Preparation of a mixed Al/Sc nano-oxide derived from the bauxite residue (red mud) via the sulfuric acid roasting–leaching–precipitation process

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Abstract

   In this study, three methods were used and compared for the selectable extraction of aluminum/scandium with the least amount of iron in red mud (RM) samples from the Iran alumina plant in Jajarm as follows: 1) RM direct acid leaching with H_2SO_4, 2) RM washing with hydrochloric acid and oxalic acid before leaching with H_2SO_4, and 3) RM sulfuric acid roasting-leaching-precipitation. The aim was to extract the highest amount of scandium while preventing the leaching of other metals, especially iron. Due to any discriminative features, the selective separation of Al/Sc with methods 1 and 2 was impossible practically. While, method 3 resulted in 73.7% of extracted scandium under optimal conditions with only 0.6% of iron found in the final product. The characterization of the final oxide product was done via inductively coupled plasma mass spectrometry (ICP-MS) and energy-dispersive X-ray analysis (EDX). The morphology of the oxide product was examined by field emission scanning electron microscopy (FE-SEM). This mixture oxide had a nanosize spherical shape and was distributed uniformly. The pH of the remaining red mud after the acid roasting-leaching-precipitation method was 8, which was far more environmentally desirable than the primary red mud with a pH = 12.

1. Introduction

Bauxite residue, or red mud (RM), is an alkaline sludge waste produced via the alumina extraction process in bauxite mines. Depending on the source of bauxite, this residue can be considered as a potential source of scandium [1-3]. The major chemical compounds in RM include Fe_2O_3, CaO, Al_2O_3, SiO_2, TiO_2, and Na_2O, as well as a small number of rare earth elements of approximately 500 ppm to 1700 ppm [4]. The red color of the RM may be attributed to the hydrated iron (III) oxides $Fe_2O_3 \cdot nH_2O$, e.g., hematite, while large quantities of goethite $FeO(OH)$ are responsible for the formation of its yellow-red color [5,6]. During aluminum ore refining, about 35-40% of the bauxite ore is converted into a high alkaline RM (pH = 10-12.5) sludge, which is known to be toxic due to its alkalinity [7,8]. Since RM has characteristics such as a large surface area, a very good distribution of particle size, high water adsorption capacity, and long-lasting alkalinity stability, [9,10] the disposal of large amounts of RM is not only costly but also has significant environmental risks such as groundwater and soil contamination as well as dust pollution and particulate matter suspensions. Therefore, the strategic use of RM is an important challenge for the alumina industry around the world.

Since the 1950s, many studies have been carried out to access and use RM as a secondary source. They mainly investigated its use in the preparation of materials such as cement [11,12], geopolymers [13,14], catalysts [15,16], adsorbents [17,18], and ceramics [19,20]

as well as the recovery of valuable elements such as Fe, Al, Na, Ti, V, Ga, Sc, and other rare earth elements [21,22]. Accordingly, the use of RM to produce materials is a potential means to utilize the bauxite residues in large quantities. Nowadays, one of the most interesting commercial materials is the scandium-containing alloys especially aluminum-scandium master alloys. These alloys exhibit an improved weldability, low specific gravity, high strength, great resistance to hot cracking, reduced grain size, and high recrystallization temperature [23-25]. The amount of scandium in the RM varies between 15-170 ppm depending on the type of bauxite, the mining location, and the aluminum refining process [26,27]. The presence of Sc in the Earth's crust is 22 ppm on the average [1], which indicates a notable enrichment of Sc in RM. The materials with a scandium content of 20-50 ppm are considered an ore. Therefore, bauxite residues containing a higher scandium concentration can be investigated as scandium resources [28,29]. An increase in the recovery of scandium from the high volumes of RM that are produced in the world could boost its supply, reduce the environmental hazards of RM, and economically enhance the refinement of aluminum.

According to many studies [30-33], it is clear that the extraction process of scandium from RM depends on the type of RM. Indeed, the mineralogical and morphological properties of the RM determine the process steps and leaching agents. Many studies have focused on direct leaching using mineral and organic acids (e.g., H_2SO_4, HNO_3, HCl, $C_2H_4O_2$, and $C_6H_8O_7$), alkali (hydrogen) carbonates like $NaHCO_3$, microorganisms (bioleaching), and ionic liquids.

Direct leaching has the disadvantage of a high co-extraction of other associated metals, especially iron, as an impurity [1,34-37]. Multi-stage leaching has been considered to overcome this limitation, which is based on the pretreatment of RM followed by acid or water leaching. Narayanan *et al.* [3] recovered all the rare earths (Sc-La-Ce …) with 88% efficiency at a relatively low Fe recovery (5%) from Jamaican bauxite residue using three-stage acid/roasting (concentrated H_2SO_4/700°C)-water leaching-precipitation. Borra *et al.* [38] used sulfation-roasting (700°C)-leaching to recover ~60% of Sc at a low Fe and Ti recovery (~1% and ~2%, respectively) from Greece Bauxite Residue. Anawati and Azimi [31] used two-stage acid baking (200°C and 400°C)-water leaching for scandium recovery from Canada bauxite residue. Based on mechanistic and kinetic investigations, they concluded that baking at 200°C resulted in the rapid water leaching of iron (<5 min) with a low-efficiency extraction of scandium (58%), but baking at 400°C resulted in slower iron leaching (>45 min) with a higher extraction efficiency of scandium (80%). In order to investigate the possibility of selectable extraction of aluminum/scandium while preventing the leaching of other metals especially iron from Iran alumina plant bauxite residue, this study investigated and compared the following three methods: 1) RM direct acid leaching with H_2SO_4, 2) RM washing with hydrochloric acid and oxalic acid before leaching with H_2SO_4, and 3) RM sulfuric acid roasting-leaching-precipitation. The high amounts of Al, Sc, Fe, and Ti that were leached without any discriminative features make the selective separation of Al/Sc practically impossible with methods 1 and 2. Based on this result and also the results of previous studies [1,3,31,34-38], an alternative three-stage extraction method 3, namely sulfuric acid-selective roasting-water leaching-selective precipitation was selected to optimize the parameters. Selective roasting based on the difference of thermal decomposition temperatures of metal sulfates reduced energy consumption and effective trapping of Fe. Selective precipitation by pH adjustment prevented the presence of small amounts of Fe remaining from the leach stage in the final deposition including Sc and Al.

