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Abstract

Reductive smelting trials were undertaken on a bauxite residue (red mud) sample via SAF (submerged arc furnace) treatment to produce pig iron (achieved Fe recovery > 95 %) and a critical metal enriched slag. Lignite coke was the selected reductant and CaO was used for fluxing achieving low operating temperatures (1500 – 1550 °C) and good slag-metal separation. The slag and the original bauxite residue as reference were subjected to leaching using 2.5 M H_2SO_4 and a 2.5 M H_2SO_4: 2.5 M H_2O_2 acid mixture with a liquid-to-solid ratio of 10 at 100 °C for 30 minutes. Decomposition of H_2O_2 at higher temperatures and formation of oxygen bubbles in the system introduce mechanical intensification of the leaching process. Leaching efficiencies for Ti and Sc were evaluated in a comparative manner between bauxite residue and slag. Selective precipitation route was followed after leaching to recover Ti and Sc from the leachate. In this precipitation process, Fe was removed by the addition of ammonia in the pH range between 3.3-3.8 with a dual stage step. Subsequent to removal of 95 % of the Fe in the solution, Sc was selectively precipitated as $ScPO_4$ with the introduction of a dibasic phosphate solution.

Keywords: Bauxite residue, pig iron, reductive smelting, titanium, scandium.

1. Introduction

During the production of alumina from bauxite via the Bayer process, a by-product is inevitably produced, namely bauxite residue. A wide range of components are contained in bauxite residue, the major components generally include Fe, Al, Ca, Si, Ti and Na [1]. The contained elements are usually present in lower concentrations compared to primary raw materials, however, bauxite residue offers a possibility for recovery of numerous product streams [2 - 3].

Iron is the most predominant element in this bauxite residue. Albeit found in high quantities, literature reports that iron recovery on its own is not economically viable [4]. The bauxite residue contains high value Ti and Sc which are attractive for recovery. An iron deficient feed material is beneficial for hydrometallurgical processing aiming for Ti and Sc due to minimising of waste (precipitation sludge) and therefore justifies upstream removal of iron. This is attributed to poor selectivity of Ti over the major constituents of bauxite residue during acidic leaching as reported in literature [5]. Methods that are explored widely in literature for Sc recovery from bauxite residue include solvent extraction and ion exchange. The presence of ions such as Fe and Al in the leachate is unfavourable for Sc extraction. Hence, intensive purification steps are necessary for Sc recovery from bauxite residue leach solutions [6 - 7].

The innovation of the present study is on a combined pyrometallurgical and hydrometallurgical processing of bauxite residue concentrate production through carbothermic reduction of bauxite residue to produce a slag concentrate and to apply leaching and precipitation conditions to the produced slag concentrate for recovery of Ti and Sc [8]. Similar leaching and precipitation conditions were applied directly to bauxite residue in order to compare recovery efficiencies of Ti and Sc.

2. Experimental Procedure

The bauxite residue of interest was sourced from Aluminium of Greece. Sample preparation entailed drying of the bauxite residue over a period of 24 hours at 105 °C. The dried lumpy sample was subsequently mixed with lignite coke and lime containing 87 % fixed carbon and 95 % 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 mould where the material cooled down and the metal settled at the bottom of the mould. 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. The original bauxite residue and slag sample were analysed by X-ray diffraction (XRD). Furthermore the dried bauxite residue and the milled slag were analysed via X-ray fluorescence (XRF) for the bulk chemical analysis and by inductively coupled plasma optical emission spectrometry (ICP-OES) for the trace elements as shown in Table 1.

Table 1. Chemical analysis of the dried bauxite residue and the produced slag concentrate.

Components (wt. %)	**Fe_2O_3**	**Al_2O_3**	**CaO**	**SiO_2**	**TiO_2**	**LOI**	**Sc (mg/kg)**	**Y (mg/kg)**	**Nd (mg/kg)**
Bauxite residue	43.5	24	10.2	5.5	5.6	10.1	130	90	110
Slag concentrate	1.8	38.3	43.2	7.6	7.6	-1.0	200	167	181

All leaching tests were carried out with the following: a glass beaker, heating plate and magnetic stirrer for controlling the reaction temperature and stirring speed. The bauxite residue and slag were each ground into fine particles and poured into pre-heated (70 °C) acid solution to start the leaching process. The experiments were carried out over a fixed leaching time of 120 minutes at a set temperature of 70 °C, 360 rpm with a solid: liquid ratio of 1:10. For both starting materials, two acid concentrations were utilised; 2.5 M sulfuric acid (H_2SO_4) and 2.5 M sulfuric acid (H_2SO_4): 2.5 M hydrogen peroxide (H_2O_2) mixture; which were based on preliminary studies about red mud leaching optimised for Ti and Sc recovery.

