Academic Platform Journal of Engineering and Science 8-3, 478-482, 2020

Academic Platform Journal of Engineering and Science

journal homepage: http://apjes.com/

Performance of Organic and Inorganic Acids in the Extraction of Vanadium from Silica Sand by Leaching Method

*[1]Hasan Hacifazlioglu, [2]Ilgin Kursun, [3]Mert Terzi
[1]Istanbul University Cerrahpasa, Department of Mining Engineering, hasanh@istanbul.edu.tr,
[2]Istanbul University Cerrahpasa, Department of Mining Engineering, ilginkur@istanbul.edu.tr,
[3]Istanbul University Cerrahpasa, Department of Mining Engineering, mert.terzi@istanbul.edu.tr,

Research Paper Arrival Date: 21.02.2019 Accepted Date: 07.07.2020

Abstract

In this study, performance of organic acids in the extraction of vanadium from silica sand, a potential vanadium source, were investigated by leaching method. Silica sand samples used in this study was obtained from a silica sand beneficiation plant operating in Istanbul, Turkey. In the context of experimental studies, detailed characterization tests and leaching tests with organic and inorganic acids were performed on the representative samples obtained from the desliming unit of the plant, and the optimum extraction conditions for vanadium were determined. The obtained results showed that the best result for vanadium extraction was obtained with hydrofluoric acid. The extraction efficiency of vanadium was found to be 76% under optimal leaching conditions of 2 h of leaching time, 800 kg/ton of HF amount and 40°C pulp temperature. On the other hand, the best results among the organic acids were obtained with oxalic acid. The extraction efficiency of vanadium was found to be 50% under optimal leaching conditions of 2 h of leaching time, 200 kg/ton of oxalic acid amount and 40°C pulp temperature.

Keywords: Vanadium, silica sand, leaching method, organic acids, inorganic acids

1. INTRODUCTION

The existence of vanadium was discovered by Spanish mineralogist Manuel Del Rio in 1801 in Mexico as a result of the studies performed on lead vanadate ore [1-2]. Vanadium is a relatively abundant trace element found in the Earth's crust and it occurs within many minerals and ore deposits. While it does not found in its native metal form in the nature; it co-exists with other elements in many different mineral species. Vanadium minerals are classified into seven groups which are namely oxides, phosphates, silicates, sulphates, sulphurs, titanates and vanadates [3]. Most common vanadium bearing minerals are carnotite, mottramite, patronite, roscoelite and vanadinite [2, 4]. Production data for 2015-2018 and the current reserves of vanadium were presented in Table 1.

Table 1. Worldwide production of vanadium and vanadium reserves [5]

	Production					Reserves
	2013	2014	2015	2016	2017	(x1000 mton)
U.S.A.	591				-	45
Australia	400				-	2,100
Brazil	-	1,030	5,800	8,000	8,400	-
China	41,000	45,000	42,000	45,000	43,000	5,100
Russia	15,000	15,100	16,000	16,000	16,000	5,000
S. Africa	21,000	21,000	14,000	10,000	13,000	3,500
Others	600	580	-	-	-	-
Total	79,000	82,700	77,800	79,000	80,000	14,000

Vanadium is almost only significant by-product used in ferrous and non-ferrous alloys owing to its physical properties such as high tensile strength, hardness and fracture strength. It is used in a wide range of alloy combinations with iron, titanium, nickel, aluminium, chrome and other metals for various commercial applications such as railroads, steel tools, catalysts and aviation. Global demand for vanadium is met by several primary resources as feedstock, concentrates, metallurgic slags and petroleum wastes. Moreover, mine tailings and waste ashes have a significant economic potential as they can contain high amounts of vanadium and nickel [4, 6].

*Corresponding Author: Istanbul University Cerrahpasa, Department of Mining Engineering, hasanh@istanbul.edu.tr, Tel: 05368711337

Doi: 10.21541/apjes.530467

Hydro-metallurgical and pyro-metallurgical methods are used for the recovery of vanadium. Most common methods are direct acid or alkali leaching and post-roasting acid, alkali leach or water leaching. Alkali leaching is generally preferred method for the selective recovery of vanadium from iron. However, this method may also resulting a partial dissolution of silica in addition to vanadium. Moreover, it is somewhat an expensive method due to the reagents used in the process. On the other hand, dissolution of silica in sulphuric acid is relatively limited; but selective recovery with this method is not possible in terms of simultaneous recovery of nickel and vanadium. At the same time, it is a cost-effective and efficient method [2].