2. Experimental

The chemical analysis of an RM sample obtained from the air-dried waste landfill of the Iran Alumina Co. (Jajarm Alumina Plant) was made via XRD (X-ray diffraction, PANalytical X'Pert Pro MPD), XRF (X-ray fluorescence, Shimadzu-7000), ICP-MS (Agilent 7800 Quadrupole), and FE-SEM (Hitachi SU3500).

The acid leaching of the scandium from the RM was carried out using H_2SO_4 (98%, Merck), and the optimum leaching condition based on acid concentration, leaching time, and the temperature was determined.

To remove the calcium, sodium, and magnesium and then iron, the RM was washed with hydrochloric acid (37%, Sigma-Aldrich) and oxalic acid (98%, Sigma-Aldrich), respectively. The pH of the aqueous solutions were measured with a pH meter model HANNA HI991001. For precipitation of the the Al/Sc from the leaching solution, NaOH (≥ 97.0%, Merck) was used to increase and set the pH.

In acid leaching with H_2SO_4 (method 1), we designed 36 experiments under different conditions of acid concentration (1-4 M), temperature (25-75°C) and leaching time (60-180 min). In each experiment, 5 g of the Jajarm alumina RM sample was mixed with 50 ml of sulfuric acid at the desired concentration at a specified temperature and time in a magnetic stirrer. After the reaction, the solution was filtered, collected, and analyzed via ICP-MS to achieve the leach percentage of the main elements (Sc, Fe, Al, Ca, and Ti).

In method 2, 10 g of RM were weighed after being washed with distilled water (L/S ratio of 30); next, it was passed through filter paper and dried in an oven for 48 h at 65°C. It was then contacted with HCl at concentrations of 1, 2, and 3 M (L/S ratio of 2) for 30 min and re-washed with distilled water in the same L/S ratio as before to remove the probable salts. Then, the weighed RM from the previous stage along with the oxalic acid with 0.5, 1.0, 1.5, and 2.0 ratios were poured into the distilled water (L/S ratio of 16); the solution was then washed at 75°C for 80 min. After washing, the solution was filtered, and the remaining RM entered the final stage of leaching by H_2SO_4. The leaching conditions were the same as the optimum point obtained from the method 1.

In method 3, for the optimization of the H_2SO_4 concentration, roasting temperature, and water required for leaching to achieve the selective recycling of scandium besides iron trapping, the following experiments were performed. Initially, 15 g of the Jajarm RM was washed with distilled water (L/S ratio of 30). After filtering, the washed RM was dried at 65°C for 48 h in an oven. It was necessary to wet the sample to allow for the sulfation reactions to occur. For this purpose, distilled water was used (L/S ratio of 0.5-1.5), and then concentrated sulfuric acid (98%) was added to this compound (L/S ratio of 0.5, 0.75, 1.0). The sample was then placed in an oven for 48 h at 65°C to dry. At this step, the sulfated RM sample was ready to be roasted in a furnace for 1 hour at 600, 650, and 700°C. In the last step, the sulfated-roasted samples were leached with distilled water (L/S ratio of 10, 20, 30, 40, 50) at room temperature for 1-7 days.

The concentrations of the metal ions were used to obtain the leaching percentage according to:

$$leaching\ percentage\,(\%) = \frac{[M^{n+}]_i - [M^{n+}]_f}{[M^{n+}]_i} \qquad (1)$$

where, $[M^{n+}]_i$ and $[M^{n+}]_f$ represent the metal ions concentrations in the initial RM and final leached RM, respectively.

3. Results and discussion

According to the XRD pattern (Figure 1), hematite (Fe_2O_3; **H**), calcite ($CaCO_3$; **C**), and katoite ($Ca_3Al_2(SiO_4)(OH)_8$; **K**) are the major phases, while cancrinite ($Na_6Ca_{1.5}Al_6Si_6O_{24}(CO_3)_{1.6}$; **Ca**), kaolinite ($(Mg,Fe)_3(Si,Al)_2O_5(OH)_4$; **Ka**), and perovskite ($CaTiO_3$; **P**) are the minor phases of the RM at room temperature.

The main chemical compositions and the rare earth element contents of the Jajarm RM sample were obtained using XRF and ICP-MS, respectively. The results of these analysis are summarized in Table 1. The amount of scandium in the Jajarm sample (43.1 ppm) was compared with other samples containing scandium (Australian RM; 54 ppm, Canadian RM; 31.1 ppm, Jamaican RM; 55 ppm, Greek RM; 120 ppm) [13,31,34,39]. The results indicated that this sample was a suitable RM source for the recovery of scandium.