Dibasic phosphates were preferred since the pH effect on precipitation could be also investigated. 1 M dibasic phosphate ($(NH_4)_2HPO_4$) solution was chosen as phosphate donor and added until the target pH was reached. All precipitation stages were performed under mild stirring at room temperature. The resulting suspension for each case was then stabilised and homogenised at a given pH and temperature for 2 hours and subsequently filtered through fine filter paper via suction filtration. The separated solid residue was washed with distilled water and dried at 110 °C for 24 hours. Both filtered solutions and the solid residues as well as the concentrations of constituent ions in the liquid samples were assayed byICP-OES. The complete process flowsheet including smelting, leaching and precipitation is shown in Figure 1.

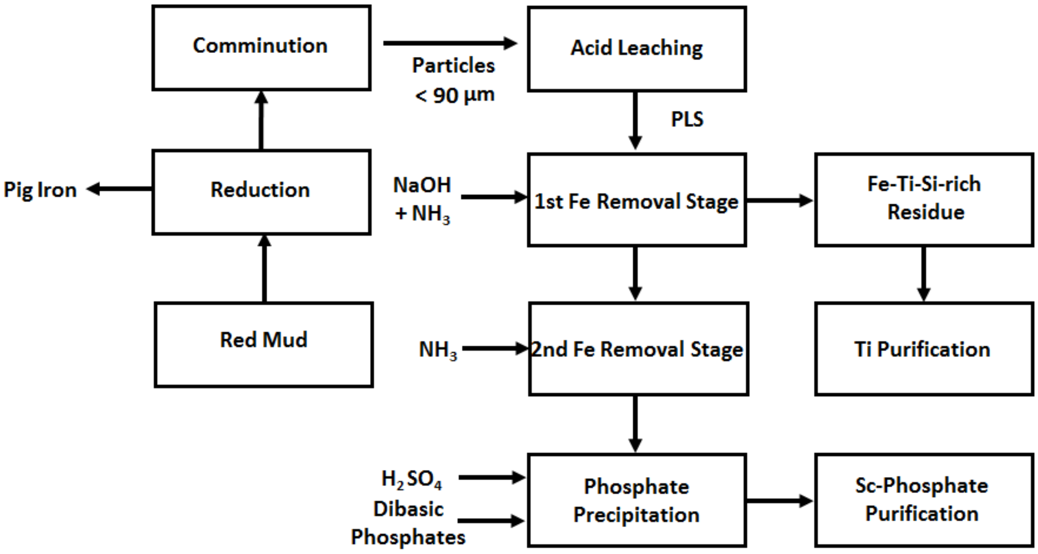

Figure 1. Process flowsheet for combined pyrometallurgical and hydrometallurgical treatment of bauxite residue to recover Fe, Ti and Sc.

3. Results and Discussion

The smelting process was undertaken for iron recovery while targeting low operating temperatures. The phase diagram below shows that low T_m slags are achieved either in the silica rich region or in the calcium oxide rich region.