Li et al., (2010) have investigated the feasibility of vanadium recovery from black shale using sulphuric acid and hydrochloric acid leaching routes. The obtained results showed that the dissolved vanadium was in the form of VO^{2+} and VO_2^+ in an aqueous solution with high potential and low pH value. Optimum parameters were determined as 87.5 g/L sulphuric acid concentration, 6-hours reaction time, 15 g/L hydrochloric acid concentration, 1 g/L sodium hypochloride concentration, 95 °C pulp temperature and 4 mL/g solid/liquid rate. Under these optimum conditions, vanadium recovery was found to be 86% [7]. Li et al., (2011) have investigated vanadium production from a low grade vanadium slag using oxidization process in the presence of Na_2CO_3. Oxidization conditions were investigated with the techniques of XRD, SEM/ DS and TG-DSC. The obtained results showed that vanadium slag was oxidized in the temperature range of 273 °C and 700 °C and the optimum oxidizing temperature range was found to be 500-600°C as water-soluble sodium vanadates are formed at this temperature range. On the other hand the samples are sintered at 800°C, which negatively affects the leaching rate of vanadium [8]. Aarabi-Karasgani et al., (2010) also investigated the vanadium recovery from Linz–Donawitz (LD) converter slag production using alkali roasting-acid leaching route and determined the effects of different parameters on vanadium dissolution kinetics. Under optimum leaching conditions, which were 70°C pulp temperature, 3 M acid concentration and 150 minutes leaching time, approximately 95% vanadium recovery was achieved [9]. Fan et al., (2013) have investigated the feasibility of both bulk and column tests for the recovery of vanadium from the vanadium containing chromate solutions using a mild base resin named D314 [10].

Several studies have also been conducted for the recovery of vanadium from hard coal [11-12]. In this regard, Wang et al., (2013) have performed a study for vanadium recovery from the hard coal using flotation. A concentrate with 1.88% V_2O_5 grade was obtained with a recovery rate of approximately %77. Moreover, 72.51% of the feed mass was removed as tailings after this process [12].

In this study, investigation of the applicability of the leaching method using organic and inorganic acids for the extraction of vanadium from silica sand were aimed, and silica sands were evaluated as a potential vanadium resource.

2. EXPERIMENTAL STUDIES

2.1. Material

The sample used in the experimental studies was taken from the desliming unit of a silica sand beneficiation facility operating in Sile, Istanbul. In the facility, raw silica sand was firstly subjected to scrubbing and filtering, then classified by hydrocyclones and other hydraulic classifiers and, finally transferred to the beneficiation plant. The samples used in the experimental studies were representatively taken from stockpiled silica sand which were pre-processed in the desliming unit. Several chemical, physical and mineralogical analyses were performed to characterize the sample before leaching experiments. The results of the chemical analysis carried out with XRF and ICP methods are given in Table 2.

Table 2. Results of chemical analysis of the deslimed sample

Content	**Assay Value**	**Content**	**Assay Value**
SiO_2 **(%)**	81.63	Cr_2O_3 **(%)**	0.07
Al_2O_3 **(%)**	15.66	P_2O_5 **(%)**	0.07
TiO_2 **(%)**	1.15	SO_3 **(%)**	0.05
Fe_2O_3 **(%)**	0.54	BaO **(%)**	0.05
K_2O **(%)**	0.37	Na_2O **(%)**	0.04
ZrO_2 **(%)**	0.17	V (ppm)	50.00
CaO **(%)**	0.12	Other (%)	0.01
MgO **(%)**	0.07	Total	100.00

