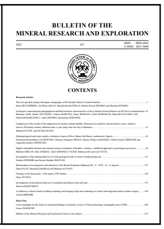
Bull. Min. Res. Exp. (2022) 167: 179-188

Bulletin of the Mineral Research and Exploration

http://bulletin.mta.gov.tr



Investigation of dissolution behavior of scandium and lithium from red mud

Hüseyin BAŞTÜRKCÜ[a*]

[a]*Esan Eczacıbaşı Industrial Raw Materials Company, İstanbul, Türkiye*

Research Article

Keywords:
Red Mud, Scandium, Lithium, Two-Stage Leaching, Kinetics.

Received Date: 14.12.2020
Accepted Date: 14.05.2021

ABSTRACT

In this study, scandium and lithium extractions were investigated using the atmospheric pressure agitation leaching method at acidic medium. The leaching tests were carried out at two stages. To remove the ionic impurities such as Na and Al first stage leaching was performed at relatively higher pH. Following solid-liquid separation of leach cake of the first stage leaching, it was subjected to the second stage leaching. The second stage leaching resulted in 95.1% Sc and 94.7% Li extractions. The overall Sc and Li recoveries were determined as 82.4% and 86.5%, respectively. Regarding the kinetic studies, it was understood that scandium and lithium leaching processes were controlled by a combination of chemical reaction and ash diffusion models. In this case, the activation energies were determined as 29.52 and 30.22 kJmol^{-1}, respectively for scandium and lithium. As a result, while direct H_2SO_4 leaching of red mud is a challenge due to physical and chemical problems, an alternative solution was suggested using H_2SO_4 even at high solids ratios.

1. Introduction

Red mud is defined as the residue of the Bayer process used in the production of aluminum from bauxite ores. 1.5 tons of red mud is generated from the production of 1 ton of aluminum (Zhang et al., 2011; Evans, 2015). There are economic and environmental risks in the storage of these high alkalinity residues considering such high amounts. For this reason, the management of red mud stands out as a very important issue for aluminum producers (Liu et al., 2007; Wang et al., 2013*a*).

Recently, a number of studies have been carried out to obtain different products from red mud. Among these, some products such as construction materials, cement and glass ceramics draw attention (Liu et al., 2012; Chen et al., 2013; Teixeria et al., 2014). On the other hand, the red mud can also be evaluated as a secondary raw material used in the recovery of some precious metals. According to the literature data, the average chemical composition of red mud is 14-45% Fe, 5-14% Al, 1-9% Si, 1-6% Na and 2-12% Ti. In terms of REEs and radioactive elements, the presence of scandium (60-120 ppm), gallium (60-80 ppm), yttrium (60-150 ppm), uranium (50-60 ppm) and thorium (20-30 ppm) occurrences are mentioned (Erçağ and Apak, 1997; Smirnov and Molchanova, 1997; Kumar et al., 2006). In addition, although there is no detailed study on Li recovery from red mud in the literature, there is certain information about the Li contents of some bauxite ores. For instance, Li contents ranging from 460-1.620 ppm have been found in some bauxite lenses located in the French Alps, while Li contents up to 2.691 ppm were detected in the Dazhuyuan bauxite deposit in China (Verlaguet

Citation Info: Baştürkcü, A., 2022. Investigation of dissolution behavior of scandium and lithium from red mud. Bulletin of the Mineral Research and Exploration 167, 179-188.
https://doi.org/10.19111/bulletinofmre.941073

Corresponding author: Hüseyin BAŞTÜRKCÜ, hbasturkcu@gmail.com

et al., 2011; Wang et al., 2013*b*; Christmann et al., 2015).

Hydro and/or pyrometallurgical methods should be used for the recovery of these metals from red mud. In recent years, studies particularly on vanadium, gallium and cerium have been carried out (Okudan et al., 2015*a*, 2015*b*; Abdulvaliyev et al., 2015; Gladyshev et al., 2015; Baral et al., 2016). As a general result of the studies, it is noteworthy that metal dissolution increases with increasing acid concentration and decreasing solid ratio. This results in the transfer of Fe and Al, S, P, Na, Ca, Mg, Si ions into the solution in large quantities. The removal of these impurities in the pregnant solution takes place in stages such as precipitation, cementation or solvent extraction after dissolution. In these stages, the movement of precious metals with impurities causes losses (Fulford et al., 1991; Hammond et al., 2013; Borra et al., 2015). Details of some previous studies are presented below in Table 1.