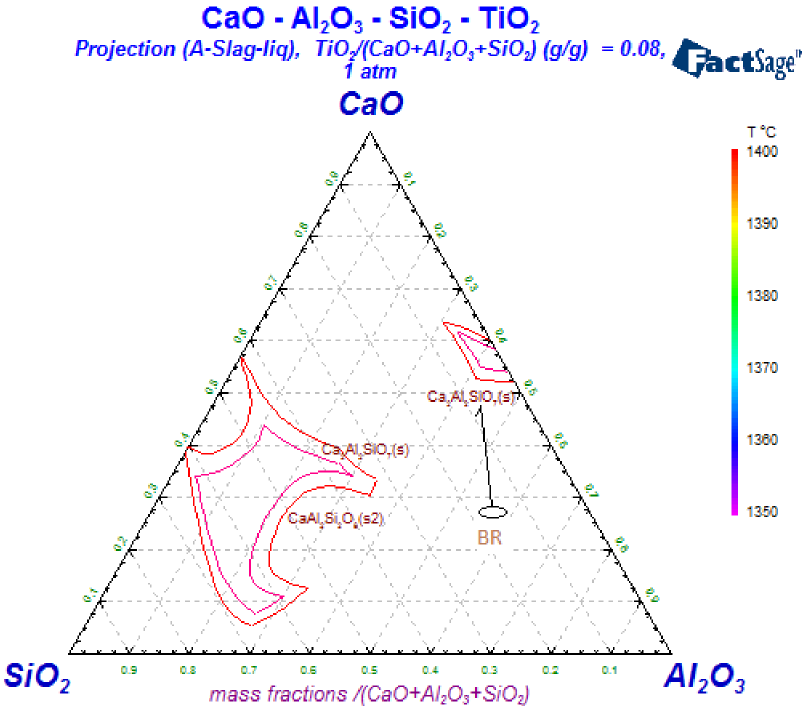

Figure 2. Ternary phase diagram as predicted by FactSage 7.0 software for CaO-Al$_2$O$_3$-SiO$_2$-TiO$_2$, detailing liquid slag phase at 1350°C and 1400°C as well as compositions for starting bauxite residue and final slag.

To avoid the risk of high silica enrichment in the slag, the high calcium oxide region was the preferred choice. Consequently, lime was used as the fluxing agent to adjust the slag composition so as to operate in the calcium oxide rich region. One disadvantage of this approach is high acid consumption in the downstream leaching stage.

An upgrade in concentration of the major and trace gangue components contained in the bauxite residue was achieved during the smelting process as can be seen when comparing the analysis of bauxite residue to that of the slag in Table 1. It is important to note that during the smelting process a small but noticeable amount of feed material was lost to the off-gas as fume or as feed carryover and this to an extent compromised the accounting of the elements.

The slag reported a low FeO content and this is important for both iron recovery to the metal and for downstream processing of the slag concentrate. The corresponding iron recovery to the slag was below 3 % which translates to good iron recovery. Therefore, the reductant addition of 10% can be deemed sufficient for effective removal of iron from bauxite residue during the smelting process. However, only 87 % Fe was recovered as the metallic block that settled at the bottom during slag metal separation; small metal prills were visible in the periphery of the slag with more iron entrainment also observed in the slag. Recovery of this metal during crushing and milling, and also accounting for mass losses during the smelting process resulted in about 95 % of iron recovery to the metal.

The XRD patterns below show clearly that the bauxite residue undergoes a transformation during the smelting process. The gehlenite phase ($2CaO.Al_2O_3.SiO_2$) was formed during the smelting and cooling process as confirmed by both the slag XRD results in Figure 3 and the phase diagram in Figure 2. Titanium is contained in the perovskite ($CaTiO_3$) phase which would have crystallised during the relatively slow cooling of the slag, the formation of this perovskite phase is expected to have an effect on the subsequent recovery of Ti via leaching. Furthermore, calcium silicate and calcium aluminate phases were also formed during the smelting process.