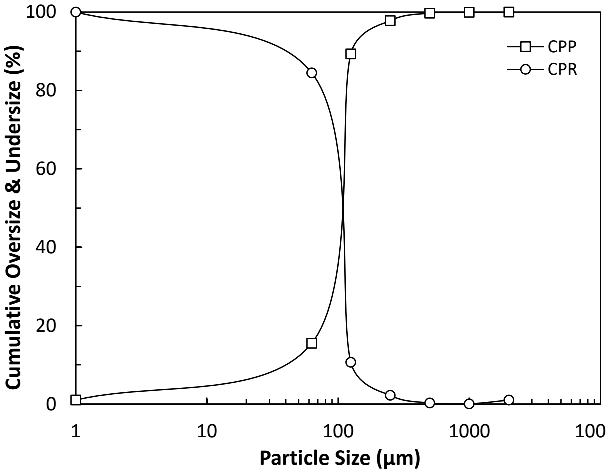
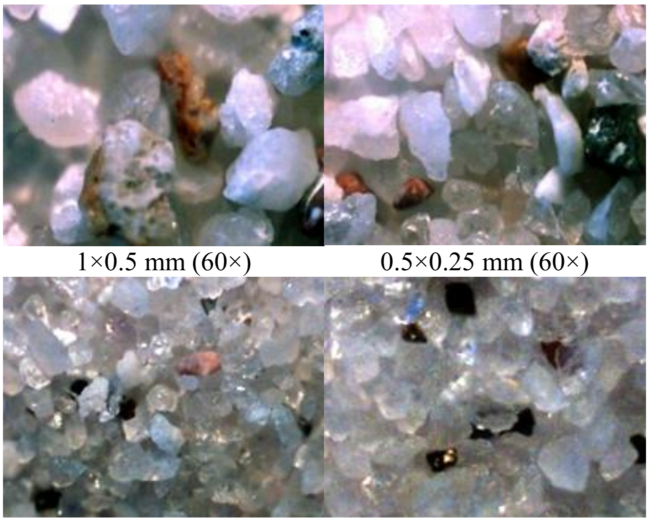


Figure 1. Particle size distribution of the sample

As seen in the particle size distribution graph of the sample (Fig. 1), the d_{50} and d_{80} sizes of the sample are 0.08 mm and 0.12 mm, respectively. Therefore, it can be said that the sample has a suitable particle size distribution for the leaching procedure without a need for further size reduction. Results of the optic and scanning electron microscope examinations showed that the sample is mainly consisting of hematite, ilmenite, magnetite and rutile minerals in addition to the dominant mineral phase, quartz (Fig.2).

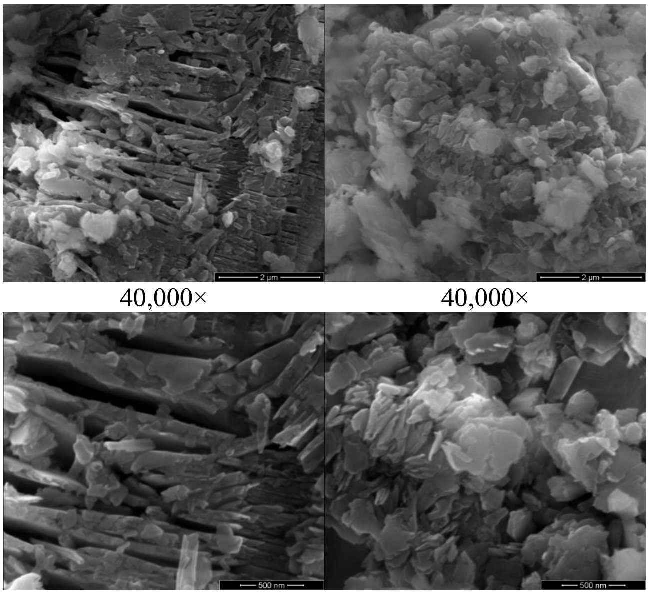


1×0.5 mm (60×) 0.5×0.25 mm (60×)

0.25×0.125 mm (60×) 0.125×0.063 mm (200×)

Figure 2. Optic microscope images of the particle size fractions

According to SEM images (Fig. 3), quartz particles within the sample have generally preserved their overall euhedral structures. On the other hand, due to the weathered conditions in the deposit, a considerable roundness in several quartz particles were also observed. Additionally, it was seen that the iron bearing particles, such as magnetite and hematite, in the sample have also preserved their euhedral crystal structures. Results of SEM analysis have also confirmed that the vanadium content in the sample is commonly distributed within magnetite particles.



