DRY ACID DIGESTION AND WATER LEACHING OF LATERITE-BASED PIG IRON SLAG FOR SCANDIUM EXTRACTION

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ABSTRACT: *Slag materials generated during laterite smelting study were found to contain a significant amount of scandium (Sc) with an average grade of 99 ppm. However, its high silica (SiO_2) content makes it difficult to be processed via conventional acid leaching due to silica gel formation. Thus, dry acid digestion followed by water leaching was investigated in this study. It was done by adding concentrated sulfuric acid (H_2SO_4) into the slag material in a water-deficient system succeeded by washing. The method demonstrated effectiveness in inhibiting the formation of silica gel even at ambient temperature yielding a scandium leaching efficiency rate of 57.45%. This relatively low leaching rate was affected by the formation of gypsum which acts as a barrier hindering further reaction between the acid and slag particles. To improve the leaching kinetics and aid in the solubility of the gypsum layer, external heat was added in the set-up which increased the scandium leaching efficiency rate to 70.00%. This successful leaching of Sc from slag without silica gelation will enable further recovery and concentration steps to convert Sc into marketable product specifically as concentrates.*

Keywords: Scandium, Silica gelation, dry acid digestion-water leaching

1. INTRODUCTION

The unique properties of scandium make it one of the world's most valuable metals. It is mainly used as a minor alloying element to aluminum alloys to improve the alloys' mechanical, corrosion, and welding properties [1], which are important for many advanced structural applications such as in aerospace engineering. It is estimated that aircraft from welded aluminum-scandium alloys are 15% lighter and 15% cheaper to build compared to present materials [1]. Moreover, the use of scandium in other applications like in laser and lighting, transmission lines and marine industry, and solid oxide fuel cells (SOFCs) for improved cell efficiency and prolonged cell life, are important emerging uses of the metal driving its market demand. Yet, the demand is being controlled by the lack of dependable supply [2,3]. Most countries around the world like the United States of America, the European Union, Australia [4], and Brazil [5] among others, consider scandium as one of their critical metals. Such metals are called critical due to possible challenges in the supply chain attributed to several reasons as cited by Junior et al. (2021): *i) high economic importance; ii) localized resources in limited mining regions; iii) practically irreplaceable in green technologies application; and iv) low recycling rate*. Compared with other rare earth elements which have recycling rates between 3% and 8% [5], scandium has zero recycling rate [6,7].

The abundance though of scandium in the earth's crust is not rare. In fact, it is more abundant than silver, cobalt, lead, and tin [2]. However, it is widely dispersed, lacking the affinity to form exploitable, high-grade primary scandium deposits [1], making it difficult to extract in commercial quantities [2]. Currently, it is mainly obtained as byproducts from various hydrometallurgical processing such as iron-uranium, titanium, rare earth elements, tungsten, and zirconium ores, tailings, and residues [1]. The criticality of scandium alongside its growing demand and poor recycling rate highlights the need to search for new sources and extraction technologies to minimize, if not prevent, supply disruption.

Recent studies have shown that scandium can be greatly enriched in laterite deposits [3,8]. In the Philippines, scandium is being recovered as a byproduct of high-pressure acid leaching of nickel laterite. However, the presence of iron results in increasing complexity of recovering scandium [9]. Hence, the use of laterite-based pig iron slags with low iron and high scandium was explored in this study as a potential source of scandium. Laterite was smelted using a shaft furnace that produced crude pig iron with almost 90% Fe and yielded a slag with about 99 ppm Sc. According to Liu and Li (2015) and Shaoquan and Suqing (1996), a scandium resource is worthy of exploitation if it contains scandium ranging between 20 ppm - 50 ppm. Nevertheless, these laterite-based slags have significant SiO_2 and calcium oxide (CaO) as a result of the pyrometallurgical treatment. Such compounds, especially the SiO_2 pose difficulty for direct acid leaching due to silica gel formation, representing drawbacks in extracting the desired metal because the gel can no longer be filtered and the gelatinous precipitate may hinder further dissolution of the ore particles and significantly reduce the leaching kinetics [12].