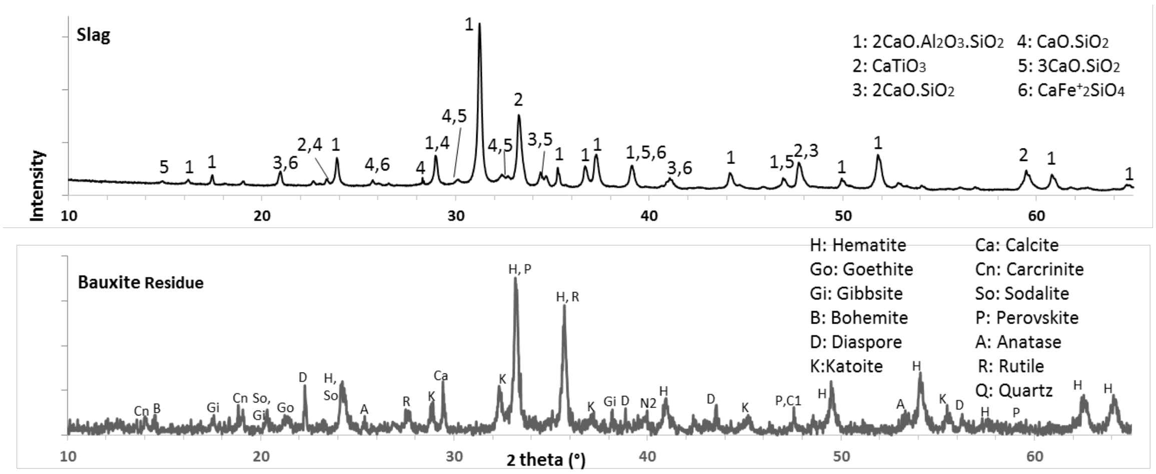

Figure 3. XRD patterns of bauxite residue and produced slag concentrate.

One of the main shortcomings about direct leaching of bauxite residue is the high Fe content. This high amount of Fe negatively affects both the recovery rates and the leaching conditions [9]. Removal of Fe from bauxite residue and collecting it into a pig iron product by smelting while keeping and concentrating the recoverable elements into a slag concentrate creates an advantage for leaching. Leaching efficiencies of bauxite residue and slag for the recovery of Ti and Sc under two different acid leaching conditions are represented in Figure 4 in a comparative manner.

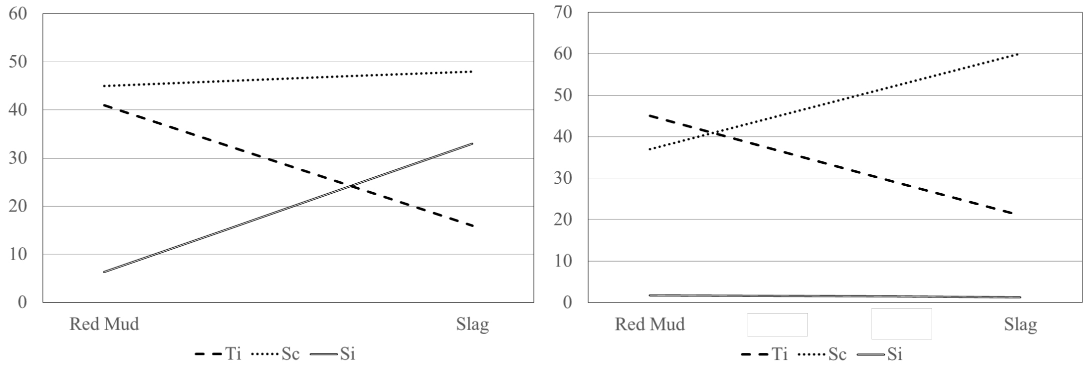

Figure 4. Ti, Sc and Si leaching efficiencies of bauxite residue and slag: 2.5 M H_2SO_4 (left), 2.5 M H_2SO_4: 2.5 M H_2O_2 (right); (t = 2 h, T = 70°C, S/L = 1:10).

The slag leaching is more promising in terms of Sc leaching efficiency for both investigated acid treatments, especially with combined use of 2.5 M H_2SO_4: 2.5 M H_2O_2, a recovery rate of 60 % was obtained compared to 48 % recovery from bauxite residue. Since a major amount of Sc in the bauxite residue is found within the structure of Fe containing phases, iron removal via smelting minimises iron containing phases, therefore, the leaching mechanism for Sc is expected to be different between the Fe depleted slag and the bauxite residue [9]. The Si leaching rates from the slag with sulfuric acid were significantly higher compared to the bauxite residue. Moreover, it is worth to emphasise that the utilisation of hydrogen peroxide in combination with sulfuric acid on the treatment of slag decreases the Si leaching rates considerably and therefore minimises the gelation problems (see Figure 4).

However, for both acidic conditions, there is a low Ti leaching efficiency observed for the slag concentrate. This seems to be attributed to re-precipitation of Ti in a more stable phase during relatively slow cooling post smelting in an EAF, the presence of perovskite in the slag was confirmed by XRD analysis shown in Figure 3. Although the extraction efficiency of Ti is low, the relatively higher Ti concentrations in pregnant leach solutions (PLS) are promising for Ti precipitation. In parallel with Sc, especially peroxide including slag yielded higher concentrations as can be seen in Table 2.

Table 2. PLS of slag concentrates before the precipitation procedure.

