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Release kinetics of vanadium from vanadium titano-magnetite: The effects of pH, dissolved oxygen, temperature and foreign ions

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ABSTRACT

As part of a broader study of the environmental geochemistry behavior of vanadium (V), the release kinetics of V from the dissolution of natural vanadium titano-magnetite under environmentally relevant conditions was investigated. In both the acidic and basic domains, the V release rate was found to be proportional to fractional powers of hydrogen ion and dissolved oxygen activities. The dependence of the rate on dissolved oxygen can also be described in terms of the Langmuir adsorption model. The empirical rate equation is given by: $r = k' \alpha (\text{H}^+)^{\alpha} \frac{K \alpha (\text{O}_2)}{1 + K \alpha (\text{O}_2)}$ where, $\alpha = 0.099\text{--}0.265$, $k' = 3.2 \times 10^{-6}\text{--}1.7 \times 10^{-5}$, $K = 2.7 \times 10^4\text{--}3.9 \times 10^4 \text{ mol/L}$ in acid solution (pH 4.1), and $\alpha = -0.494\text{--}(-0.527)$, $k' = 2.0 \times 10^4\text{--}2.5 \times 10^{-11}$, and $K = 4.1 \times 10^3\text{--}6.5 \times 10^3 \text{ mol/L}$ in basic solution (pH 8.8) at 20°C. Based on the effect of temperature on the release rate of V, the activation energies of minerals at pH 8.8 were determined to be 148–235 kJ/mol, suggesting that the dissolution of vanadium titano-magnetite is a surface-controlled process. The presence of Na^+ , Ca^{2+} , Mg^{2+} , K^+ , NO_3^- , Cl^- , SO_4^{2-} and CO_3^{2-} was found to accelerate the V release rates. This study improves the understanding of both the V pollution risk in some mine areas and the fate of V in the environment.

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Introduction

Concerns over the potential adverse health effects of vanadium (V) have led the Chinese Ministry of Environmental Protection to list it as a priority prevention and control hazardous heavy metal. The U.S. Environmental Protection Agency has placed V

on the top of its list of contamination candidates (Imtiaz et al., 2015). Extensive mining and smelting activities have had major environmental impacts in mines or nearby regions, resulting in abnormally elevated concentrations of V in the water and soil near mines or smelting sites. For example, the concentration of V in mostly unpolluted surface water

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resources is approximately 3 $\mu\text{g/L}$ or less, but the value increases to approximately 70 $\mu\text{g/L}$ near high level geochemical sources (Hamada, 1998; WHO, 2001). The V concentration in water from the Colorado River basin (USA) near mining areas for uranium-vanadium was 49.2 $\mu\text{g/L}$ (Linstedt and Kruger, 1969). Our latest analysis data also showed that in a downstream river of a shut-down smelter located in Hubei province in China, the concentration of V reached up to 200–6700 $\mu\text{g/L}$, while in the control sites, the values were only 10–30 $\mu\text{g/L}$. The average V content in various soil types varied from 10 to 220 mg/kg dry mass, while the soils in mining areas contained V concentrations up to 738–3505 mg/kg (Małuszynski, 2007; Panichev et al., 2006; Poledniok and Buhl, 2003; Teng et al., 2006, 2011).

Mineral dissolution is considered to be an important source of heavy metals in the environment. For example, weathering and leaching of minerals causes elevated concentrations of a broad range of potentially toxic elements, such as As, Pb and Sb, which are enriched in metal minerals (Hu et al., 2014, 2016a, 2016b; Shi and Stone, 2009; Walker et al., 2006). Vanadium-containing ore deposits are found in many parts of the world and are usually associated with other elements, such as iron, phosphorus, and uranium (Baroch, 2006; Lide, 2008). Titano-magnetite deposits are the primary source of V. In China, an estimated 40% of V production is from vanadiferous slag. As the most important base of V production in the world, the giant Panzhihua Vanadium Titanium Magnetite ($\text{Fe}(\text{V}, \text{Ti})_3\text{O}_4$) deposit provides 20% of the Fe, 64% of V, and 53% of Ti for China (Teng et al., 2002). However, despite the growing economic importance of V and its compounds and alloys, the kinetic and mechanistic aspects of the weathering of V-containing ores have received little attention. The weathering rate under favorable geochemical conditions and the type of V-bearing source rock were identified as important controlling factors for fluvial dissolved V at high (≥ 50 $\mu\text{g/L}$) and moderate (25 to 49 $\mu\text{g/L}$) concentrations, while the solution chemistry of V or anthropogenic influences were not considered to be important controlling factors (Shiller and Boyle, 1987; Wright and Belitz, 2010). Given the growing recognition of V as an emerging and important contaminant, there is a real need to develop a better understanding of the geochemistry of V in the weathering zone, especially its release behavior from its predominant source, vanadium titanium magnetite minerals.

