



The leaching of vanadium pentoxide using sulfuric acid and sulfite as a reducing agent



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ABSTRACT

Vanadium has been produced from both primary and secondary sources having various compositions. One of the most available sources of vanadium is vanadium pentoxide. In this paper, vanadium pentoxide leaching was investigated using three chemistries. First, vanadium leaching and the solubility of pentavanadyl ion (VO_2^+) at different pHs and temperatures were investigated in the sulfuric acid system. It was shown that decreasing pH and temperature as well as increasing sulfate concentration in the solution will increase the solubility and extraction of vanadium. The extraction of vanadium (V) was found to be limited by solubility. To overcome the solubility problem of vanadium (V), the kinetics of vanadium leaching from vanadium pentoxide at mildly basic pHs and reductive leaching in the low acidic pHs were then investigated. The kinetics of leaching was reasonably fast in both cases. Moreover, the progressive-conversion model was applied to model reductive leaching of vanadium using sodium sulfite. The rate of the reaction was reported as:

$$\text{rate} = k^* \frac{[\text{H}^+]}{(K_e + [\text{H}^+])^{0.5}} [\text{SO}_2]_{\text{total}}^{0.57}$$

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1. Introduction

Vanadium is a valuable rare metal found in over 50 different minerals (Gupta and Krishnamurty, 1992; Moskalyk and Alfantazi, 2003). As well as using vanadium in metal alloys, other applications such as catalysts, biological application, and vanadium batteries have recently increased the importance of vanadium (Gupta and Krishnamurty, 1992; Habashi, 1998). The increasing demand for vanadium requires increased knowledge of the possible routes to vanadium recovery from a variety of raw materials.

A significant number of reports about vanadium leaching have been published in recent years. Table 1 summarizes some of the important research studies on vanadium leaching from different resources. Vanadium is produced from primary and secondary sources such as fly ash, spent catalyst, and steel slags (Izquierdo and Querol). Vanadium leaching has yielded a wide range of results. Varying conditions, such as solvent pH and temperature range as well as solid to liquid ratio, have been applied in order to obtain reasonable recovery of vanadium from different sources. In addition to this wide variety of results, some studies have shown opposite effects by varying certain parameters in the vanadium leaching process. For instance, regarding the effect of additives, Li et al. (2009) and Xiang-yang et al. (Chen et al., 2010)

investigated NaClO and MnO_2 , respectively, as an oxidizer to increase vanadium recovery in leaching. Furthermore, Okuwaki et al. (1988) and Li et al. (2010c) studied H_2SO_3 and FeSO_4 , respectively, as a reductive agent to increase leaching recovery. Moreover, Li et al. (2009) showed that FeSO_4 has no effect on vanadium leaching while Xiang-yang et al. (Chen et al., 2010) reported that FeSO_4 decreases vanadium recovery. The lack of primary research on vanadium leaching as well as contradictory results in the literature has prompted an interest in studying vanadium (V) leaching in a more fundamental way. Therefore, the leaching of vanadium (V) at different pHs and reductive leaching of vanadium (V) to vanadium (IV) have been investigated.

2. Materials and methods

Pure vanadium pentoxide (V_2O_5) from Fisher Scientific was used for leaching experiments. The purity of vanadium pentoxide was greater than 99.6% with low levels of iron (0.01% max), aluminum (0.03% max), silicon oxide (0.01% max), sulfur (0.01% max), and phosphorus (0.01% max). The phase composition of vanadium pentoxide was also confirmed by XRD analysis. The effect of impurities was not considered in our experiments. The vanadium pentoxide was screened to various particle size fractions for the study. The leaching/solubility procedure using 90 μm average (75–106 μm) particle size was performed in a Pyrex reactor equipped with a magnetic stirrer and a reflux condenser. A water bath was used for controlling the temperature. The final

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Table 1
Vanadium leaching reports in literature.

