A PARAMETRIC STUDY ON THE SULFURIC ACID LEACHING OF VANADIUM OF AN IRANIAN THERMAL POWER PLANT ASH

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Abstract: *Vanadium recovery of Thermal Power Plant Ash (TPPA) is an attractive process which simultaneously satisfies the pollution control standards regarding TPPA disposal and provides a valuable source of vanadium for industrial demands. In the present research work, sulfuric acid leaching route has been employed for vanadium recovery from an Iranian TPPA. Effects of acid concentration, temperature, acid/TPPA ratio, leaching time as well as TPPA particle size on the leaching efficiency of vanadium have been investigated. Experimental results showed that leaching efficiency of vanadium is significantly affected by the leaching conditions. The results revealed that with acid concentration of about 15%, temperature around 75 °C, acid/TPPA ratio~15, leaching time about 120 minutes and particle size of 75 - 150 µm, almost 92% of vanadium can be dissolved.*

Keywords: *Vanadium, Acid Leaching, Thermal Power Plant Ash*

1. INTRODUCTION

The main application of V is in ferrous and non-ferrous alloys where its use improves mechanical properties such as high-temperature strength, fatigue behavior and hardness of these alloys. Vanadium and/or its compounds have also been used in batteries, cemented carbides, coating materials, superconductors and catalysts [1, 2].

Average concentration of V in the earth crust is about 150 g/t [1]. Pure vanadium has never been found in the nature [3] and vanadium resources exist in combination with several minerals such as Roscoelite, Montroseite, Carnotite, Francevillite and Magnetite [1, 4]. Since vanadium abundance is limited and world vanadium demand is increasing fast [5], current trend in vanadium extraction is the use of secondary resources. For example, it has been reported that 23% of vanadium in 1981 in USA and 14% of vanadium in 1986 in Japan came from oil ash [6].The main secondary resources of vanadium are spent catalysts [7, 8], black shale [4, 9], LD converter slag [10], special alloys [5] and Thermal Power Plant Ash (TPPA) [2, 11, 12].

Vanadium recycling from secondary resources is accomplished through pyro-metallurgical and hydro-metallurgical as well as pyro-hydrometallurgical processes.

Pyro-metallurgical process has been performed through two main routes as follows:

A. Vanadium is recovered by conversion to its chlorides ($VOCl_3$ or VCl_4) through the reaction with chlorine [13]. Afterwards, a reducing agent is used for reducing the chloride to elemental vanadium.

B. Vanadium is recovered via direct reduction of vanadium oxides by use of some active metals such as Ca and Al [1].

Hydro-metallurgical recycling of vanadium involves leaching of vanadium compounds in acids such as HCl [14], HF [15], H_2SO_4 [9], H_3PO_4 [16] and oxalic acid [17] or alkalines including NaOH [18] or NH_4OH [19] and even water [20], depending on the type of vanadium compounds. Effects of various leaching parameters (time, pulp density, temperature, solution concentration, additives, etc.) on the leaching efficiency of vanadium have been examined by many researchers. The leached vanadium ions could be recovered from the solution through various routes such as solvent extraction, ion exchange and sedimentation [1].

In order to increase the leaching efficiency of vanadium (specially for hard soluble compounds) [21], roast-leach method has been proposed which is a combination of Pyro-metallurgical (roasting) and Hydro-metallurgical (leaching) processes. It has been shown that roasting of vanadium compounds with some salts such as NaCl [22], sodium hypochlorite [23] and Na_2CO_3 [24] converts the insoluble compounds to the soluble ones [25].

In the cases that hydrometallurgical process is applicable, this process is preferred in sense of lower capital cost, ease of performance and lower energy consumption [5].

Among the secondary sources of vanadium, more attention has been paid to the recycling of vanadium from TPPA. TPPA consists of toxic vanadium compounds and should be treated adequately before disposal [2]. TPPA exists in the form of fly ash (dust and fine particles) and bottom ash (scale and small agglomerates) which are solid residues of the combustion of liquid fuels in thermal power plants. Vanadium concentration of TPPA depends on the type of combusted fuel as well as the concentration of vanadium in the fuel. High amount of vanadium in TPPA reveals the importance of this secondary resource.