The study reveals that red mud is a possible source of lithium in addition to scandium. It was aimed, by removing the impurities moving with these metals, to increase the Sc and Li recovery yields. In this way, the applicability of H_2SO_4 leaching under atmospheric pressure and at high solid ratio was investigated. Thus, the applicability of H_2SO_4 leaching under atmospheric pressure and high solid ratio was investigated. This process was carried out in 2 successive steps. In this way, unlike previous studies, ionic impurities such as Na, Ca, K and Al were removed. In the literature, there is a study carried out by the author on the subject (Baştürkcü, 2020). Besides, dissolution behaviors of scandium and lithium in the recovery from red mud have been demonstrated for the first time.

2. Material and Method

2.1. Material

During the characterization of the red mud sample (Seydişehir), XRD (X-Ray Diffraction) method was utilized in order to determine the mineral phases. ICP (Inductively Coupled Plasma) method was used to determine the elemental content for chemical analysis. According to the results given in Table 2, it was determined that the red mud sample contains 25.00% Fe, 9.45% Al and 7.17% Na. In addition, 120 ppm Sc and 165 ppm Li concentrations, and the hematite, sodalite, rutile and magnetite mineral phases

Table 1- A summary of literature studies on red mud.

Author	Details
Ochsenkuhn-Petropulu et al. (1995)	Roasting with borate and carbonate at 1,100 ºC for 20 minutes
	Leaching at a concentration of 1.5 M HCl
	Fe, Al, Ti, Na removal with Dowex-50 W X8
	Sc-Y separation by using HDHEHP (di-(2-ethylhexyl) phosphoric acid)
Ochsenkuhn-Petropulu et al. (1996)	H_2SO_4, HNO_3, HCl
	80% Sc, 96% Y yield with 0.5 M HNO_3
	It was stated that roasting is unnecessary
Zhou et al. (2008)	Leaching with 6 M HCl at 60 ºC for 4 hours
	There is high amount of Na, Fe, Al, Ti in the pregnant solution
	Sc recovery using TBP (tributyl-phosphate) modified with activated carbon
Borra et al. (2016)	Sulfation-roasting-leaching process
	After 1 hour at 700 ºC, Fe and Al change into oxide form
	60% Sc and >80 REE recovery after 48 hours leaching
Deng et al. (2017)	Roasting with the Na salt addition
	Magnetic separation on calcined product
	The magnetic product was used as iron concentrate
	The non-magnetic part was leached with phosphoric acid
	Si-rich leaching solution was obtained
	Al was obtained by dissolving the leach cake in alkaline medium
	Alkaline leaching cake contains Sc and Ti

Table 2- Chemical analysis of red mud sample.

Component	Content
Fe_2O_3, %	35.7
Al_2O_3, %	17.9
TiO_2, %	4.9
Na_2O, %	9.7
CaO, %	1.7
K_2O, %	0.3
Sc, ppm	119
Li, ppm	165
LOI, %	14.5

were determined in the sample (Figure 1). Besides, in the size distribution analysis by Malvern particle sizer 2000, d_{80} and d_{50} sizes were determined as 7 and 3.5 µm, respectively.

2.2. Method

It is seen in chemical analyzes that alkali ions such as sodium and aluminum are very high. These ions are expected to dissolve quickly and pass into solution during the leaching. In order to prevent this undesired situation, an application including dissolving at 20% solid ratio and pH 3 (by using H_2SO_4) for 2 hours was carried out.

The resulting leach cake formed the feed of the second stage leach. First of all, leaching kinetics were investigated on this product under specific conditions. Then, the effects of different solid ratio, H_2SO_4 concentrations and leaching times on extractions were investigated at 90°C. Solid ratio expresses the solid/liquid ratio by weight.

Leaching tests were carried out in a 500 mL cylindrical beaker at a constant stirring speed of 500 rpm. The pH was measured by an acid resistant probe and analytical grade H_2SO_4 was preferred. Total acid consumption was determined in the presence of masking reagent and 1 M NaOH. The experimental program followed throughout the study is presented in Figure 2.

3. Experimental Results

Leaching tests were examined in two main groups and will be presented respectively in this section. The purpose of two-stage leaching is to obtain a Sc- and Li-rich solid material by removing undesired ions (Na^+ and Al^{3+}).