Due to the high iron content in RM, this study attempted to prevent iron leaching along with the scandium and aluminum leaching.
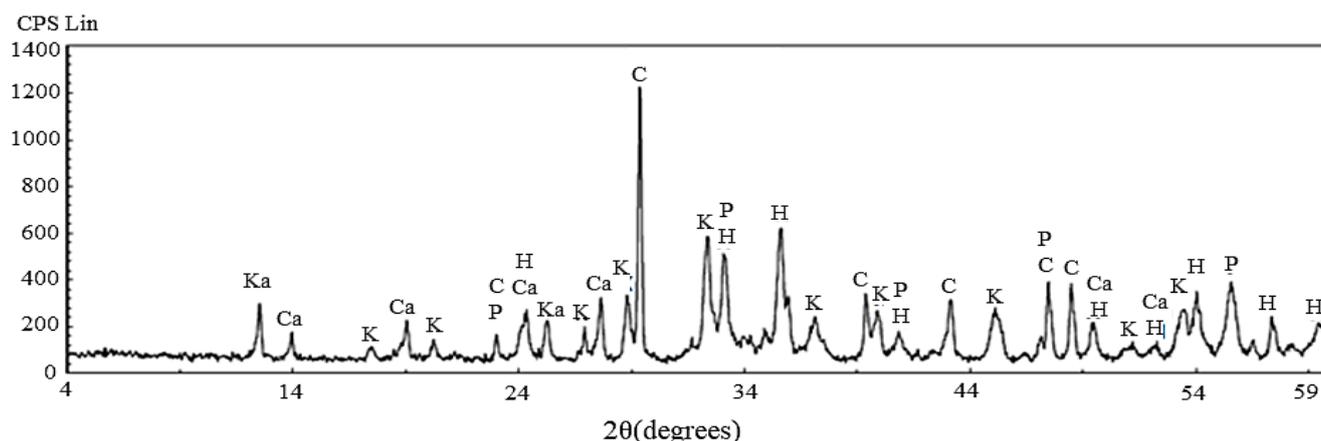
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Figure 1. XRD pattern of the Jajarm RM sample.

Table 1. The concentration of the main oxides and the rare earth elements of the Jajarm RM sample.

Main oxide	(wt%)	Rare earth	(ppm)
Fe_2O_3	30.22	Ce	231
Al_2O_3	18.26	La	68
CaO	16.34	Nd	58.3
SiO_2	14.02	Sc	43.1
TiO_2	5.21	Y	38.9
Na_2O	3.22	Pr	19.22

It also attempted to minimize the amount of some other elements, such as calcium and sodium in the leaching solution containing scandium and aluminum. For this purpose, the following three methods: 1) RM direct acid leaching with H_2SO_4, 2) RM washing with hydrochloric acid and oxalic acid before leaching with H_2SO_4, and 3) RM sulfuric acid roasting-leaching-precipitation were investigated and the results were compared.

3.1 RM direct acid leaching with H_2SO_4

The summary of [40-42] showed that the less volatile sulfuric acid was a good agent for the leaching of scandium from RM because it had a lower iron solubility. Therefore, our study investigated the effective factors (acid concentration, reaction temperature, and leaching duration) in acid leaching with H_2SO_4. Figure 2(a) shows the changes in the leaching percentage versus the H_2SO_4 concentration in which the temperature was 25°C and the leaching duration was 60 min. Increasing the concentration of the H_2SO_4 as a leaching agent increased the amount of iron leached, but it did not significantly affect the amount of leaching of the other metals. At ambient temperature, the best acid concentration for high scandium leaching and low iron leaching was 2 M. The changes in the leaching percentage versus the leaching duration are shown in Figure 2(b), where the temperature is 25°C and the H_2SO_4 concentration is 2 M. According to the data obtained, a 120 min duration was well suited for the high leaching of all the desired elements.

Figure 2(c) shows the changes in the leaching percentage versus the temperature where [H_2SO_4] is 2 M and the leaching duration is 120 min. Based on the obtained data, with increasing temperature,

the leaching amount of all the examined metals increased, which was higher for iron than for other metals.

The highest amount of Sc, Fe, and Ti leaching (63.81, 49.55, and 65.07%) was achieved at the upper limit of all the applied conditions, e.g., temperature: 75°C, [H_2SO_4]: 3 M, and leaching duration: 180 min. Due to the importance of achieving the maximum leaching of scandium, these conditions continued to apply.