A method called dry acid digestion is deemed effective in inhibiting silica gel formation. It is defined as a process of adding concentrated acid to solid materials in a water-deficient system. Several studies have already reported promising results on its application for the extraction of rare earth elements from eudialyte [13], bauxite residue [12], and bauxite slags [9]. Summarized in Table 1 was a comparison of scandium leaching efficiencies from previous studies of treating bauxite residue and bauxite slag by direct leaching and dry acid digestion & water leaching, respectively, which highlights the potential of the novel method. At present, there are no available literature reports yet on the use of dry acid digestion to laterite slags.

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Table 1: Comparison of scandium leaching efficiencies between direct leaching and dry acid digestion & water leaching

References	Sample	Process	Reagent	Efficiency (%)
Alkan et al., 2019 [19]	bauxite residue	direct leaching	2.5M H_2SO_4	45
	basic bauxite slag	direct leaching	2.5M H_2SO_4	84
	bauxite residue	dry digestion & water leaching	98% H_2SO_4	50
	acidic bauxite slag	dry digestion & water leaching	98% H_2SO_4	70
	basic bauxite slag	dry digestion & water leaching	98% H_2SO_4	70
Alkan et al., 2018 [14]	bauxite residue	direct leaching	2.5M H_2SO_4 & 2.5M H_2O_2	68
Marin Rivera et al., 2018 [12]	bauxite residue	dry digestion & water leaching	37% HCl	40
	bauxite residue	dry digestion & water leaching	95-97% H_2SO_4	25
Junior et al., 2021 [5]	bauxite residue	direct leaching (25°C)	20% H_2SO_4 & 15 g/L H_2O_2	10
	bauxite residue	direct leaching (25°C)	20% H_2SO_4 & 4mL/h H_2O_2	25
	bauxite residue	direct leaching (90°C)	20% H_2SO_4	92
	bauxite residue	direct leaching (90°C)	20% H_2SO_4 & 1.40 mol/L H_2O_2	92
	bauxite residue	direct leaching (90°C)	60% H_2SO_4	89
	bauxite residue	direct leaching (25°C)	60% H_3PO_4	35
	bauxite residue	direct leaching (90°C)	60% H_3PO_4	>90

This study investigated the effectiveness of dry acid digestion followed by water leaching in extracting Sc from laterite-based slag

2. MATERIALS AND METHODS

2.1 ***Sample preparation:*** The slag material from crude smelting of laterite ore was used in this study. The slag was prepared by crushing and grinding to obtain a slag fraction of -200/+325 mesh, equivalent to 74-53 μ.
The samples were treated with direct acid leaching and dry acid digestion for comparison.

2.2 ***Direct Leaching:*** The slag was leached in a glass beaker with 2.5M H_2SO_4 solution at 75°C and 500 rpm using a hot plate with magnetic stirring, and solid-to-liquid (S/L) ratio of 1/10 for 1 h.

2.3 ***Dry acid digestion and Water Leaching:*** The experiments were done by manually mixing concentrated sulfuric acid (97% wt. H_2SO_4) to 15g of slag samples at varying amounts of acid (10, 15, and 20 mL), equivalent to an acid-to-solid (A/S) ratio of 0.67, 1.00, and 1.13, respectively, and in each case, 10 mL of deionized water was also added to the mixture to ensure complete wetting, ionization, and diffusion [9]. After ensuring complete mixing, the mixture was kept constant at ambient temperature and a hot plate set at a temperature of 120°C, respectively, for 1 hour. Then, the pasty mixture was washed and stirred magnetically with deionized water with a liquid-to-solid (L/S) ratio of 3 and

2.4 a stirring speed of 500 rpm for 1 hour. These parameters were adopted in the preliminary studies using the dry acid digestion method in red mud slag leaching for scandium recovery. Illustrated in Figure 1 is the process flow of the methodology.