The aim of the present work is to study the release kinetics of V from the dissolution of vanadium titanium magnetite minerals and to establish kinetic rate laws that are applicable under environmentally relevant conditions. The effects of pH, dissolved oxygen, temperature and ionic strength on the release rates of V were considered.

1. Materials and methods

1.1. Materials

Vanadium titano-magnetite raw mineral was purchased from the National Research Center for Certified Reference Material (Beijing, China). The main composition by weight percent of the mineral provided is total Fe 27.55%, SiO_2 25.47%, TiO_2 9.72%, MgO 6.17%, CaO 7.50%, Al_2O_3 10.29%, and V_2O_5 0.258%.

The X-ray diffraction (XRD) pattern of the ore showed that its dominant component phases are magnetite (Fe_3O_4 , PDF#19-0629) and iron titanium oxide ($(\text{Fe}_{2.5}\text{Ti}_{0.5})_{1.04}\text{O}_4$, PDF#51-1587) (Fig. 1). Its specific surface area is 1.71 m^2/g and the point of zero charge (PZC) is pH 6.3. According to the solubility characteristics of different oxide states of V, through chemical separation, it can be found that V contained in the vanadium titano-magnetite is mainly in the form of trivalent (1.2 mg/g) and pentavalent (1.3 mg/g) oxidation states. The characterization results for natural vanadium titano-magnetite by Liang et al. (2010) indicated that trivalent V in titano-magnetite cannot exist in the form of vanadium oxides, but occupies the octahedral site of magnetite. The pentavalent V was recognized as pentavalent vanadium oxide by X-ray photoelectron spectroscopy (XPS) analysis (Fig. 1). The other chemicals used had a purity of analytical grade or better and were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All aqueous solutions were prepared using deionized water (18.2 M Ω /cm at 25°C) from a Milli-Q water purification device. Highly pure O_2 and N_2 gases (>99.999%) were purchased from Beijing Hai Ke Yuan Chang practical gas Co., Ltd. (China).

1.2. Dissolution experiments

The release rates of V under different conditions were measured using a dynamic mixed flow reactor, avoiding saturation of V in the aqueous solution. The application of the mixed flow reactor in the study of mineral dissolution kinetics was first described and discussed by Rimstidt and Dove (1986) and it has since become a well-established technique. The feed solution was pumped into a reactor (Amicon Ultrafiltration Cell, Model 8200, of nominal volume 200 mL, with diameter 75 mm, Merck Millipore, China) containing 5.0 g of vanadium titano-magnetite using a variable speed peristaltic pump at a rate of 10 mL/min. Then, the reactor was immersed in a water bath that had a constant temperature. Once every hour, 200 mL of reacted feed solution was discharged into a measuring cylinder; simultaneously, fresh feed solution was injected into the reactor. Then, 10 mL was removed from the collected 200-mL solution and filtered using a 0.45- μm cellulose acetate membrane for analysis. The experiments on the effect of the filter procedure on the measured concentration of V were also conducted using 1, 5 and 10 mg/L V standard solutions. After filtering, the loss rates of V ranged from 0.5% to 1.0%, within acceptable limits. The experimental period for each condition was 12 hr. Each experiment was performed once and only repeated when inconsistencies were found in the results.

To test the effect of pH on the release kinetics of V, the pH of the feed solution was adjusted to 4.1, 5.9, 6.9, 7.9, 8.8 and 9.8 using 2-(N-morpholino)-ethanesulfonic acid (MES), 3-(N-morpholino)-propanesulfonic acid (MOPS) and a 1 mol/L NaOH solution. The total concentration of the buffer was 0.05 mol/L. The ionic strength of the solution was adjusted to 0.05 mol/L using NaClO_4 . To test the effect of dissolved oxygen, the feed solution was sparged with oxygen–nitrogen mixtures (5%, 10%, 40%, 60% and 80% O_2) to achieve different concentrations of dissolved oxygen. Feed solutions containing 5 mmol/L and 50 mmol/L Na^+ , Ca^{2+} , Mg^{2+} , K^+ , NO_3^- , Cl^- , SO_4^{2-} and CO_3^{2-} at pH 6.9 were used to test the effects of common ions on the release rate of V. They were prepared by dissolving the corresponding salts in Milli-Q water.