3.2 RM washing with hydrochloric acid and oxalic acid before leaching with H_2SO_4.

In this method, hydrochloric acid and oxalic acid were used simultaneously to precipitate troublesome elements such as calcium, sodium and magnesium, aluminum, and iron before acid leaching to selectively separate scandium in direct leaching with H_2SO_4. Based on researches [43,44], the use of HCl to wash RM before washing it with oxalic acid reduced the consumption of oxalic acid. The diagrams relating to the effect of HCl and oxalic acid concentrations (in washing) on the leaching percentage are shown in Figure 3(a)-3(d). The highest amount of Sc leaching (90.32%) was achieved at an [HCl]: 3 M and an oxalic acid ratio of 1.0. The leaching percentage of other important elements at this condition is given in Table 2. It was found that high levels of iron and titanium make the direct separation of scandium practically impossible with this treatment before acid leaching. Aluminum behaved quite the opposite of other elements. Washing with HCl and oxalic acid before the leaching process dramatically reduced the amount of aluminum leaching, which was more pronounced as the concentration of HCl and oxalic acid increased.
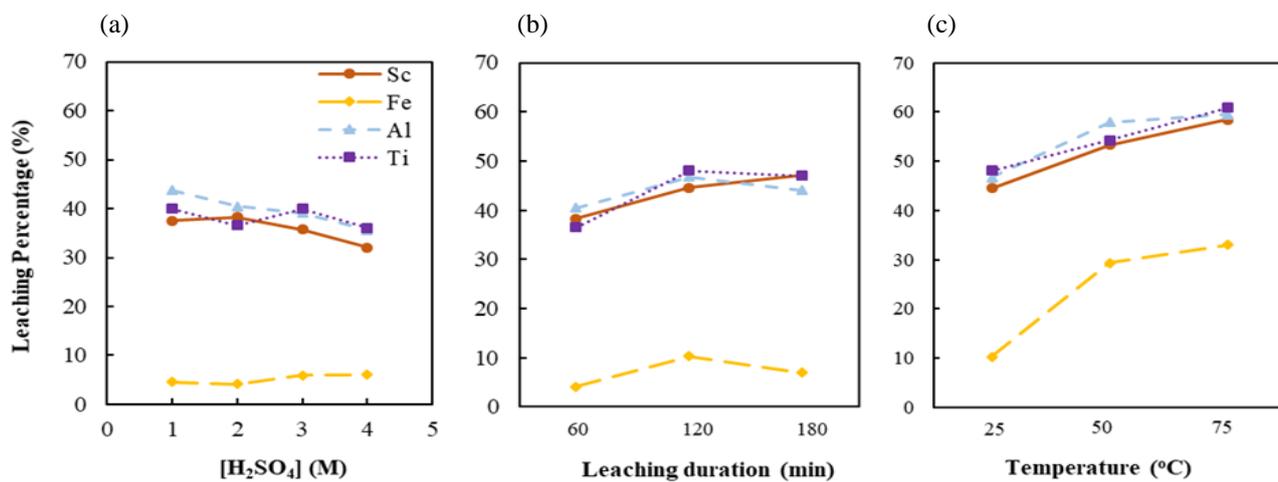
Figure 2. Effect of (a) H₂SO₄ concentration (T: 25ºC, leaching duration: 60 min), (b) leaching duration (T: 25ºC, [H₂SO₄]: 2 M), and (c) leaching temperature ([H₂SO₄]: 2 M, leaching duration: 120 min) on leaching of Sc, Fe, Al, and Ti.
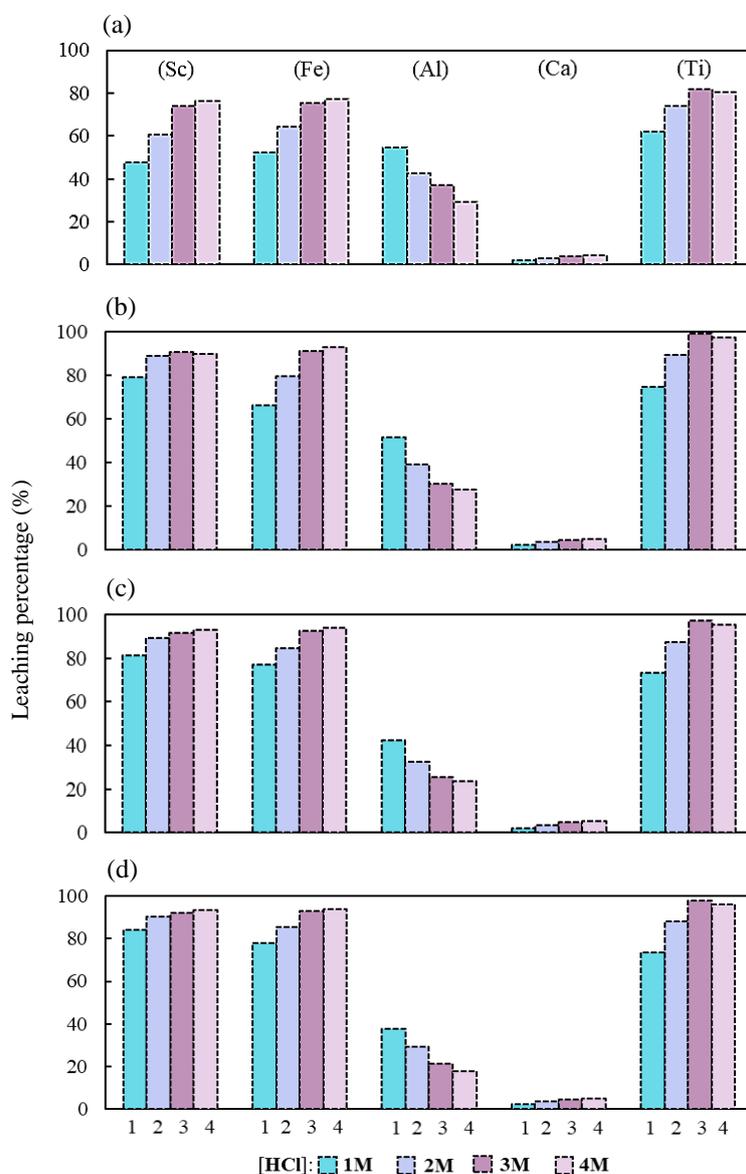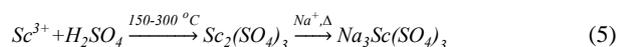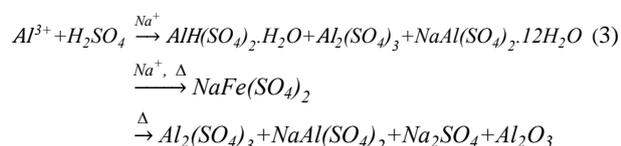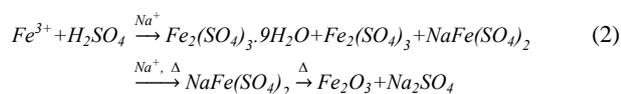

Figure 3. Effect of HCl concentration on leaching of Sc, Fe, Al, Ca and Ti. Oxalic acid/RM ratio: (a) 0.5, (b) 1.0, (c)1.5, and (d) 2.0.