40,000× 40,000×

100,000× 100,000×

Figure 3. SEM images of the sample

2.2. Method

In the context of leaching tests, direct acid leaching method were applied using different organic and inorganic acids as lixiviant for the selective vanadium extraction from silica sand. The organic acids used were citric, tartaric and oxalic acids whereas the inorganic acids were sulphuric (H_2SO_4), hydrochloric (HCl) and hydrofluoric (HF) acids. The silica sand samples was subjected to the leaching process for 2 hours under an average leaching temperature (40^{o}C) at different acid amounts (100, 200, 400, 600, 800 and 1000 kg/t). The leaching tests were performed in 250 cc of conical flasks in a shaking water bath under shaking rate of 250 rpm. After the leaching procedure, solid-liquid separation was performed by filtration, then the obtained residues were dried at 105^{o}C and finally the vanadium content was analysed using the ICP method. The vanadium extraction rate was calculated according to Equation 1.

$$\mathrm{V.E.}\,(\%) = \frac{[\mathrm{V}_{feed} - \mathrm{V}_{residue}]}{\mathrm{V}_{feed}} * 100 \qquad (1)$$

3. FINDINGS

The results of leaching experiments performed with different organic and inorganic acids were given in Fig. 4 and Fig. 5, respectively. As seen in Fig. 4, a linear increase in the vanadium extraction rate was observed up to the acid quantity of 800 kg/tons with citric acid. The vanadium extraction rate was found to be 36% at 800 kg/ton citric acid amount. However, approximately 4% decrease was observed after a further increase in acid amount to 1000 kg/ton. On the other hand, despite the fact that vanadium extraction has increased up to 200 kg/ton acid amount, no significant change was observed after this point in the leaching tests performed with tartaric acid. Consequently, the best vanadium extraction were obtained with oxalic acid among the organic acids investigated. The vanadium extraction rate was found to be 50% after the leaching process performed under 2-hours leaching time, 40^{o}C pulp temperature and 200 kg/ton oxalic acid amount conditions.

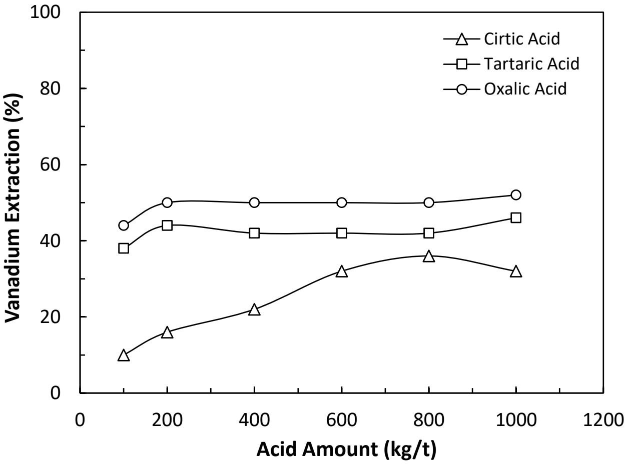


Figure 4. The results of leaching experiments performed with different organic acids

As seen in Fig. 5, no significant change was observed in vanadium extraction up to the acid amount of 600 kg/ton in sulphuric acid leaching experiments. On the other hand, vanadium extraction has considerably increased at 800 kg/ton and it decreased to 46% at 1000 kg/ton acid amount. The decrease in vanadium extraction rate can be associated with the dissolution of unwanted minerals resulting of a possible precipitation of extracted vanadium, which should be investigated in terms of the solution chemistry. In hydrochloric acid leaching, vanadium extraction rate has increased up to 400 kg/ton acid amount. At this acid amount, vanadium extraction was 62%. However, similar to sulphuric acid leaching, vanadium dissolution efficiency showed a decrease tendency after further increase in acid amount. It is clear that the excessive lixiviant amount hindered the selectivity of leaching in both sulphuric and hydrochloric acid leaching experiments. In the leaching experiments performed with inorganic acids, the best results in terms of vanadium extraction were obtained with hydrofluoric acid. In comparison to vanadium extraction rate obtained with 100 kg/ton hydrofluoric acid amount, a significant increase of about 20% was achieved at 200 kg/ton. Although the increase trend in vanadium extraction rate has remained constant up to 800 kg/ton but it was slowed down after 200 kg/ton as seen in Fig. 5. It can be concluded that the optimum acid amount was 800 kg/ton in hydrofluoric acid leaching where the best result was obtained as 76% vanadium extraction rate.