3.1. First Stage Leaching

The red mud sample had an original pH value of 10.4, and this value was reduced to 3 by the addition

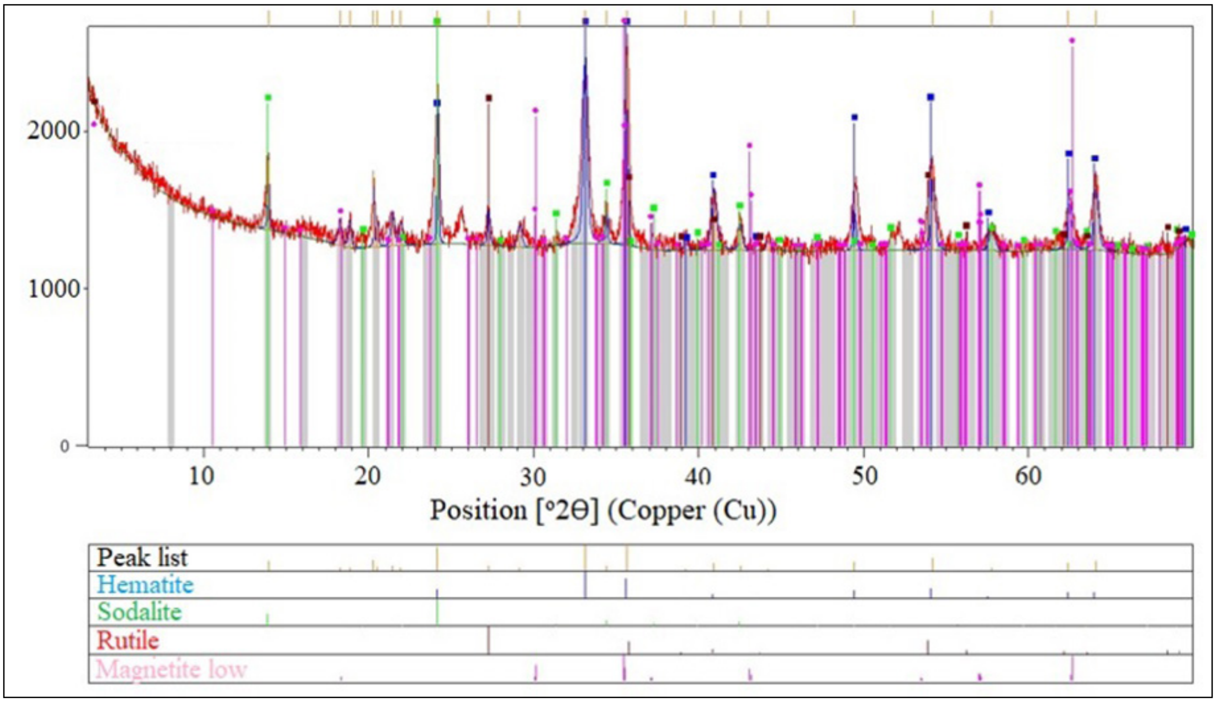


Figure 1- XRD pattern of red mud sample (Baştürkcü, 2020).

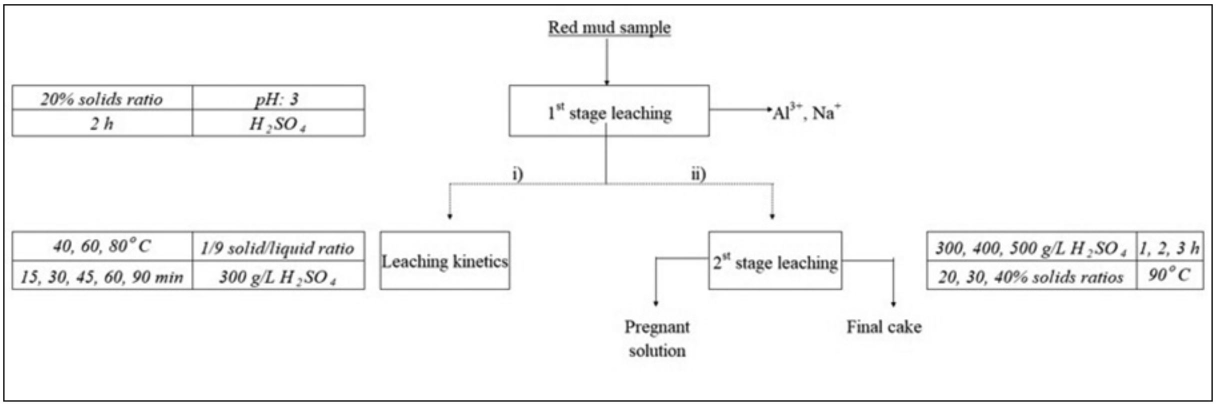


Figure 2- Experimental studies conducted on red mud sample.

of H_2SO_4. As a result of the leaching, Na and Al dissolutions were obtained as 97.2% and 69.3%, respectively (Baştürkcü, 2020). In the XRD analysis performed on the leach cake, it was observed that the sodalite $[Na_8(Al_6Si_6O_{24})Cl_2]$ peaks disappeared (Figure 3), revealing that the chemical and mineralogical analyzes are compatible and confirming.