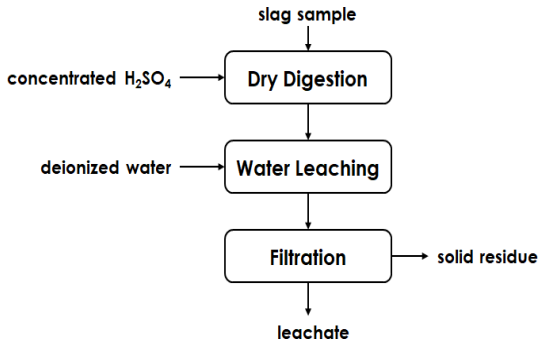

Figure 1. General process flow of methodology

2.5 ***Analysis:*** The mineralogical composition of the solid samples was analyzed using a Malvern PANanalytical X'Pert Pro MPD. The analyses of leachates and solid residues were performed by an external laboratory using direct read ICP-OES and four-acid digestion ICP-OES, respectively.

3. RESULTS AND DISCUSSION

Tables 2 and 3 show the mineralogical phases and chemical analyses of the laterite-based pig iron slag.

Table 2: Mineralogical composition of the slag sample

Minerals	Chemical Formula	%
Spinel	$Mg_2Al_2O_4$	44
Melilite	$(Ca,Na)_2(Al,Mg,Fe^{2+})(Si,Al)_2O_7$	56

Melilites, the main mineral phase identified, are sorosilicates containing groups of SiO_4^{4-} and $Si_2O_7^{6-}$ dimers [15]. It is one of the most frequently reported phases in ferrous slags with compositions between gehlenite ($Ca_2Al_2Si_2O_7$) and åkermanite ($Ca_2MgSi_2O_7$) [16]. Meanwhile, spinel-group phases (AB2O4, where A=Fe^{2+}, Mg, or Mn, and B=Al, Cr, or Fe^{3+}) are one of the common types of oxides found in ferrous slags. The mineral phases containing rare earth elements cannot be confirmed due to their low concentration in the slag material; however, it is known that rare earth elements are found in wide range of minerals including silicates, carbonates, oxides, and phosphates [17].

Table 3: Chemical composition of the slag sample

Fe_2O_3	Al_2O_3	CaO	MgO	SiO_2	Sc (ppm)
4.0%	34.9%	26.6%	5.2%	21.8%	99

In Table 3, the ratio of CaO and MgO with respect to SiO_2 was at 1.45 which was indicative of the basic nature of the slag material and was consistent with the above XRD results. In the study by Yagmurlu et al. (2019), the predominant mineral phase present in the basic slag cooled under ambient conditions was found to be gehlenite.

The slag treated with direct leaching experienced silica gelation after 4 hours as shown in below Figure 2, affecting further analysis of the supposed leached solution.

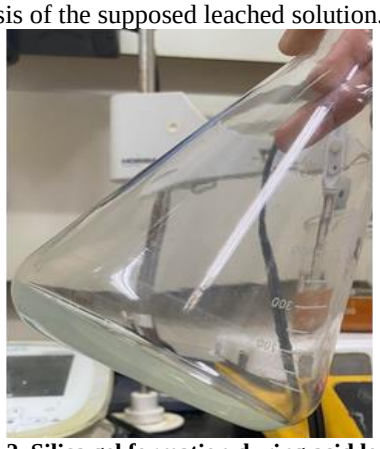

Figure 2. Silica gel formation during acid leaching

Many experiments on direct acid leaching highlighted the impact of acid concentration in the formation of silica gel, such that as the acid concentration increases, the leaching of silicon also increases [5,12]. Using direct leaching in this study, the scandium leaching rate was computed at 65.05%, however, gelation rapidly occurred preventing subsequent recovery steps. On the other hand, in dry acid digestion followed by water leaching, silica gel formation was successfully inhibited at ambient temperature, with the highest scandium leaching efficiency rate of 57.45% at 1.13 A/S ratio. The dissolution of silicon was low due to the minimal amount of water used in the process. It is hypothesized that in a water-deficient system, the interaction between the metal and the acid scavenges the available water, such that no hydration of silica takes place [12].