The aim of the present research work has been the use of sulfuric acid leaching route for the recovery of vanadium from a type of TPPA received from a thermal power plant in the vicinity of Saveh (Iran). In order to determine the optimum leaching conditions, effects of different leaching parameters including acid concentration, temperature, acid/TPPA ratio, leaching time and TPPA particle size on the dissolution efficiency of vanadium have been investigated.

2. EXPERIMENTAL PROCEDURE

TPPA sample used in this research work belongs to Rudshur thermal power plant (Saveh, Iran). The ash was a residue of combustion of heavy oil in the power plant heart. X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) analysis showed that in addition to vanadium, the sample contains various amounts of S, Ni, Fe, Al, Si, and Na mainly in the form of complicated oxide compounds. Wet chemical analysis showed that vanadium concentration in the sample is around 22 wt%.

As received TPPA was milled for 1 hour in a laboratory ball mill and then classified into four size fractions. In this research work sulfuric acid leaching has been employed. For this purpose, laboratory grade (95-98% purity) sulfuric acid was used. The leaching process was performed under the air atmosphere in a Pyrex cylindrical beaker of 400 ml volume. Temperature of the solution was measured by use of a contact thermometer with the accuracy of + 3°C. A hotplate accompanied by a magnetic stirrer was used for heating and mixing the solution. Stirrer speed was fixed at 600 rpm.

Leaching experiments were done in five steps in order to investigate the effects of influencing parameters including acid concentration, temperature, acid/TPPA ratio, leaching time and TPPA particle size. Experimental conditions are summarized and presented in table 1.

After the termination of each leaching experiment, solid residue was filtered and vanadium content of the solution was determined by spectrophotometeric technique.

The leaching efficiency was calculated from the ratio of vanadium transferred to the solution to the amount of vanadium in the initial sample.

3. RESULTS AND DISCUSSIONS

The present study has been aimed on the evaluation of the effects of influential parameters on the leachability of a typical vanadium bearing TPPA in order to determine the optimum conditions for maximum vanadium recovery. For this purpose, effects of acid concentration, temperature, acid/TPPA ratio, leaching time and TPPA particle size have been examined. Experimental results are presented and discussed in this section.

3. 1. Effect of acid concentration

The vanadium leaching efficiency as a function of acid concentration is plotted in Fig. 1. Other constant parameters are presented in table 1. The figure shows that acid concentration has a significant effect on the vanadium leachability, so that leaching efficiency increases as a direct function of acid concentration. Increase of

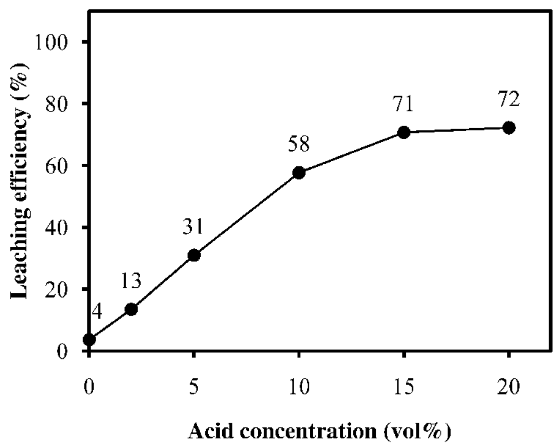

Fig. 1. Effect of acid concentration on the vanadium leaching efficiency. Other constant parameters are: temperature: 60 °C, acid/TPPA ratio: 10, leaching time: 120 minutes and particle size of 75 - 150 μm.