At this stage, 314 kg/t H_2SO_4 consumption was realized while Sc and Li losses were determined as 13.4% and 9.6%, respectively. The first stage leach cake contains 5.5% Al, 46% Fe, 0.3% Na, 184 ppm Sc and 197 ppm Li.

3.2. Second Stage Leaching

This section of the study is divided into two. They are the investigation of the Sc and Li dissolution kinetics (3.2.1) and the effect of the H_2SO_4 concentration-leaching time relationship at different solid ratio (3.2.2).

3.2.1. Leaching Kinetics

Various kinetic models, among which the shrinking core model is the most frequently used, have been developed to explain the leaching mechanism. In the detailed study of Sc and Li leaching kinetics, a series

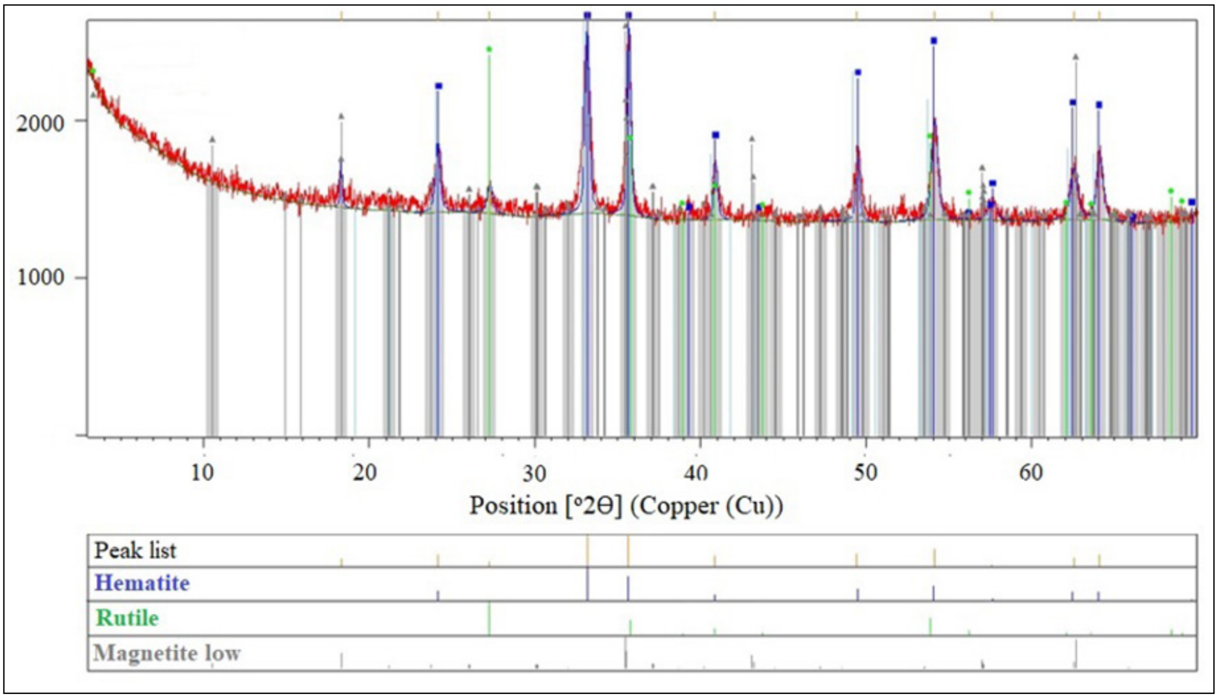


Figure 3- XRD pattern of the first stage leach cake.

of leaching tests using first-stage leach cake were performed. In the tests where the solid/liquid ratio was 1/9 and the H_2SO_4 concentration was constant as 300 g/L, leaching times of 15, 30, 45, 60 and 90 minutes were tested for 40, 60 and 80 °C. According to the results given in figures 4 and 5, it has been inferred that there is a substantial increase in metal dissolution with the increase in temperature, thus giving rise to data on which kinetic models can be applied have been obtained and calculations have been made.

According to the equations in the shrinking core model: equation 1 describes volumetric diffusion control, equation 2 describes ash film diffusion, and equation 3 describes chemical reaction control.

$$x = kt \tag{1}$$

$$1\text{-}3(1\text{-}x)^{2/3} + 2(1\text{-}x) = kt \tag{2}$$

$$1\text{-}(1\text{-}x)^{1/3} = kt \tag{3}$$

where x is the dissolved metal fraction, k is the apparent rate constant and t is time.