Elements (mg/l)	Al	Fe	Ti	Si	Sc	Y	Nd
2.5 M H_2SO_4	10570	770	1191	2400	7.8	9.8	3.2
2.5 M H_2SO_4 + 2.5 M H_2O_2	14674	1176	1596	100	14.8	10.4	3.4

PLS obtained after leaching were introduced into precipitation procedure in order to produce a Sc and Ti concentrate. In the first two stages of precipitation, the major aim was to decrease the amount of Fe and Al presented in the PLS, since, the major problem of the scandium recovery by precipitation from a multicomponent solution is co-precipitation with ions presented in the system, especially with iron. For this purpose, ammonia solution was added into the PLS until target pH was reached. Addition of ammonia was done in two stages to avoid Sc losses with co-precipitation with Fe in the system. The pH values of dual Fe removal stages were 3.4 and 3.8 respectively [8, 10]. Resulting liquid was passed for phosphate precipitation step to recover Sc from the solution much more selectively. The pH was adjusted to a value 2 by adding sulfuric acid with the intention of preventing unwanted hydroxide precipitation. Figure 5 shows the precipitation procedure as described above detailing the concentration of the elements of interest as a function of pH.

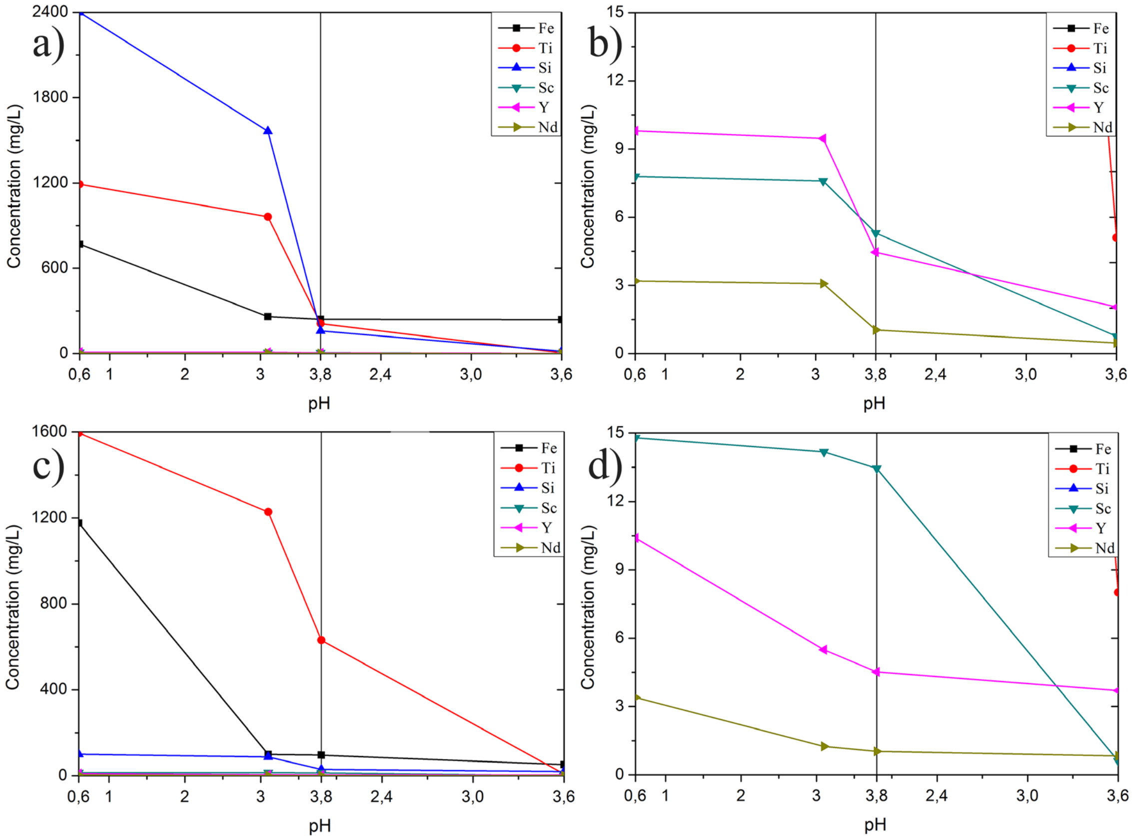

Figure 5. Precipitation procedure with PLS obtained from upstream leaching with: 2.5 M H_2SO_4 (a, b), 2.5 M H_2SO_4: 2.5 M H_2O_2 (c, d); where the vertical line at pH 3.8 indicates the point of sulfuric acid addition decreasing the pH to 2.