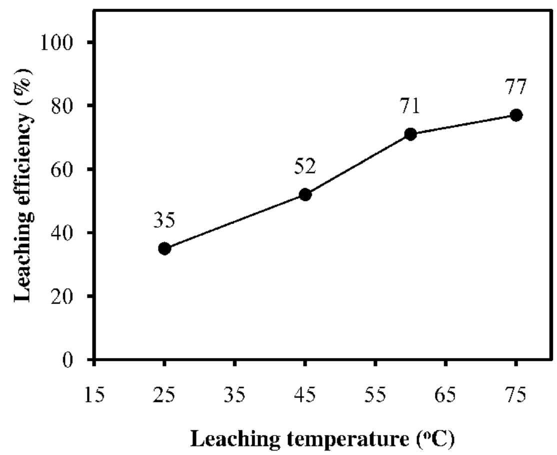

Fig. 2. Effect of leaching temperature on the vanadium leaching efficiency. Other constant parameters are: acid concentration: 15%, acid/TPPA ratio: 10, leaching time: 120 minutes and particle size of 75 - 150 μm.

vanadium leaching efficiency as a result of increasing acid concentration has also been reported by Chen [3], Vitolo [15], Li [23] and Zhou [26]. Chen believes this behavior is related to the fact that at higher acid concentration, H^+ ions have more chance to attack the sample [3].

According to Fig. 1, leaching efficiency reaches the maximum value of about 70% and after that changes very slowly. Since the higher acid concentration makes the process more corrosive and dangerous, optimum acid concentration was concluded as being about 15%.

3. 2. Effect of Leaching Temperature

Fig. 2 shows the effect of temperature on the leaching efficiency of vanadium. Other constant parameters are presented in table 1. As figure shows, the temperature has a significant effect on the leaching efficiency so that the efficiency increases from around 30% to about 77% as the temperature increases from 25°C to 75°C.

Significant effect of temperature on the leaching efficiency of vanadium has also been observed by Li et al. [23] during their study on the acid leaching of black shale. Li has reported that leaching efficiency reaches to about 85% when the temperature rises up to 95°C. Similar results have been reported by Aarabi-Karasgani et al. [10] during sulfuric acid leaching of LD converter slag. According to the collision theory, it may be concluded that pronounced increase of leaching efficiency as a result of temperature is related to the increase of vibrations of H^+ ions in the solution which increases the possibility of their efficient attack. Although higher efficiency is anticipated at higher temperatures as Fig. 2 shows, optimum leaching temperature was decided as 75°C, because of the difficulties accompanied with working at higher temperatures in industrial scale. Furthermore, longer leaching time compensates the effect of lower temperature.

3. 3. Effect of acid/TPPA ratio

The effect of acid/TPPA ratio on the leaching efficiency of vanadium is shown in Fig. 3. Other constant parameters are presented in table 1. Since increasing this ratio increases the collision between H+ and TPPA particles, it could be predicted that by increase of acid/TPPA ratio, the leaching efficiency would be increased. Fig. 3 reveals that this prediction is true and leaching efficiency reaches to about 96% with an acid/TPPA ratio of around 20. The role of contact between particles and leachants has been confirmed by Vitolo et al. [15] during their study

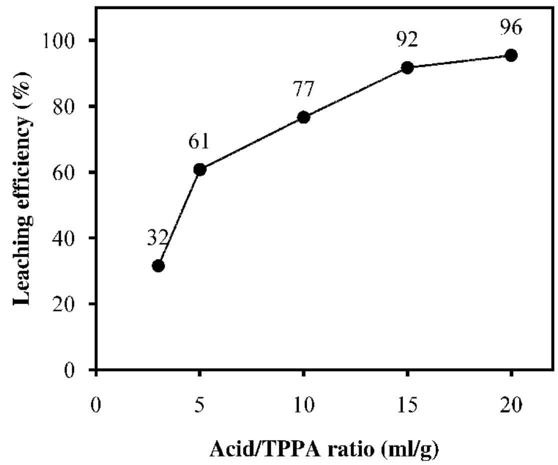

Fig. 3. Effect of acid/TPPA ratio on the vanadium leaching efficiency. Other constant parameters are: acid concentration: 15%, temperature: 75 °C, leaching time: 120 minutes and particle size of 75 - 150 µm.

on the recovery of vanadium from fly ash. Zhou et al. [26] have also reported the enhancement of vanadium recovery from carbonaceous shale as a consequence of increasing the liquid to solid ratio. In Zhou's opinion, this phenomenon could be related to the decrease of viscosity and consequently ease of mass transport in the system at higher acid/TPPA ratios.