With the results obtained from the shrinking core model, the activation energy is calculated by the Arrhenius equation (4). Ea (kJ mol^{-1}) is the activation energy, R (8,314 J K^{-1} mol^{-1}) is the ideal gas constant, k0 (min^{-1}) pre-exponential factor and T (K) is the absolute temperature.

$$k = k0e^{-Ea/RT} \tag{4}$$

Accordingly, R^2 correlation coefficients were calculated as ~0.98 for Sc and Li in accordance with the ash film diffusion equation. Figures 6 and 7 present the resulting kinetics. In other equations, lower values were obtained. Additionally, in order to calculate the activation energy by using the Arrhenius equation, a graph of ln K value vs. temperature was plotted (Figures 7 and 8). Activation energies of 29.52 and 30.22 $kJmol^{-1}$ were determined for Sc and Li, respectively.

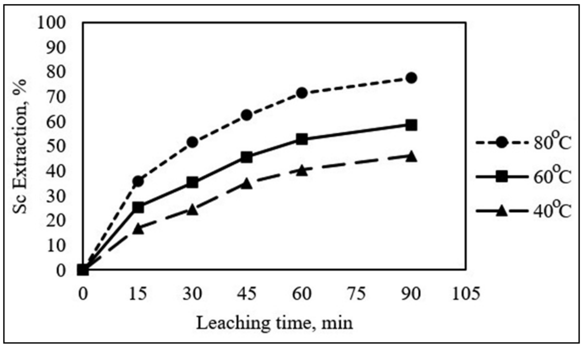


Figure 4- Sc dissolution efficiency versus temperature.

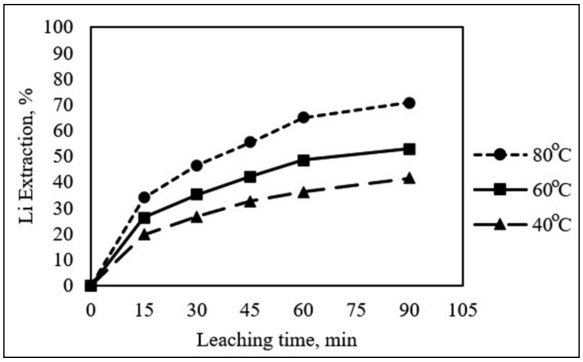


Figure 5- Li dissolution efficiency versus temperature.

Activation energies in reactions under the control of ash film diffusion are generally between 4-12 kJ

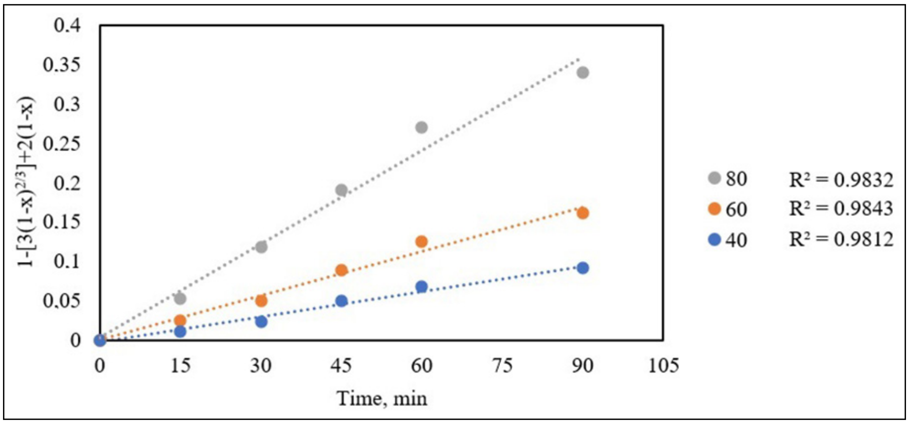


Figure 6- Distribution of ash film diffusion for Sc.

