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The kinetics of oxidative leaching of vanadium trioxide

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ABSTRACT

The oxidative leaching of vanadium trioxide was studied in sulfuric acid solutions from 30 °C to 90 °C. This study was performed in three stages. First, the kinetics of leaching using oxygen was investigated. It was shown that this oxidative leaching is chemically-controlled with an activation energy of around 69 kJ/mol. Secondly, vanadium(III) oxidative leaching was studied using ferric ions and oxygen. The presence of ferric enhanced kinetics significantly. Finally, oxidative leaching using a constant ferric–ferrous ratio from 1 to 300 was investigated. Potassium permanganate ($KMnO_4$) was found to be a suitable oxidant for controlling solution potential. The oxidation rate using a constant ferric–ferrous ratio was very sensitive to temperature, giving a large activation energy (38 kJ/mol) and was proportional to the Fe(III)/Fe(II) ratio to the power of 0.47. The leaching rate using the shrinking sphere model was modeled as:

$$\frac{\partial d}{\partial t} = 12,088 \times \exp\left(-\frac{4580}{T}\right)\left(\frac{C_{\mathrm{Fe(III)}}}{C_{\mathrm{Fe(II)}}}\right)^{0.47} \quad \frac{\mu\mathrm{m}}{\mathrm{min}}.$$

1. Introduction

Vanadium has been used in a wide variety of applications such as metal alloys, catalysts, biological application and mass storage batteries. The extraction of vanadium from ore uses processes such as roasting followed by leaching, while direct atmospheric or pressure leaching has been used to leach vanadium from primary and secondary resources (Gupta and Krishnamurthy, 1992; Zeng and Cheng, 2009). Roasting of vanadium ore is effective; but, roasting requires high temperatures and a significant amount of chemical additive to make sodium metavanadate (Biswas et al., 1985; Chen et al., 2006; Holloway and Etsell, 2004).

A wide range of conditions have been investigated for the direct leaching of vanadium from various ores (Tavakoli et al., 2014). Sulfuric acid solutions were tested at a concentration of 0.5 M for fly ash leaching (Okuwaki et al., 1988), 1 M for stone coal and spent catalyst leaching (Chen et al., 2010; Mishra et al., 2010), 2 M for fly ash and black shale leaching (Li et al., 2009, 2012; Navarro et al., 2007; Vitolo et al., 2000; Vitolo et al., 2001) and even 4 M for oil-fired fly ash leaching (Tsai and Tsai, 1998). Likewise in kinetics studies, Aarabi-Karasgani et al. (2010) reported diffusion control in the first 15 min followed by chemical control for the rest of the leaching of vanadium from steelmaking converter slag. Lozano and Juan (2001) determined that the dissolution kinetics of vanadium from spent catalysts is diffusion-controlled and reported an activation energy of 18 kJ/mol. However, since the oxidation state of vanadium in the raw material was often unknown in most reports, behavior of vanadium oxides leaching was not studied sophisticatedly.

Vanadium trioxide (V_2O_3) is one the most stable and well-known forms of vanadium oxide. However, the kinetics of dissolution of this oxide has been insufficiently studied. Amer (1994) showed that the most favorable conditions for the extraction of 95% of the vanadium present as vanadium trioxide in black shale are: 180 °C, around 1 M sulfuric acid, 61–88 μm in size and 40 min leaching. It was indicated that the kinetics of vanadium dissolution was mixed-controlled and the overall activation energy was reported to be 30 kJ/mol. Li et al. (2012) observed that oxidative conditions using oxygen can increase leaching efficiency from black shale containing a mixture of vanadium(IV) and (III) oxides. The activation energy was reported as 40 kJ/mol. Zhou et al. (2012) showed that vanadium trioxide can be completely leached in about 20 min in 1 M sulfuric acid with an oxygen partial pressure of 1 MPa at 140 °C. A chemically-control mechanism was reported with an activation energy of 43 kJ/mol. A shrinking core model was used for the leaching of pure vanadium trioxide. There was no ash layer reported for leaching of the pure vanadium trioxide. In another research, Qiu et al. (2011) investigated pressure oxidative leaching of vanadium trioxide using sodium hydroxide. They found that about 90% of vanadium can be dissolved in a solution of 2 M sodium hydroxide, oxygen partial pressure of 500 kPa and 130 °C in about 40 min. They offered a two-stage kinetics model: the chemically controlled regime for the initial step and diffusion for the second step.

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This study investigates the acid oxidative leaching of vanadium using vanadium trioxide (V_2O_3). The kinetics of atmospheric oxidative leaching of pure V_2O_3 in sulfuric acid was studied using oxygen alone, oxygen and ferric, and ferric separately. The effect of the main factors of the oxidative leaching of V_2O_3 was examined and the shrinking sphere model was applied to describe the kinetics model.