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Table 2. The leaching percentage of investigated metals resulting from the RM washed by hydrochloric acid (HCl) and oxalic acid ($H_2C_2O_4.2H_2O$) before leaching.

Element	Sc	Fe	Al	Ca	Ti
Leaching percentage (%)	90.32	91.15	30.09	4.72	98.95

3.3 RM sulfuric acid roasting-leaching-precipitation

Studies conducted on the pretreatment methods of RM before leaching indicate their usefulness for the selective separation of the desired metal or metals [31,40]. Therefore, we used such a pretreatment in this step to extract and, in particular, to better separate the scandium element and reduce the disturbing elements, especially iron. The sulfuric acid roasting of RM was done by moistening the dried RM with distilled water and concentrated H_2SO_4 in a crucible, heating it in a vacuum oven, and then roasting the sulfated RM in a furnace to decompose the sulfates to oxides. After that, the roasted RM was leached by distilled water in a magnetic stirrer. In this method, the scandium selective leaching is based on the differences in the phase transfer of various metal sulfates during the roasting process, which is given in Equations 2-6 [45]. As seen, scandium appears in the $Na_3Sc(SO_4)_3$ compound, which is completely different from the crystalline phases of Fe, Ti, Al and Ca, and is easily leachable in water. The presence of sodium ions plays an important role in the formation of these phases. In addition to the selectivity of scandium recycling by sulfate-roasting-water based leaching, this method has other advantages, including the reuse of H_2SO_4 and better solid-liquid separation efficiency.

$$Fe^{3+}+H_2SO_4 \xrightarrow{Na^+} Fe_2(SO_4)_3.9H_2O+Fe_2(SO_4)_3+NaFe(SO_4)_2 \qquad (2)$$
$$\xrightarrow{Na^+, \Delta} NaFe(SO_4)_2 \xrightarrow{\Delta} Fe_2O_3+Na_2SO_4$$

$$Al^{3+}+H_2SO_4 \xrightarrow{Na^+} AlH(SO_4)_2.H_2O+Al_2(SO_4)_3+NaAl(SO_4)_2.12H_2O \quad (3)$$
$$\xrightarrow{Na^+, \Delta} NaFe(SO_4)_2$$
$$\xrightarrow{\Delta} Al_2(SO_4)_3+NaAl(SO_4)_2+Na_2SO_4+Al_2O_3$$

$$TiO_2+H_2SO_4 \xrightarrow{<150\ ^oC} Ti(SO_4)_2 \xrightarrow{\Delta} TiOSO_4 \xrightarrow{\Delta} TiO_2 \qquad (4)$$

$$Sc^{3+}+H_2SO_4 \xrightarrow{150-300\ ^oC} Sc_2(SO_4)_3 \xrightarrow{Na^+,\Delta} Na_3Sc(SO_4)_3 \qquad (5)$$

$$Ca^{2+}+H_2SO_4 \rightarrow CaSO_4 \qquad (6)$$

Studies have shown that scandium sulfate exhibits a higher decomposition temperature compared to iron sulfate [46-48]. The thermal decomposition temperatures of some pure sulfates of the relevant metals are given in Table 3. Therefore, during roasting, the SO_3 exits at higher temperatures to form oxide from unstable sulfates, and all the iron in the sample turns into insoluble oxide, while the scandium sulfates remain soluble in $Na_3Sc(SO_4)_3$ form. The thermal decomposition temperature of the metal sulfates in the RM sample, due to the presence of metal ions such as Na^+, is different from the temperature of the pure metal sulfates. For this reason, the roasting temperature was optimized for the RM sample.

Figure 4(a) shows the effect of the magnitude of sulfuric acid used in the sulfation on the metal's leaching. Other conditions included a roasting temperature of 700°C, a leaching time of 30 min, and distilled water for leaching with an L/S = 50 at a room temperature of 25°C. As can be seen, the application of high sulfuric acid (L/S = 1.0) yielded the 62% leaching of scandium. Also, the leaching percentage of iron, calcium, titanium, and aluminum was very high, and therefore, the scandium selectivity decreased. With a decrease in the consumption of H_2SO_4 to a ratio of 0.75, the leaching percentage of iron, titanium, and aluminum decreased significantly. Under this condition, although the scandium leaching was reduced, it provided very good selectivity for the scandium. Figure 4(b) shows the effect of the roasting temperature on the metal's leaching. As the roasting temperature rises, the amount of scandium leaching decreased. The amount of calcium leaching remained almost constant due to the high temperature required to decompose its sulfate. Although the disturbance of iron and aluminum was greatly reduced at 700°C, the significant reduction in the scandium leaching prompted us to choose 600°C as the optimum roasting temperature.

In order to investigate the effect of the amount of distilled water used for leaching, five experiments were carried out at five different L/S ratios: 10, 20, 30, 40, and 50; the other parameters were fixed based on the optimum amounts obtained from the previous steps (the results are shown in Figure 4(c)). As the temperature increased, the scandium leaching increased, and the scandium had the highest leaching percentage (61.5%) at an L/S = 50 ratio. Based on the data obtained, the amount of water used for leaching had an important effect on the amount of scandium and aluminum leaching percentage, while the leaching percentage of the other elements was mostly unaffected. The L/S = 50 valuable ratio is a very good choice for scandium and aluminum selective leaching compared to those of iron, calcium, and titanium.