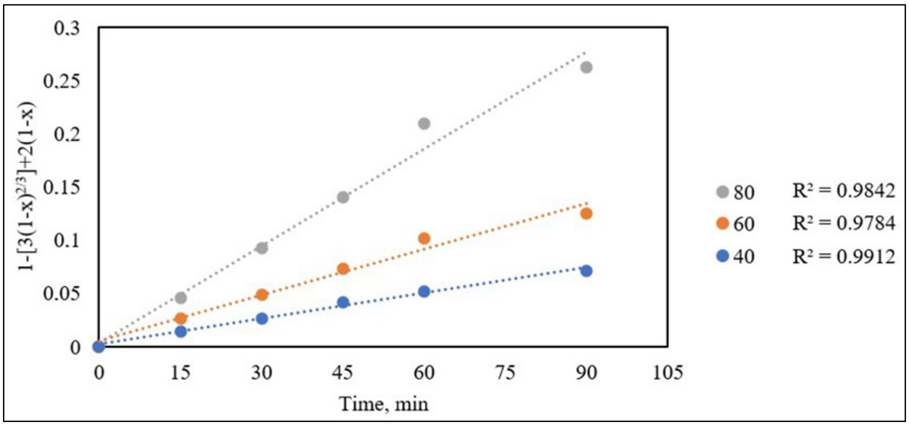


Figure 7- Distribution of ash film diffusion for Li.

mol^{-1}. If the Ea value is 41.8 kJ mol^{-1} or higher, it can be interpreted that it is a leaching process under chemical reaction control (Figures 8 and 9). If the Ea value is between 12-41.8 mol^{-1}, it is concluded that the reaction was conducted under the control of both ash film and chemical reaction (Wang et al., 2017; Xu et al. 2018). Therefore, it can be stated that the Sc and Li leaching reaction occurs in collaboration with ash film diffusion and chemical reaction.

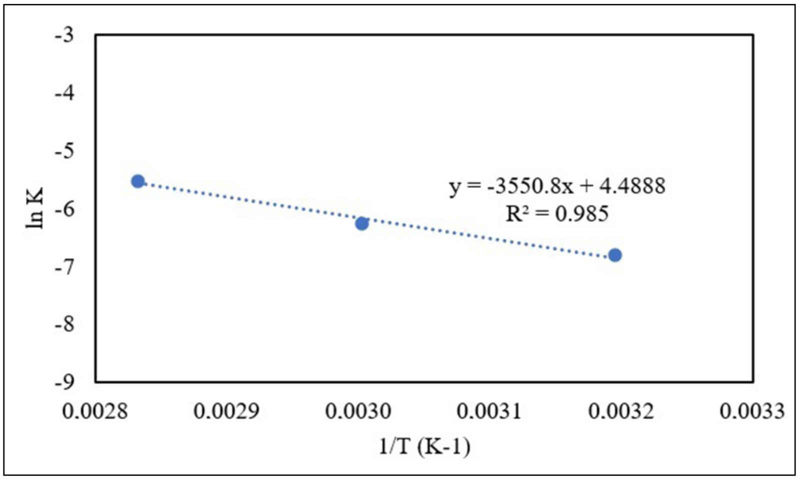


Figure 8- Plot of ln K versus temperature of Sc leaching.

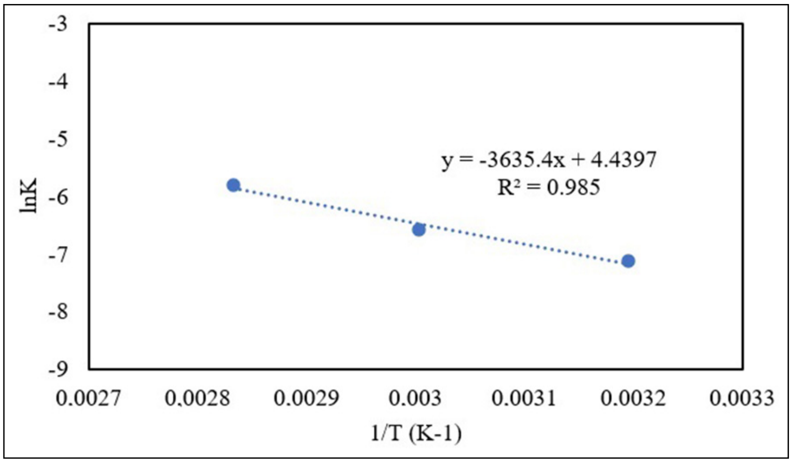


Figure 9- Plot of ln K versus temperature of Li leaching.

3.2.2. The Effect of Leaching Parameters

The effect of leaching parameters was investigated under such conditions as: temperature of 90 °C, H_2SO_4 concentrations of 400, 500, 600 g/L, leaching times of 1, 2, 3 hours, solid ratio of 20%, 30%, 40%. Based on the results given in Figures 10 and 11, it is understood that the Sc and Li extractions were in similar characteristics.