No.	Source	Vanadium content (%)	Extraction (%)	Solvent	Solvent conc.	Temp. (°C)	S/L ratio (g/L)	Time (min)	Ref.
1	HDS catalyst	15	81.8	H ₂ O	–	Boiling	–	–	Biswas et al. (1985)
2	EP ash	1.93–3.36	95	H ₂ SO ₄	0.5 M	70	0.125	45	(Okuwaki et al. (1988)
3	Fly ash	1.8	63	Na ₂ CO ₃	2 M	25	0.2	420	Akita et al. (1995)
			10	NH ₄ Cl	2 M	25	0.2	420	Akita et al. (1995)
			20	(NH ₄) ₂ CO ₃	2 M	25	0.2	420	Akita et al. (1995)
4	Fly ash	0.41 & 1.91	95	H ₂ SO ₄	2 M	30	0.2	120	Tsai and Tsai (1998)
			75	NaOH	2 M	30	0.2	120	Tsai and Tsai (1998)
			48	NH ₄ OH	2 M	30	0.2	120	Tsai and Tsai (1998)
5	Spent petroleum catalyst	27.28 (V ₂ O ₅)	90	NH ₃	15 M	95	100	1440	Villarreal et al. (1999)
			90	NaOH	pH = 8	95	100	1440	Villarreal et al. (1999)
6	Fly ash	1.3–3.3	80–95	H ₂ SO ₄	2 M	Boiling	333.34	30	Vitolo et al. (2000)
7	Fly ash	3.8 (19 wt.% after burning)	97	H ₂ SO ₄	2 M	Boiling	142.85	60	Vitolo et al. (2001)
8	Boiler ash	20	98	H ₂ SO ₄	0.6 M	220	0.5	30	Amer (2002)
9	Fly ash	0.93	80	NaOH	5 M	–	100	5760	Guibal et al. (2003)
		0.93	90	H ₂ SO ₄	0.5 M	Ambient	100	1440	Guibal et al. (2003)
10	Spent catalyst	0.42	90.1	Water	–	80–90	0.5	15	Chen et al. (2006)
11	Fly ash	1.6	98	H ₂ SO ₄	0.5 M	Ambient	250	1440	Navarro et al. (2007)
			56	NaOH	2 M	Ambient	250	1440	Navarro et al. (2007)
			60	Na ₂ CO ₃	0.66 M	Ambient	250	1440	Navarro et al. (2007)
12	Black shale mine	3.26 (V ₂ O ₅)	75	H ₂ SO ₄	2 M	180	833.34	240	Li et al. (2009)
13	Black shale mine	0.56 (V ₂ O ₅)	86	H ₂ SO ₄	0.87 M	95	250	8640	Li et al. (2010a)
14	Stone coal	1.09	85	H ₂ SO ₄	1 M	95	333.34	120	Chen et al. (2010)
15	Steel slag	8.46 (V ₂ O ₅)	90	NaOH	0.4 M	240	500	350	Xiao et al. (2010)
16	LD convertor slag	1.97 (V ₂ O ₅)	90	H ₂ SO ₄	3 M	70	0.067	140	Aarabi-Karagani et al. (2010)
17	Black shale mine	6.15 (V ₂ O ₅)	70	H ₂ SO ₄	2 M	150	14.28	60	Li et al. (2010b)
18	Calcium vanadate	65.5 (V ₂ O ₅)	95	Na ₂ CO ₃	1.2 M	80	40	60	Wang-xing et al. (2010)
19	Spent petroleum catalyst	9	80	H ₂ SO ₄	1 M	30	0.1	120	Mishra et al. (2010)
20	Stone coal	1.82	91	H ₂ SO ₄	0.3 M	150	0.833	240	Deng et al. (2010)

solution was filtered using an ashless syringe filter paper and analyzed for vanadium content with Inductively Coupled Plasma spectroscopy (ICP, made by PerkinElmer; model Optima 7300). The pH was continuously monitored by a controller connected to the computer. The pH was kept constant (± 0.01) during the leaching process by the addition of concentrated sulfuric acid from the acid stock tank on the digital scale connected to an accurate pump and controller. The vanadium extraction was confirmed using mass balance by weighting the remaining solid after each test and calculating the extent of leaching. In the second step, the kinetics of vanadium pentoxide leaching by weak acid solution (pH = 5) and dilute sodium hydroxide solution (pH = 8) was studied. In these tests, pH was kept constant by adding sodium hydroxide during the experiment. Vanadium (V) concentration was also analyzed by Inductively Coupled Plasma spectroscopy (ICP).

In the third step, the kinetics of reductive leaching of vanadium (V) using sodium sulfite was also investigated. The effect of pH, temperature, and sulfite concentration on the kinetics was studied. For this part of the project, UV–Visible spectroscopy (made by PerkinElmer; model Lambda 35) was applied to analyze vanadium (IV) concentration in the solution (Kanamori et al., 1999; Yang and Gould, 2003). UV–Visible spectroscopy showed a suitable accuracy for vanadium (IV) standard solutions in sulfuric acid.

3. Results and discussion

3.1. Solubility

The kinetics of V₂O₅ leaching at different solid to liquid ratios was studied. As Fig. 1 shows, the kinetics of vanadium (V) leaching is fast at 90 °C. However, at a high solid to liquid ratio, the leaching halted abruptly after a short time, apparently because the vanadium solution had reached its solubility limit. In fact, the solution has been saturated by vanadium to the same concentration for the experiments performed at 5 and 10 g/L solid to liquid ratio. This means that when there is enough sulfuric acid in solution, the leaching can be completed quickly. However, acid concentration must be kept high through the leaching process. This suggests that the final leach solution will have significant

amounts of sulfuric acid which should be neutralized by sodium hydroxide before the purification step.

The solubility of VO₂⁺ was studied at different pHs from 0.3 to 1.4 and at various temperatures. Fig. 2 represents vanadium extraction versus time in different pHs at 90 °C. The limiting concentration reached in each experiment after 8 h of leaching represents the solubility of pentavalent vanadium in solution. The same calculations have been made for temperatures 30, 50 and, 70 °C and the results were reported in Table 2.

The results show that the kinetics of leaching vanadium to VO₂⁺ is fast, but that this species suffers from low solubility. Thermodynamic data was studied for comparison with the experimental results. Table 3 shows the thermodynamics data for the following reaction which can occur in acidic media:

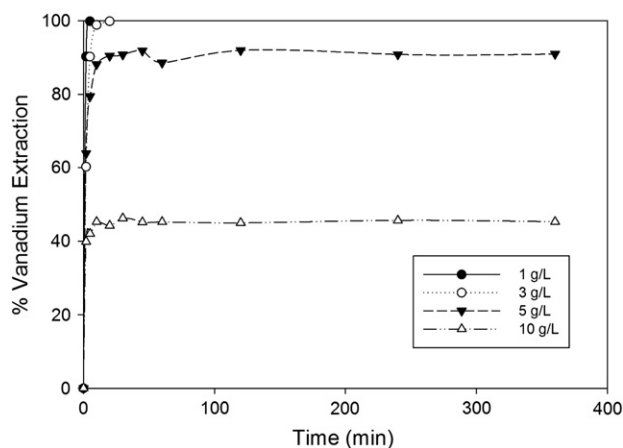


Fig. 1. The effect of solid to liquid ratio on V₂O₅ leaching (30 g/L H₂SO₄, 90 °C, 90 μm and 600 rpm).

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