As Fig. 3 shows, by increasing acid/TPPA ratio from 15 to 20, leaching efficiency increases only slightly. Hence, acid/TPPA ratio of 15 was decided as the optimum value, because this condition needs less sulfuric acid in the system.

3. 4. Effect of Leaching Time

Fig. 4 represents the effect of leaching time on the recovery efficiency of vanadium. As figure shows, by increasing the leaching time up to 100 minutes, vanadium leaching efficiency increases rapidly. The rate of leaching becomes sluggish after this stage and reaches to around 95% after 150 minutes of leaching. Similar trends have been observed by Li et al. [23] and Chen et al. [3] during the acid leaching of black shale and stone coal, respectively. Improvement of leaching efficiency between 120 to 150 minutes of reaction time is so small that with an economic logic it seems better to determine 120 minutes as the optimum reaction time for the specific conditions reported in table 1.

3. 5. Effect of Particle Size

Fig. 5 shows the effect of TPPA particle size on the leaching efficiency of vanadium. As figure shows, by decreasing the particle size, leaching efficiency has been increased from around 66% to about 95%. Mazurek et al. [8] and Aarabi-

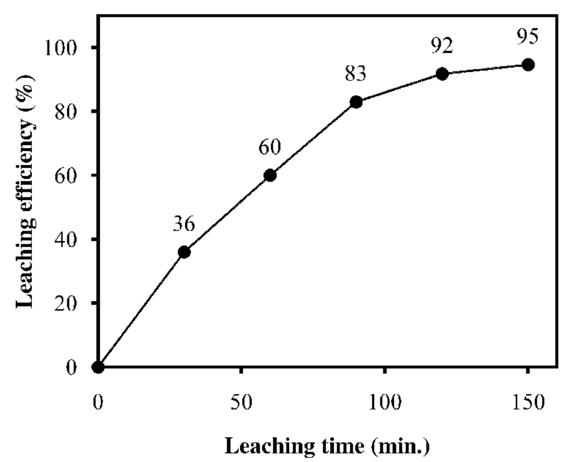

Fig. 4. Effect of leaching time on the vanadium leaching efficiency. Other constant parameters are: acid concentration: 15%, temperature: 75 °C, acid/TPPA ratio: 15 and particle size of 75 - 150 µm.

Table 1. Summary of the experimental conditions.

Step	Investigated parameter	experiment variable				
		Concentration (Vol. %)	T (°C)	acid/TPPA (ml/g)	Time (min)	Particle size (µm)
1	Acid concentration	0	60	10	120	75 - 150
		2	60	10	120	75 - 150
		5	60	10	120	75 - 150
		10	60	10	120	75 - 150
		15*	60	10	120	75 - 150
		20	60	10	120	75 - 150
2	Temperature	**	25	10	120	75 - 150
		**	45	10	120	75 - 150
		**	60	10	120	75 - 150
		**	75*	10	120	75 - 150
3	Acid/TPPA ratio	**	**	3	120	75 - 150
		**	**	5	120	75 - 150
		**	**	10	120	75 - 150
		**	**	15*	120	75 - 150
		**	**	20	120	75 - 150
4	Time	**	**	**	30	75 - 150
		**	**	**	60	75 - 150
		**	**	**	90	75 - 150
		**	**	**	120*	75 - 150
		**	**	**	150	75 - 150
5	Particle size	**	**	**	**	<75
		**	**	**	**	75 - 150*
		**	**	**	**	150 – 250
		**	**	**	**	> 250
*: Optimum value		**: Optimum values found in the previous steps				

Karasgani et al. [10] have also observed similar trends during the dissolution of vanadium from spent catalyst and LD convertor slag, respectively. This phenomenon could be related to the fact that the smaller particles have larger specific area and consequently react with acid sooner and easier. Fig. 5 reveals that decreasing the particle size of TPPA from 75 - 150 µm to less than 75 µm has no appreciable effect on the vanadium leaching efficiency. This means that further milling of TPPA sample is not practically necessary.