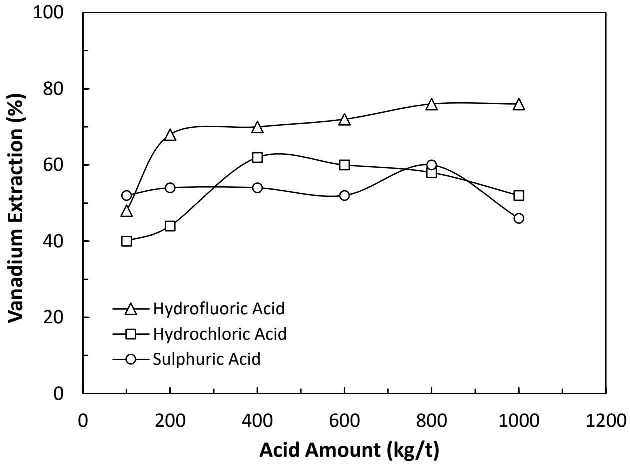


Figure 5. The results of leaching experiments performed with different inorganic acids

Fig. 6 shows the residues obtained after leaching process performed with hydrofluoric and oxalic acids. As seen in Fig. 6, hydrofluoric acid was more efficient than oxalic acid in terms of total decomposition of mafic minerals including vanadium bearing magnetite particles.

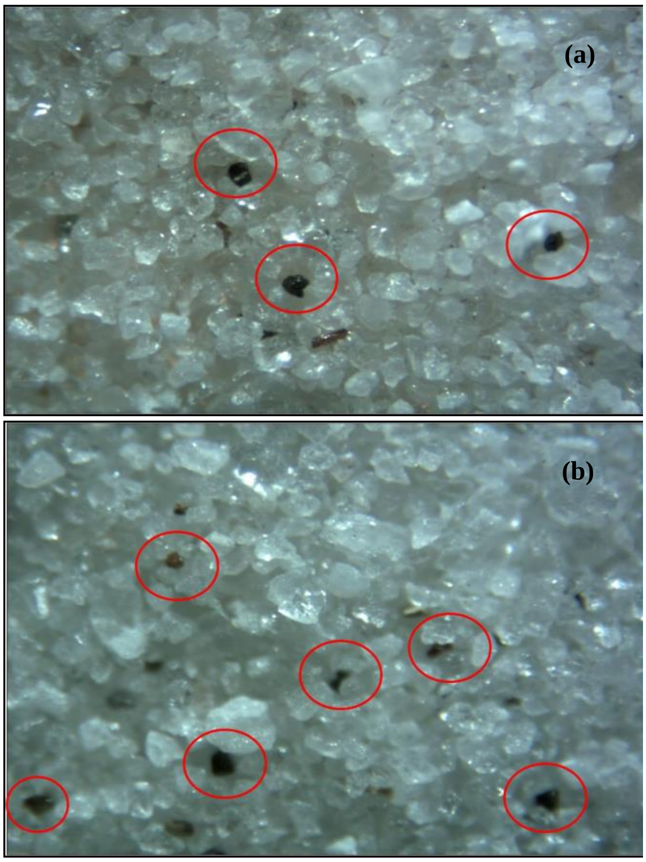


Figure 6. Images of residues after hydrofluoric (a) and oxalic (b) acid leaching

4. DISCUSSION AND CONCLUSION

In this study, performance of organic acids in the extraction of vanadium from silica sand, a potential vanadium source, were investigated by leaching method. Leaching tests were performed using different organic and inorganic acids as lixiviants. In the experiments, leaching time (2-hours), pulp temperature (40ºC) and mixing speed (250 rpm) parameters were kept constant and the effect of acid amount (100, 200, 400, 600, 800 and 1000 kg/t) of the organic (citric acid, tartaric acid and oxalic acid) and the inorganic acids (sulphuric, hydrochloric and hydrofluoric) were investigated.