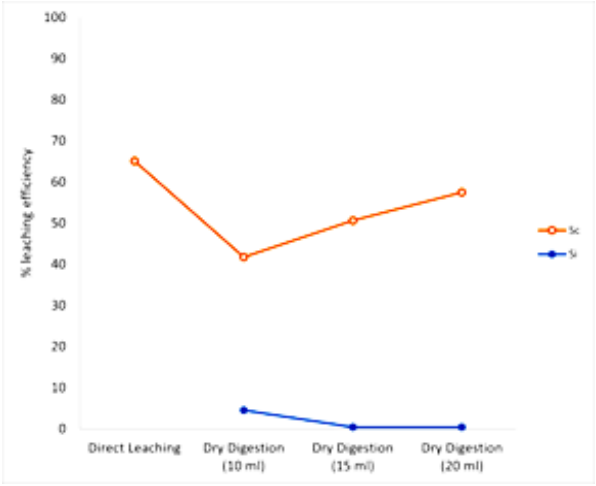

Figure 3. Leaching efficiency rates of Sc and Si

Marin Rivera et al (2018), further explained the phenomena in the below chemical equations. According to Eq. (1), a silicate compound that is in contact with an excess of water in acidic media (i.e., direct leaching), will liberate silicon and will generate silicic acid resulting in the formation of silica gel.

$$M_2SiO_{4(s)} + 2H_2SO_{4(l)} + H_2O \xrightarrow{excess\ H_2O} 2MSO_4 + H_2O + H_4SiO_{4(aq)}$$

If, however, the amount of water is limited, the reaction will proceed according to Eq. (2):

$$M_2SiO_4 + 2H_2SO_4 + nH_2O \rightarrow 2MSO_4 \cdot nH_2O + H_4SiO_4$$

Although, such is an intermediate step. The partially hydrated metal ions further react with silicic acid, reducing the condensation of monomeric silicic acid according to Eq. (3).

$$2MSO_4 \cdot nH_2O + H_4SiO_4 \rightarrow 2MSO_4 \cdot (n+2)H_2O + SiO_{2(filterable)}$$

The overall reaction is presented in Eq. (4):

$$M_2SiO_4 + 2H_2SO_4 + nH_2O \rightarrow 2MSO_4 \cdot (n+2)H_2O + SiO_{2(filterable)}$$

A further increase in the acid volume corresponding to A/S ratio of 1.5 and 2.0 did not increase leaching efficiencies, instead crystallization of the solutions was observed during filtration also posing difficulty in the analysis as well as in the next steps.

XRD analyses of the solid residues were also conducted to examine the change in mineral phases of the slag materials

after dry acid digestion and water leaching. The results revealed the formation of mostly gypsum ($CaSO_4 \bullet 2H_2O$) and anhydrite ($CaSO_4$) from the reaction between calcium aluminates and sulfuric acid [18]. This formation of gypsum layer acts as a diffusion barrier suppressing further leaching of the desired metal [9]. Nonetheless, the solubility of gypsum is influenced by temperature [19]. Thus, the application of additional heat in the set-up using a hotplate at 120 ^{0}C improved the leaching kinetics, thereby, increasing the scandium leaching efficiency rate to 70.00% from 57.45%.

4. CONCLUSION

Scandium tends to concentrate on the slag generated during laterite smelting. The concentration is within the cut-off grade making it a potential secondary source of such valuable metal. However, the considerable amount of silica in the material poses a challenge in processing it via conventional leaching routes due to silica gelation. The dry acid digestion followed by water leaching method used in the study demonstrated effectiveness in inhibiting silica gel formation while obtaining a fair leaching efficiency of 70.00% at the following experimental conditions – 1.13 A/S at 120 ^{o}C for 1 hour followed by water leaching at L/S ratio of 3 with mixing speed of 500 rpm for 1 hour. At ambient temperature, the method yielded lower scandium leaching efficiency rate of 57.45% due to the formation of gypsum layer hindering further leaching reaction. This successful leaching without the challenges posed by the formation of silica gel will enable further metal recovery steps for the eventual production of marketable Sc product in the form of concentrate.

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