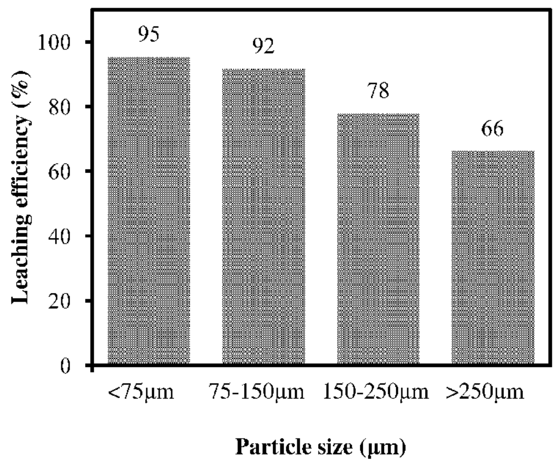

Fig. 5. Effect of particle size on the vanadium leaching efficiency. Other constant parameters are: acid concentration: 15%, temperature: 75 °C, acid/TPPA ratio: 15 and leaching time: 120 minute

4. CONCLUSIONS

In this research work, the effects of different leaching parameters on the sulfuric acid leaching of vanadium in a type of Iranian TPPA have been examined. Experimental results showed that increase of acid concentration, temperature, acid/TPPA ratio and leaching time increase the leaching efficiency. Leaching efficiency also increases by decreasing the particle size of TPPA. Optimum leaching conditions which bring about around 92% recovery was concluded as: acid concentration~15%, temperature~75 °C, acid/TPPA ratio~ 15, leaching time~ 120 minutes and particle size of 75 - 150 μm.

REFERENCES

1. Habashi, F., "Handbook of Extractive Metallurgy", Volume 3, WILEY-VCH; 1997.
2. Meawad, A. S., Bojinova, D. Y. and Pelovski, Y. G., "An overview of metals recovery from thermal power plant solid wastes". Waste Manage, 2010, 30, 2548.
3. Chen, X. Y., Lan, X. Z., Zhang, Q. L., Ma, H. Z. and Zhou, J., "Leaching vanadium by high concentration sulfuric acid from stone coal". Trans Nonferr Metal Soc, 2010, 20, s123.
4. Li, C. X., Wei, C., Deng, Z. G., Li, M. T., Li, X. B. and Fan, G., Recovery of vanadium from black shale. Trans Nonferr Metal Soc, 2010, 20, s127.
5. Amer, A. M., "Processing of Egyptian boiler-ash for extraction of vanadium and nickel". Waste Manage, 2002, 22, 515.
6. Tsai, S. L. and Tsai, M. S., "A study of the extraction of vanadium and nickel in oil-fired fly ash". Resour Conserv Recyc, 1998, 22, 163.
7. Salmiaton, A. and Garforth, A. A., "Multiple use of waste catalysts with and without regeneration for waste polymer cracking". Waste Manage, 2011, 31, 1139.
8. Mazurek, K., Białowicz, K. and Trypuć, M., "Recovery of vanadium, potassium and iron from a spent catalyst using urea solution". Hydrometallurgy, 2010, 103, 19.
9. Li, M., Wei, C., Fan, G., Li, C., Deng, Z. and Li, X., "Extraction of vanadium from black shale using pressure acid leaching". Hydrometallurgy, 2009, 98, 308.
10. Aarabi-Karasgani, M., Rashchi, F., Mostoufi, N. and Vahidi, E., "Leaching of vanadium from LD converter slag using sulfuric acid". Hydrometallurgy, 2010, 102, 14.
11. Alonso-Hernández, C. M., Bernal-Castillo, J., Bolanos-Alvarez, Y., Gómez-Batista, M. and Diaz-Asencio, M., "Heavy metal content of bottom ashes from a fuel oil power plant and oil refinery in Cuba". Fuel, 2011, 90, 2820.
12. Marrero, J., Polla, G., Jiménez Rebagliati, R.,