2. Experimental method

Pure (99.7%) chemical grade made by Alfa Aesar was used. The procedure involved leaching V_2O_3 having an average particle size of 90 μm (75–106 μm) in 0.5 L sulfuric acid solution in a 1 L Pyrex reactor equipped with a magnetic stirrer for agitation and a reflux condenser to prevent water loss. The pH was controlled and recorded via a data acquisition system connected to the computer. At 30 °C, 94 g/L of sulfuric acid made a solution of pH 0. For experiments at higher temperature; more sulfuric acid concentrations were added to keep an initial pH of 0. The reactor was immersed in a water bath to control temperature. Solution samples were withdrawn over time. The final slurry was filtered using ashless syringe filter paper and analyzed for vanadium content by ICP (PerkinElmer model Optima 7300) or UV–visible spectroscopy (PerkinElmer model Lambda 35). The leaching kinetics was investigated in three steps. First, the oxidation of V_2O_3 using oxygen was studied. A flow of 480 mL/min of oxygen with a purity of more than 99.5% was injected to the solution contained 1 g/L of V_2O_3 in sulfuric acid. The effect of temperature, pH, particle size and stirring speed was studied. Different particle sizes (P_{50}: 55, 90 and 128 μm) were prepared by screening the pure starting material. Secondly, a mixture of ferric and oxygen as oxidative agents was used. For these experiments, 180 mL/min of oxygen and 1 g/L of V_2O_3 were used. The effect of the initial ferric concentration, temperature and pH was studied. Finally, in the third step, the isokinetic technique (Bouffard et al., 2006) was applied to study the kinetics of vanadium oxidative leaching. For these experiments, 1 g/L of V_2O_3 was leached in sulfuric acid solution at pH 0. Leaching tests were performed under isokinetic conditions which involved the control of every relevant variable during leaching. The potential, relate to ferric/ferrous ratio, was kept constant by adding drops of potassium permanganate ($KMnO_4$) to the slurry. The mass of $KMnO_4$ solution was continually monitored via a digital scale connected to a computer for continuous data capture. Potassium permanganate is highly soluble in acidic media and rapidly re-oxidizes ferrous to ferric ion. Permanganate has a simple aqueous chemistry at pH ≤ 2; it generates five electron-moles per mole of reduced permanganate. The vanadium concentration for each sample was calculated considering the volume of the added sodium permanganate solution to the reactor and the withdrawal of samples during the test.

3. Results and discussion

3.1. V_2O_3 leaching using oxygen

The leaching of vanadium trioxide using oxygen is thermodynamically favorable and exothermic (HSC).

$$2V_2O_3 + O_{2(g)} + 8H^+ = 4VO^{+2} + 4H_2O \qquad \Delta G^\circ(\text{at } 25\ ^\circ C) = -462.35\ \text{kJ/mol}. \tag{1}$$

3.1.1. Effect of temperature

Fig. 1 illustrates the effect of temperature on vanadium extraction. Increasing the temperature from 50 °C to 70 °C increased the reaction rate significantly.

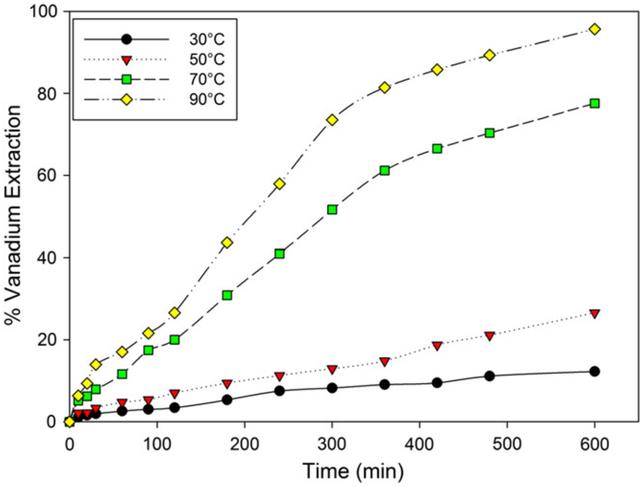

Fig. 1. The effect of temperature on vanadium leaching (at 1 g/L V_2O_3, 480 mL/min O_2, 90 μm average particle size, pH 0 and 600 rpm).

Temperature has an effect on the solubility of oxygen, the diffusion of oxygen in the solution and the chemical reaction rate. The solubility of oxygen in a solution at different temperatures can be expressed by Eq. (2) (Tromans, 1998; Tromans, 2001):

$$\left(C_{aq}\right)_I = \left[\frac{1}{1+k(C_I)^y}\right]^{\eta} P_{O_2} f(T) \tag{2}$$

where

$$f(T) = \exp\left[\frac{0.046T^2 + 203.35T\ln\left(\frac{T}{298}\right) - (299.378 + 0.092T)(T-298) - 20.591\times10^3}{8.314T}\right]$$

and where $(C_{aq})_I$ is the molal solubility of oxygen and the coefficient k and the exponent y and η are solute-specific parameters (2.02, 1.25 and 0.17 respectively for sulfuric acid solution). Based on Eq. (2), increasing acid concentration can decrease oxygen solubility. For a solution of H_2SO_4 at pH 0, the dissolved oxygen concentration was calculated at about 9.54×10^{-5}, 6.93×10^{-5}, 4.8×10^{-5} and 2.1×10^{-5}m for temperature 30, 50, 70 and 90 °C respectively.

Likewise, it should be considered that by increasing temperature, the diffusion coefficient of oxygen in the solution increases more than three times from 30 °C to 90 °C (Tromans, 2001). However, since solubility of dissolved oxygen decreases by a factor of nearly 5× when increasing temperature from 30 to 90 °C in the system, it can be assumed that the mass transfer rate for oxygen is not increasing fast enough to produce the rapid increase in vanadium leaching kinetics shown in Fig. 1. It is likely the increasing kinetics of the oxidative leaching process produces the significant increase in the observed leaching rates.

Since pure V_2O_3 was used, particles shrunk in size throughout the leaching. There is no core or ash layer; all the particles are depleted at the end. The shrinking sphere model has been chosen for describing the kinetics. When chemical reaction is the rate controlling step, the fraction of vanadium reacted at any time can be predicted by (Levenspiel, 1998):

$$\frac{t}{\tau} = 1-(1-X)^{\frac{1}{3}} \tag{3}$$

where

$$\tau = \frac{\rho R_\circ}{b k_S C}$$

and where $R_\circ$ is the average radius of a spherical particle, ρ is the molar density of the sample, b is the stoichiometric coefficient of the reaction; k_s is the rate constant for surface reaction, and C is the concentration of the reactant in the bulk solution.