As a prominent finding, it is observed that the leaching time is not necessarily required for Sc and

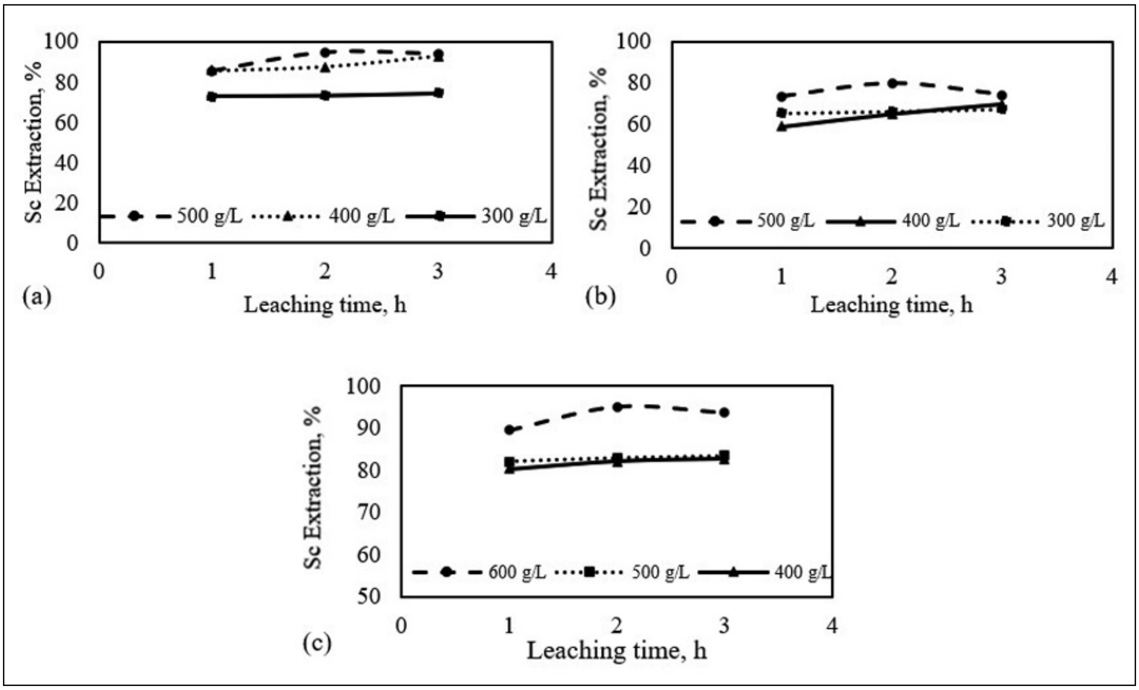


Figure 10- Sc extractions; a) 20% solid ratio, b) 30% solid ratio, c) 40% solid ratio.