Best vanadium extraction were obtained with oxalic acid among the organic acids investigated. The vanadium extraction rate was found to be 50% after the leaching process performed under 2-hours leaching time, 40ºC pulp temperature and 200 kg/ton oxalic acid amount conditions. In the leaching experiments performed with inorganic acids, the best results in terms of vanadium extraction were obtained with hydrofluoric acid. It was concluded that the optimum acid amount is 800 kg/ton in hydrofluoric acid leaching where the best result was obtained as 76% vanadium extraction rate. It was also seen that the excessive lixiviant amount hindered the selectivity in both sulphuric and hydrochloric acid leaching experiments as vanadium extraction was negatively affected after a certain acid amount in both cases. Therefore, the investigation of reasons behind these findings in terms of the solution chemistry is recommended for the future studies.

Ultimately, it can be concluded that the hydrofluoric acid was more efficient than oxalic acid in terms of total decomposition of mafic minerals including vanadium bearing magnetite particles which were observed in optic microscopy examinations on the leaching residues. However, the results obtained in this study have also revealed that the inorganic acids can be successfully applied for the extraction of vanadium from silica sands.

REFERENCES

[1].B. Lagerkvist and A. Oskarsson, Handbook on the Toxicology of Metals, Elsevier, 2007.
[2].Ozturk A. T., “Acquisition of Vanadium and Nickel out of Waste Ashes and Used Industrial Catalytic”, MSc. thesis, Suleyman Demirel University, 2008.
[3].H. Gharehbagheri, J. Safdari, R. Roostaazad and A. Rashidi, 2013, “Two-stage fungal leaching of vanadium from uranium ore residue of the leaching stage using statistical experimental design”, Ann. Nucl. Energy, vol. 56, pp.48–52, Feb 2013.
[4].R. R. Moskalyk and A. M. Alfantazi, “Processing of vanadium: a review”, Miner. Eng., vol. 16, no. 9, pp. 793–805, Jul 2003.
[5].USGS, 2018, “Vanadium”, U. S. Geological Survey, Mineral Commodity Summaries, (2018).
[6].J. Yang, Y. Tang, K. Yang, A. A. Rouff, E. J. Elzinga and J. Huang, “Leaching characteristics of vanadium in mine tailings and soils near a vanadium titanomagnetite mining site”, J. Hazard. Mater., vol. 264, pp. 498– 504, 2014.
[7].M. Li, C. Wei, G. Fan, H. Wu, C. Li and X. Li, “Acid leaching of black shale for the extraction of vanadium”, Int. J. Miner. Process., vol. 95, pp. 62–67, May 2010.
[8].X. Li, B. Xie, G. Wang and X. Li, “Oxidation process of low-grade vanadium slag in presence of Na_2CO_3”, Trans. Nonferrous Met. Soc. China, vol. 21, no. 8, pp.1860-1867, Aug 2011.
[9].M. Aarabi-Karasgani, F. Raschi, N. Mostoufi and E. Vahidi, “Leaching of vanadium from LD converter slag using sulphuric acid”, Hydrometallurgy, vol. 102, no. 1-4, pp.14–21, Apr 2010.
[10]. Y. Fan, X. Wang and M. Wang, “Separation and recovery of chromium and vanadium from vanadium-containing chromate solution by ion Exchange”, Hydrometallurgy, vol. 136, pp.31–35, Apr 2013.
[11]. Y. Min-Zhang, S. Bao, T. Liu, T. Chen and J. Huang, “The technology of extracting vanadium from stone coal in China: History, current status and future prospects”, Hydrometallurgy, vol. 109, no. 1-2, pp.116–124, Sep 2011.
[12]. L. Wang, W. Sun, R. Liu, X. Gu, “Flotation recovery of vanadium from low-grade stone coal”, Trans. Nonferrous Met. Soc. China, vol. 24, no. 4, pp.1145−1151, Apr 2013.