To evaluate the effect of the time of the leaching, the experiments were carried out for 1-7 days. The mixing of phases was performed by a magnet stirrer during the leaching time. The results are shown in Figure 4(d). The scandium, aluminum, and calcium leaching percentage increased with an increase in the leaching time. This occurred in such a way that the leaching percentage of the scandium increased from 62.2% in 1 day to 75.6% in 7 days. It is noteworthy that the iron and titanium leaching percentage was not affected by the leaching time. Accordingly, the leaching time of 7 days was chosen as the optimum time for improving the selective leaching of scandium. The leaching percentage of the desired important elements in the final solution at optimum conditions (sulfuric acid L/S ratio of 0.75, roasting temperature of 650°C, distilled water L/S ratio of 50, and leaching time of 7 days) are given in Table 4. The pH of the filtered leaching solution is 2.7, and the pH of the separated solid is 8.0. It should be noted that the pH of the primary RM was 12.0, which is very alkaline; but it dropped to 8.0 after acid roasting-leaching, which is very environmentally friendly.
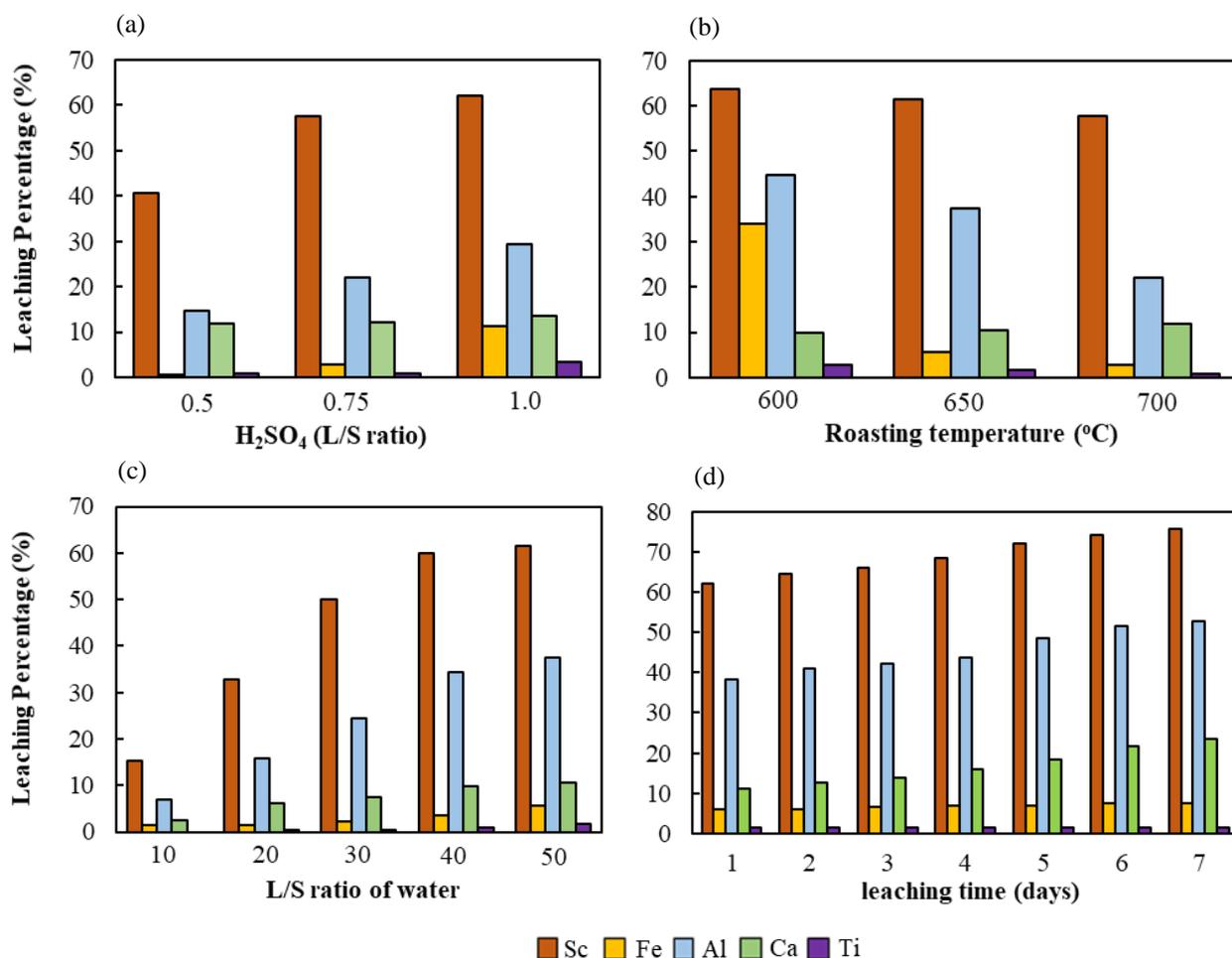
Figure 4. Effect of (a) L/S ratio of H₂SO₄, (b) roasting temperature, (c) L/S ratio of water, and (d) leaching time on leaching percentage of Sc, Fe, Al, Ca and Ti during sulfation-roasting-leaching process.

Table 3. Thermal decomposition temperatures of some metal sulfates (℃) [46,47].

Metal sulfate	Decomposition temperature (°C)	Metal sulfate	Decomposition temperature (°C)
Fe₂(SO₄)₃	545	TiOSO₄	340
Sc₂(SO₄)₃	700	Na₂SO₄	870
Al₂(SO₄)₃	524	CaSO₄	>1000

Table 4. Leaching percentage of investigated metals resulting from acid roasting-leaching at optimum conditions.