In Table 3, the precipitation yields of subsequent precipitation can be seen. As it can be understood from Figure 5 and Table 3, a majority of Fe, Ti and Si was removed from the PLS during the Fe removal step. Thus, an enhanced environment for Sc recovery is attained.

Table 3. Precipitation yields after subsequent precipitation steps.

Elements		**Fe**	**Ti**	**Si**	**Sc**	**Y**	**Nd**
2.5 M H_2SO_4	Fe-removal (%)	68.6	82.2	93.3	32.1	54.5	67.8
	Phosphate Prec. (%)	1.5	97.6	89.7	85.6	53.9	54.8
2.5 M H_2SO_4 + 2.5 M H_2O_2	Fe-removal (%)	91.8	60.5	69.5	8.1	56.5	69.7
	Phosphate Prec. (%)	46.3	98.7	34.1	94.9	18.3	19.4

The main difference in the behaviour and the yields of Fe precipitation in each case was the occurrence of Fe^{2+} and Fe^{3+} ions in the solutions during leaching. It was clearly observed that the orange colour which is one of the biggest indicators of Fe^{3+} was formed during the increase in pH in PLS obtained with H_2SO_4-H_2O_2 mixture achieving a precipitation yield of Fe as high as 90 – 95 % while Sc co-precipitation was very low. The Fe-removal rate decreased to 70 % since Fe^{2+} was also presented after smelting process and the co-precipitation of Sc was relatively high in the PLS synthesised by only using sulfuric acid.

In every case, the recovery of both Ti and Sc was better in the PLS case of H_2SO_4-H_2O_2 mixture. All of the Ti was not recovered during Fe-removal process since there might be some interactions between Ti and N. However, it is possible to recover all Ti with small addition of NaOH just before the Fe-removal stage. In a similar manner, Si may also be removed completely. The concentrate formed via precipitation was enriched in terms of Sc and Ti, the precipitate from sulfuric acid PLS contained 1 % and 52 % Sc and Ti respectively in its composition. The concentrate from the other PLS contained 1.8 % and 83 % Sc and Ti respectively. It is known that the solubility of titanium phosphate is very limited in highly acidic solutions. Both concentrates can be further upgraded by re-dissolving it in an acidic solution and removing titanium phosphate which can result in 10 % Sc content.

4. Conclusion

The recovery of iron from bauxite residue through carbothermic reduction in an electric arc furnace followed by hydrometallurgical processing for Ti and Sc recovery from the produced slag concentrate has been successfully undertaken and compared with direct recovery of Ti and Sc from bauxite residue by hydrometallurgical means. High iron recovery in excess of 95% to the pig iron was achieved resulting in a slag concentrate with low residual iron. The fluxing agent and additions were such that slag with a low melting point and a low silica content would be achieved. The Ti in the slag was found to be contained in a perovskite phase. The gangue components were concentrated in the slag and included the high value Sc.

The leaching efficiencies for Sc were higher for the slag in comparison to leaching of bauxite residue for both 2.5 M H_2SO_4 and a 2.5 M H_2SO_4: 2.5 M H_2O_2 acid mixture; on the other hand, lower leaching efficiencies for Ti were achieved for the slag under the investigated leaching conditions. The lower leaching efficiencies for the slag could be attributed to the crystalline perovskite phase found in the slag. Modification of the slag with regards to crystallinity will be investigated further with the aim to improve Ti recovery during slag leaching. The utilisation of hydrogen peroxide in combination with sulfuric acid for slag leaching decreases the Si leaching rates considerably and therefore minimises the gelation problems.

Selective precipitation route followed after leaching to recover Ti and Sc from the leachate. In this precipitation process, Fe was removed by the addition of ammonia in the pH range between 3.3-3.8 with a dual stage step. Subsequent to removal of 95 % of the Fe in solution, Sc was selectively precipitated as $ScPO_4$ with the introduction of a dibasic phosphate solution.

5. Acknowledgement

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