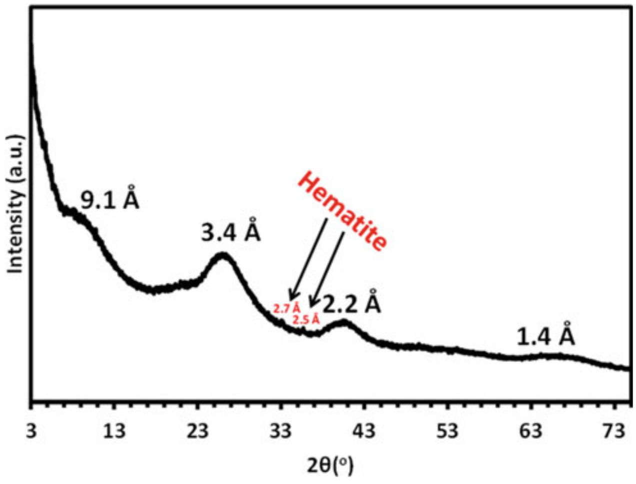

Fig. 4 XRD of amorphous aluminosilicate precipitate

purification. It is known, that the capacity of a weakly acidic resin, can significantly depend on the pH of the solution [3]. Most Ion-exchange resins are known for having the ability to first adsorb the higher valence ions [5]. The elements that are usually co-extracted together with Sc are Ti, Zr and Fe due to their high chemical affinity [4, 6]. If though, Fe^{+3} is reduced to Fe^{+2} by adding metallic iron according to reaction $2Fe^{+3} + Fe^{0} = 3Fe^{+2}$, then Fe is usually not co-extracted increasing the ion-exchange resin's performance [6].

Before testing, the PLS solution was modeled, using the HSC software (ver: 10.0.6.7). At first, the aqua module was used to calculate the ionic strength of the solution based on its concentration. The ionic strength was found to be 3.57 mol/kg. The solution was also modeled using the Eh–pH module, using the ionic strength that was calculated from the aqua module, for the H_2O/Fe/S system at 25 °C. The

Table 4 Chemical analysis of PLS sample (measured by ICP-OES or AAS at NTUA)

Elements	SO_4	Na	Al	Ca	Total Fe	Fe + 2	K	Si	Ti	Sc	Zr	V
Concentration (mg/L)	78,100*	12,800	9,800	577.5	280.9	172**	140	123	39.1	11.3	2.1	1

*Measured with a gravimetric method with the ignition of residue

**Measured by UV–VIS spectrophotometer, Fe(II) 1,10 Phenathrolin method

Eh–pH diagram produced can be seen in Fig. 5. From the graph, it can be seen that at a pH less than 4, the predominance area of Fe^{+3} species is always above 596 mV and the Fe^{+2} species predominance area is always below 538 mV depending on the pH.

To stabilize the PLS and to remove Fe interference in the ion-exchange, the PLS was studied for lowering the pH by adding sulfuric acid and metallic iron to reduce all the Fe^{+3} to Fe^{+2}.

The pH and the Oxidation/Reduction potential of the PLS were measured at room temperature. Since silica gel formation can also become a problem in such solutions, also the Si concentration was monitored in the experiments where sulfuric acid was added. The results showing the addition of sulfuric acid can be seen in Table 5 and the addition of metallic iron in Table 6. From the results, we can see that the addition of sulfuric acid did not have a great influence on the Eh or on the concentration of Fe^{+2} and Si. On the other hand, the addition of metallic iron changed greatly the Eh and the Fe^{+3} was totally reduced to Fe^{+2} from the first 0.315 g of Fe addition. Iron is reduced between 541.7 and 453.5 mV which corresponds with the theoretical calculations conducted with the HSC software.

Conclusions

The pH-driven BR leaching pilot campaign at MYTILINEOS has proven the capability to reproduce and even slightly improve the results of the previous flowmeter driven BR leaching campaign. This method of controlling the process is considered preferable as it allows for automatic corrections of the acid feed in light of changes in the BR's sodium content-pH level. Overall, the leached impurities of Fe and Ti were found to be fewer in comparison to the flowmeter campaign of 2021 with practically the same amounts of Sc recovery and acid consumption.