Plá, R., Gómez, D. and Smichowski, P., "Characterization and determination of 28 elements in fly ashes collected in a thermal power plant in Argentina using different instrumental techniques". Spectrochim Acta, Part B, 2007, 62, 101.
13. Murase, K., Nishikawa, K. I., Ozaki, T., Machida, K. I., Adachi, G. Y. and Suda, T., "Recovery of vanadium, nickel and magnesium from a fly ash of bitumen-in-water emulsion by chlorination and chemical transport". J Alloys Compd, 1998, 264, 151.
14. Kashiwakura, S., Kubo, H., Kumagai, Y., Kubo, H., Matsubae-Yokoyama, K., Nakajima, K., et al., "Removal of boron from coal fly ash by washing with HCl solution". Fuel, 2009, 88, 1245.
15. Vitolo, S., Seggiani, M., Filippi, S. and Brocchini, C., "Recovery of vanadium from heavy oil and Orimulsion fly ashes". Hydrometallurgy, 2000, 57, 141.
16. Panichev, N., Mandiwana, K., Moema, D., Molatlhegi, R. and Ngobeni, P., "Distribution of vanadium(V) species between soil and plants in the vicinity of vanadium mine". J Hazard Mater, 2006, 137, 649.
17. Szymczycha-Madeja, A., "Kinetics of Mo, Ni, V and Al leaching from a spent hydrodesulphurization catalyst in a solution containing oxalic acid and hydrogen peroxide". J. Hazard Mater, 2011, 186, 2157.
18. Navarro, R., Guzman, J., Saucedo, I., Revilla, J. and Guibal, E., "Vanadium recovery from oil fly ash by leaching", precipitation and solvent extraction processes. Waste Manage, 2007, 27, 425.
19. Al-Ghouti, M. A., Al-Degs, Y. S., Ghrair, A., Khoury, H. and Ziedan, M., "Extraction and separation of vanadium and nickel from fly ash produced in heavy fuel power plants". Chem Eng J, 2011, 173, 191.
20. Ye, P., Wang, X., Wang, M., Fan, Y. and Xiang, X., "Recovery of vanadium from stone coal acid leaching solution by coprecipitation", alkaline roasting and water leaching. Hydrometallurgy, 2012, 117-118, 108.
21. Hu, Y.-j., Zhang, Y.-m., Bao, S.-x. and Liu, T., "Effects of the mineral phase and valence of vanadium on vanadium extraction from stone coal". Int J Miner Metall Mater, 2012, 19, 893.
22. Zeng, L. and Cheng, C. Y., "A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts". Hydrometallurgy, 2009, 98, 1.
23. Li, M., Wei, C., Fan, G., Wu, H., Li, C. and Li, X., "Acid leaching of black shale for the extraction of vanadium". Int J Miner Process, 2010, 95, 62.
24. Li, X.-s. and Xie, B., "Extraction of vanadium from high calcium vanadium slag using direct roasting and soda leaching". Int J Miner Metall Mater, 2012, 19, 595.
25. Liu, Y. h., Yang, C., Li, P.-y. and Li, S.-q., "A new process of extracting vanadium from stone coal. Int J Miner Metall Mater", 2010, 17, 381.
26. Zhou, X., Li, C., Li, J., Liu, H. and Wu, S., "Leaching of vanadium from carbonaceous shale". Hydrometallurgy, 2009, 99, 97.