Element	Sc	Fe	Al	Ca	Ti
Leaching percentage (%)	75.6	7.6	52.8	23.6	1.6

Table 5. Recovery percentage of desired important elements at optimal RM sulfuric acid roasting-leaching-precipitation.

Element	Sc	Fe	Al	Ca	Ti
Leaching percentage (%)	73.7	0.6	51.6	20.1	0.0

In order to precipitate the scandium from the leaching solution, a 2 M solution of NaOH was used. A very important parameter in the selective scandium precipitation was the pH adjustment. The most suitable pH for the selective scandium precipitation was 8.0. At this pH, the Sc(OH)₃ in combination with Al(OH)₃ precipitated; then, they were collected by passing them through filter paper and converted to the white oxide of these metals under roasting. Based on the obtained data, the pH adjustment prevented the presence of iron in the final deposition. At this optimal condition, the extraction of scandium was 73.7%, with only 0.6% of iron found in the final product (Table 5).

As expected, the EDX analysis of the oxide product confirmed the ratio of Al/Sc/Ca (Figure 5(a)). The morphology of the oxide

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product was examined by FE-SEM (Figure 5(a)). This mixture oxide had a nanosize spherical shape and was distributed uniformly. These properties are very important for achieving high-strength aluminum-scandium alloys [23-25]. The FE-SEM images of the primary RM and the SRL-RM (sulfated-roasted-leached RM) after the process with a magnification of 100 µm to 500 nm are shown in Figure 5(b) and Figure 5(c), respectively for comparison. As a result of the acid roasting-leaching process, the particle size and morphology of the primary RM underwent substantial changes. The particle size changed from the micron-scale to the nanoscale. The EDX analysis comparison for the primary RM and SRL-RM showed that the SRL-RM was enriched with titanium and iron, while scandium and other rare earth elements such as Ce and La

were removed from the primary RM and accumulated in the leach solution (Figures 5(d), 5(e)). The pH of the remaining SRL-RM was 8.0, and its disposal did not present any environmental problems. A schematic of the optimized steps of the acid roasting-leaching of RM and producing of the mixed Al/Sc nano-oxide is shown in Figure 6.

Since Sc selective extraction in method 3 is based on the thermal decomposition temperature differences of the metal sulfates in the RM sample, this method can be applied to other RM samples from other areas as well. The important point is that due to the effect of the presence of metal ions such as Na^+ on the thermal decomposition temperature of the metal sulfates, it is necessary to optimize the roasting temperature for each RM sample.
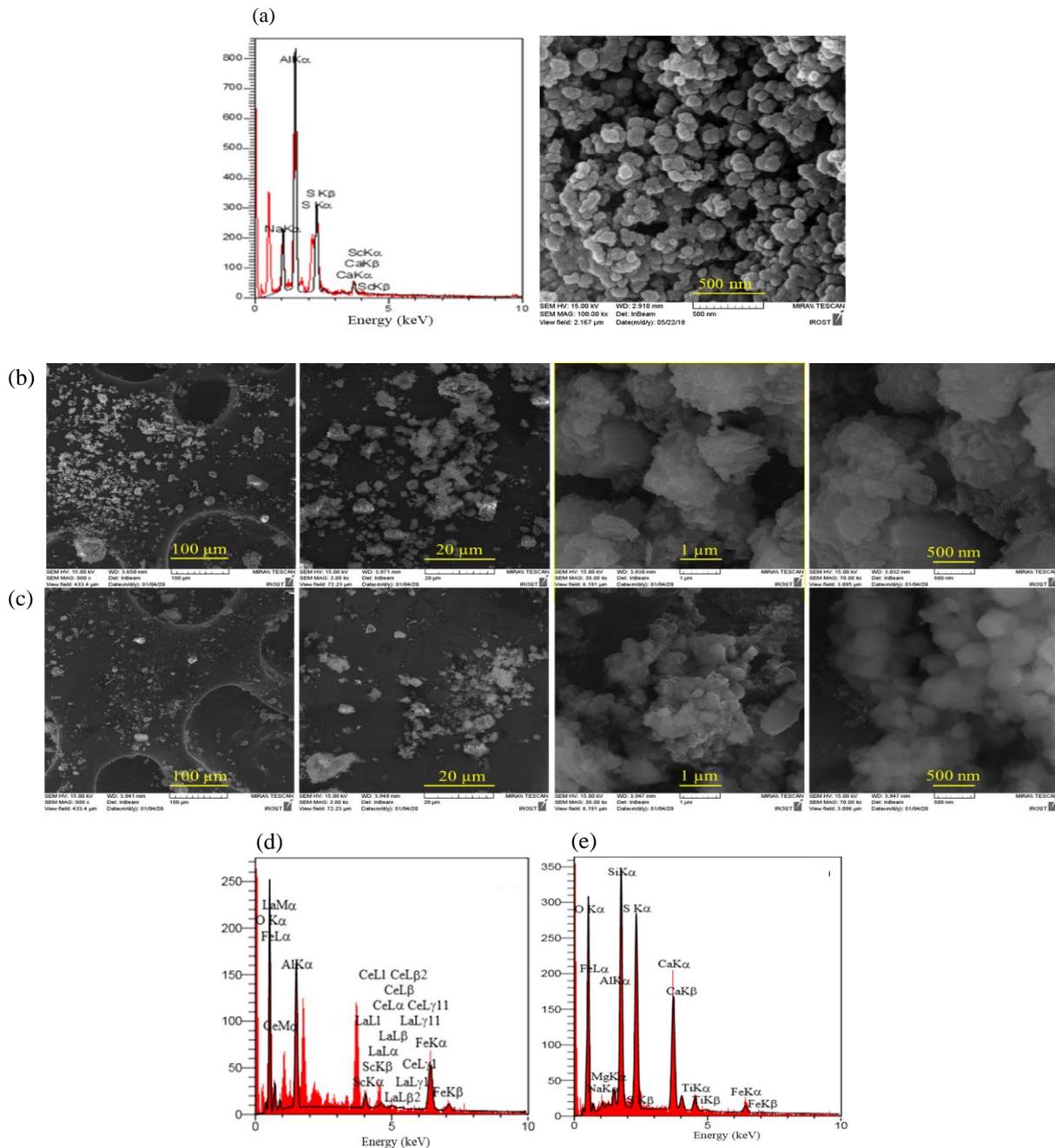