Lab scale study of the produced PLS revealed that as produced it is oversaturated in Al and Si, leading to precipitate formation over time. Sulfuric acid addition is required to stabilize the solution pH below 1.5. Approximately 60% of the dissolved iron is found to be Fe(II) cations. Addition of metallic iron as little as 3 kg/m^3 of PLS can increase this amount to 95% allowing for Sc extraction through ion-exchange without significant Fe co-extraction.

The results presented here offer insight into further potential optimizations of the process that will allow the

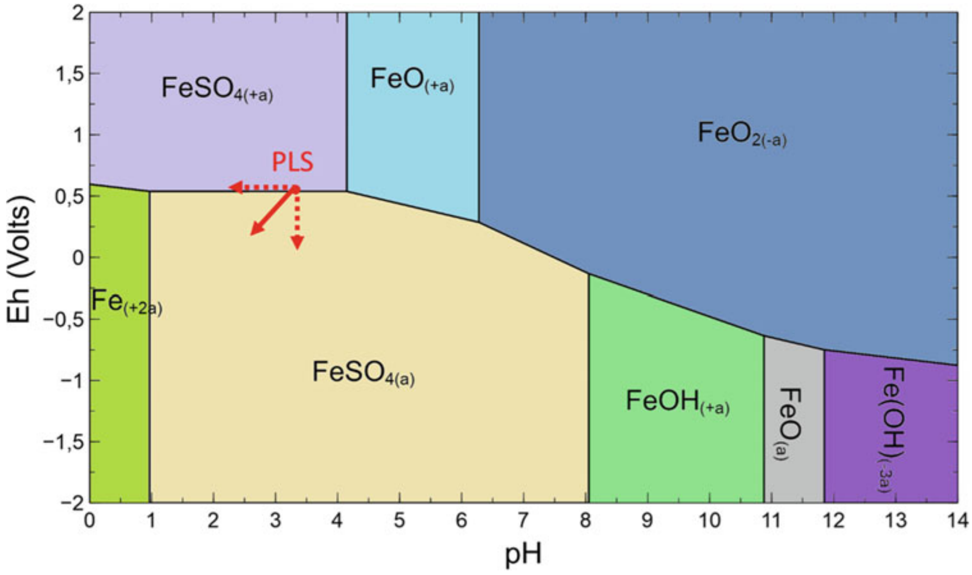

Fig. 5 Eh–pH diagram of the PLS produced in the MYTILINEOS pilot plant calculated with HSC software

Table 5 Addition of concentrated sulfuric acid and its influence on the PLS

Added	2 h agitation		24 h contact		UV	ICP-OES	
ml of concentrated H_2SO_4 / L of PLS	pH	eh (mV)	pH	Eh (mV)	Fe(II) (mg/L)	Fe total (mg/L)	Si (mg/L)
0	3.36	541.7	3.35	559.2	172.3	272.2	123
5	1.54	617	1.6	612.6	176.28	270.8	121.9
10	1.05	612.1	1.09	612.5	176.53	266.1	118.4
15	0.8	607.8	0.84	606.7	174.54	269.3	121.5
15	0.83	607	0.88	608.7	171.31	265.2	117.3
20	0.6	605.7	0.64	603.2	168.32	249.3	114.2

Table 6 Addition of metallic iron and its influence on the PLS

Added			UV	ICP-OES	
Fe^0 (g/L)	pH	eh (mV)	Fe(II) mg/L	Fe total	Fe II%
0	3.36	541.7	172.3	272.200	63.3
0.315	0.76	453.5	559.9	587.300	95.34
0.617	0.76	438.3	846.8	899.200	94.18
1.014	0.78	400.2	1268.0	1400.000	90.57
1.51	0.81	382.9	1683.2	1800.000	93.51

leaching of more than 20 g/t of Sc from BR with less than 15 kg of acid per gr of Sc, by a small adjustment of the leaching pH. The specific acid consumption is expected to be further reduced, by recycling the raffinate from the subsequent ion-exchange process to extract Sc from the PLS.

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