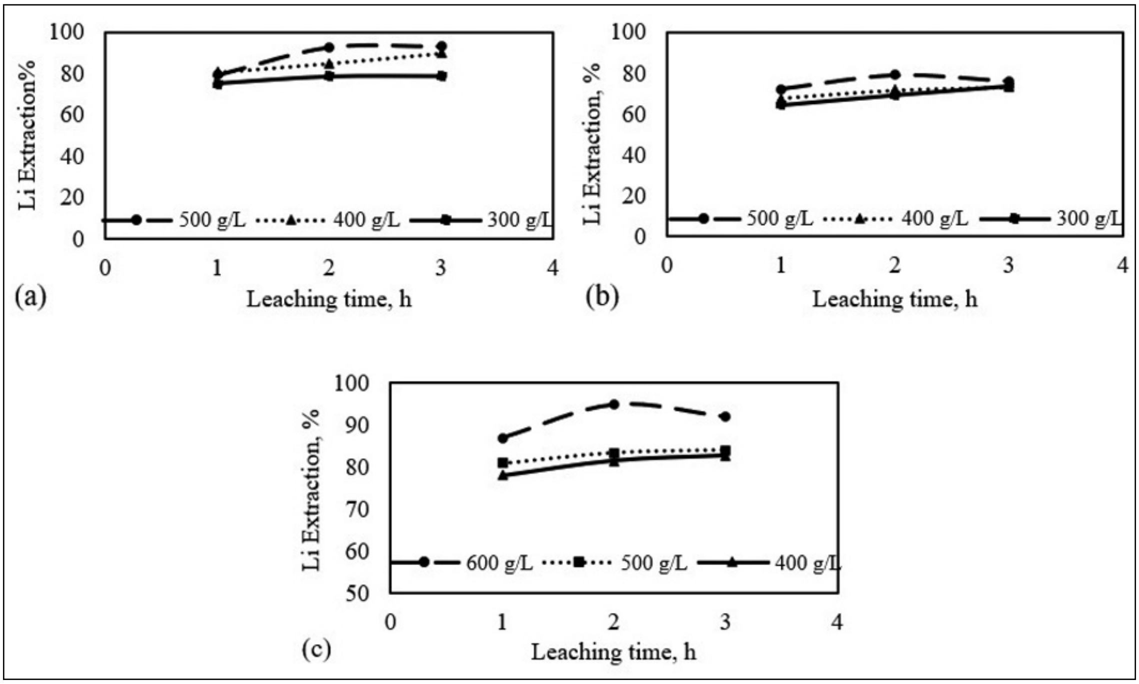


Figure 11- Li extractions; a) 20% solid ratio, b) 30% solid ratio, c) 40% solid ratio.

Li dissolution. Similar results were obtained at 300-500 g/L H_2SO_4 concentrations, and it is determined that high acid concentrations are more effective at high solid ratio. Despite the 400-500 g/L H_2SO_4 concentrations are sufficient for 20% solid ratio, in order to obtain the highest metal extractions at 40% solid ratio, high acid concentration such as 600 g/L is needed.

Since 40% solid ration will be used during industrial applications, 95.1% Sc and 94.7% Li extraction values are achieved as an optimum result for a 2-hours leaching period. At this stage, a quite high amount of H_2SO_4 was consumed (775.5 kg/t).

The resulting pregnant solution contains 0.13 g/L Sc, 0.13 g/L Li, 0.7 g/L Na and 6.92 g/L Al. In the absence of two-stage leaching, the Al+Na concentration is expected to be more than 40 g/L.

4. Results

Based on the tests performed on the red mud sample, the following overall conclusions are reached:

- As a result of the first stage, leaching applied for 2 hours at pH 3 and 20% solid ratio, 97.2% Na and 69.3% Al extractions were achieved. At this stage, Sc and Li losses were determined as 13.4% and 9.6%, respectively.
- The second stage leaching for 2 hours at 40% solid ratio resulted in 95.1% Sc and 94.7% Li extractions.
- As the result of two-stage leaching, total Sc and Li recoveries were determined as 82.4% and 86.5%, respectively.
- The final pregnant solution contains 0.13 g/L Sc, 0.13 g/L Li, 0.7 g/L Na and 6.92 g/L Al.
- It was determined that the Sc and Li dissolution occurred under the control of both ash film diffusion and chemical reaction, and the activation energies were calculated as 29.52 and 30.22 $kJmol^{-1}$ for both metals, respectively.

Most studies in the literature on metal recovery from red mud have been carried out using HNO_3 and HCl, and the average 75-80% Sc extractions have been achieved at low solid ratio, while in the use of H_2SO_4, extractions remain around 50%. Okudan et al. (2015) and Uzun and Gülfen (2007), which used H_2SO_4 in the leaching, preferred pretreatment such as roasting/calcination before leaching. As a result of the heat treatment, some phase transformations occur, thus resulting in the metal extractions increasing to 90%.

In this study, when direct H_2SO_4 leaching at high solid ratio (~40%) was applied, gelling was observed, and the mixing process stopped. This problem is not encountered when working at a low solid ratio. In the literature, it is remarkable that different acids have been tried but H_2SO_4 in direct leaching. In this study, two-stage H_2SO_4 leaching is proposed as an alternative solution. In this way, ionic impurities are removed and the problem of gelation, which hinders the mixing process, is prevented. As a result of the two-stage leaching, 82.4% Sc and 86.5% Li extractions were reached.

In addition, the final solution contains 0.7 g/L Na and 6.92 g/L Al, which is expected to exceed 40 g/L if two-stage leaching is not applied. Removing the impurity at such a high concentration at the beginning provides a big advantage.

As a result of this study, 314 and 775 kg/t H_2SO_4 consumption occurred in the first and second stages. Considering the price of scandium (3,500 USD/kg) to be obtained from this residual product, which does not require size reduction despite its high value, an economic evaluation should be made.

Revealing the recovery of hidden values of Sc and Li metals in red mud demonstrates that red mud is a residual material, not a waste. Although many evaluations have been made in terms of Sc, the dissolution behavior of Li is described for the first time. Red mud should be considered as a by-product of a process.

It is thought to be useful to study solvent extraction and/or metal precipitation processes in detail for selective recovery of these precious metals from the pregnant solution after leaching. In addition, mineralogical investigations of scandium and other rare metals will contribute greatly to hydrometallurgical processes.

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