Figure 5. EDX pattern and FE-SEM image of mixed Al/Sc nano-oxide (a), FE-SEM images of (b) the primary RM and (c) the SRL-RM after the process with a magnification of 100 µm to 500 nm. EDX pattern of (d) the primary RM and (e) the SRL-RM after the process.
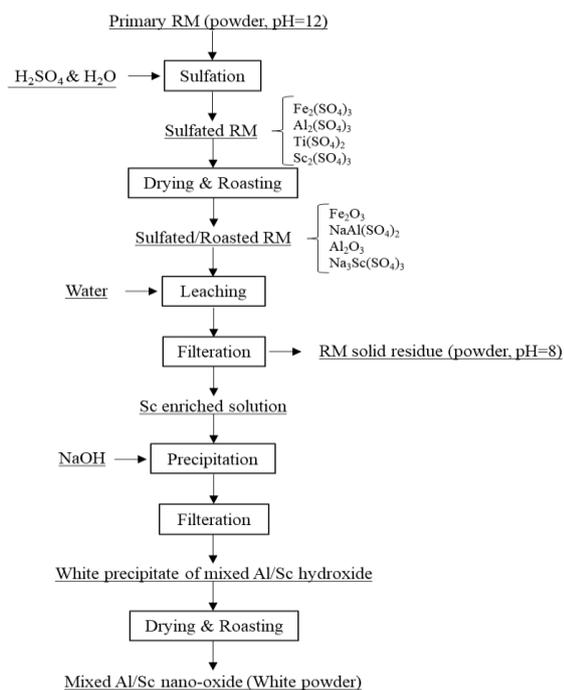
In method 3, the differences in the phase transfer of various metal sulfates during the roasting process led to selective scandium leaching. During roasting, the exiting of SO_3 at higher temperatures formed oxide from unstable sulfates, all iron sulfate in the sample turned into insoluble oxide while the scandium sulfates remained soluble in $Na_3Sc(SO_4)_3$ form. Accordingly, the applied optimal conditions (sulfuric acid L/S ratio of 0.75, roasting temperature of 650°C, distilled water L/S ratio of 50, and leaching time of 7 days) resulted in 73.7% of extracted scandium, with only 0.6% iron in the final mixed Al/Sc nano-oxide product. This mixture oxide had a nanosize spherical shape and was distributed uniformly. The pH of the remaining RM after sulfation-roasting-leaching was 8.0, which was close enough to neutral pH, and its disposal presented no environmental problems.

Considering the effect of the presence of metal ions such as Na^+ on the thermal decomposition temperature of the metal sulfates in the RM sample, method 3 can be used to Sc selective extraction from any other RM samples only with optimizing the roasting temperature.

Acknowledgements

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Figure 6. The optimized steps of the acid roasting-leaching of RM and producing of the mixed Al/Sc nano-oxide.

4. Conclusions

The results of XRD analysis of the red mud from the Iran alumina refining process in the Jajarm plant show that this residue includes hematite (Fe_2O_3), calcite ($CaCO_3$), cateoite ($Ca_3Al_2(SiO_4)(OH)_8$) as the main phases, and conservinite ($Na_6Ca_{1.5}Al_6Si_6O_{24}(CO_3)_{1.6}$) and chlorite ((($Mg,Fe)_6(Si.Al)_4O_{10}(OH)_8$) as the secondary phases. According to the XRF and ICP-MS analysis, the average amounts of the Fe_2O_3, Al_2O_3, CaO, TiO_2, and Sc in the Jajarm RM sample were 30.22%, 18.26%, 16.34%, 5.21%, and 43 ppm. This study researched and compared three methods to clarify the possibility of selectable extraction of aluminum/scandium and prevent iron leaching and minimize the leaching of the other elements such as calcium and sodium as follows: 1) RM direct acid leaching with H_2SO_4; 2) RM washing with hydrochloric acid and oxalic acid before leaching with H_2SO_4; and 3) RM sulfuric acid roasting-leaching-precipitation.

The acid concentration, reaction temperature, and leaching duration, as effective parameters, were investigated in method 1. The highest amount of Sc leaching (63.81%) was achieved at the temperature: 75°C, [H_2SO_4]: 3 M and the leaching duration: 180 min in process 1. Under optimum conditions, the amounts of Fe and Ti leaching (49.55%, and 65.07% respectively) were also close to Sc leaching amount. Accordingly, it was concluded that due to any discriminative features, the selective separation of Al/Sc practically impossible with this process.

The highest amount of Sc leaching (90.32%) was achieved at [HCl]: 3 M and an oxalic acid ratio of 1.0 in method 2. The high amounts of iron (91.15%) and titanium (98.95%) that were leached under this optimum conditions make the direct separation of scandium practically impossible with this treatment before acid leaching (method 2).

Preparation of a mixed Al/Sc nano-oxide derived from the bauxite residue (red mud)
via the sulfuric acid roasting–leaching–precipitation process

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