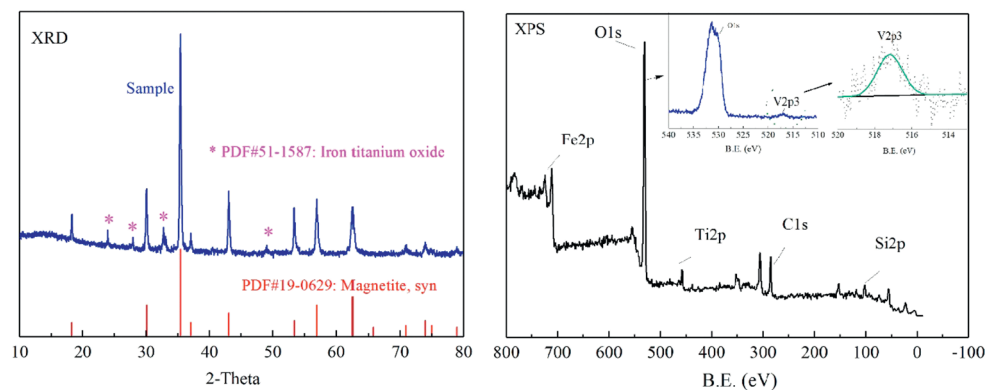


Fig. 1 – The X-Ray Powder Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) characterization of vanadium titanomagnetite.

1.3. Release rate of V

For all of the experiments, the mobilized V mass was plotted as a function of time. From the slopes of these lines, the release rates of V can be calculated from the cumulative amount (μmol) of V_{tot} migrated into the solution (Eq. (1)). Note that we do not convert these release rates of V into dissolution rates of the vanadium titanomagnetite, since the ideal chemical equation of V and the precise stoichiometry of V in the vanadium titanomagnetite are difficult to determine.

$$r = \frac{d[V_{\text{tot}}]}{dt} \quad (1)$$

To determine the quantitative relationship between the release rate of V and both hydrogen ions and dissolved oxygen, an empirical rate law was used and is given by Eq. (2):

$$r = k \cdot \alpha(H^+)^{\alpha} \cdot \alpha(O_2)^{\beta} \quad (2)$$

1.4. Analytical methods

The determination of total V was performed with inductively coupled plasma optical emission spectroscopy (NexION300, PerkinElmer Inc., USA) with a detection limit of $10 \mu\text{g/L}$. For each sample, 3 replicates were measured. The relative standard deviation for each sample was $<1.0\%$. The recoveries of V were $95\%–102\%$ in 10 sample solutions selected randomly. Some aqueous samples needed to be diluted with Milli-Q water to adjust the concentration to within the working range ($0–20 \text{ mg/L}$, $R^2 \geq 0.9990$). The main composition of the ore sample was analyzed by XRD (PANalytical B. V., Holland). The XRD pattern was recorded on a PANalytical X'Pert Pro diffractometer (conditions: $\text{Cu K}\alpha$ radiation, 40 kV and 40 mA). Its specific surface area was determined using a BET N_2 -adsorption Quantachrome Autosorb-iQ surface area measuring apparatus (Boynton Beach, FL). The point of zero charge (PZC) of vanadium titanomagnetite was identified as the pH where the zero zeta potential value was obtained. The zeta potential of the sample was measured using a micro electrophoresis apparatus (ZS90, Malvern Instruments Ltd.) at constant temperature, 298.15 K . Sufficiently dilute suspensions

were prepared with constant ionic strength, 0.05 mol/L . The pH of the suspensions was adjusted to $4.0–10.0$ by small additions of 0.1 mol/L HNO_3 or NaOH solutions. The valence state of V was determined from the X-ray photoelectron spectra (XPS) with an ESCALAB MK II apparatus (VG Scientific Ltd. UK), using Mg K radiation and the carbon $1s$ peak at 284.6 eV as standard.

2. Results and discussion

2.1. Effect of the reaction time on the V release rate

It can be seen from Fig. 2, in general, that the release rate of V gradually decreased with time. Especially at pH values of 5.9 , 6.9 and 7.8 , the release rates in the first 3 hr (751 , 1291 and $959 \mu\text{mol/hr}$) were $1.4–2.5$ times greater than the rates at 12 hr (555 , 633 and $503 \mu\text{mol/hr}$). However, as time went on, the difference in the time-dependent rates gradually diminished. The most likely reason for this decrease is that (1) the highly reactive surface of the freshly ground minerals, with sharp edges, stressed areas and adherent small grains, reacts more rapidly than the bulk solid (Rimstidt and Dove, 1986).

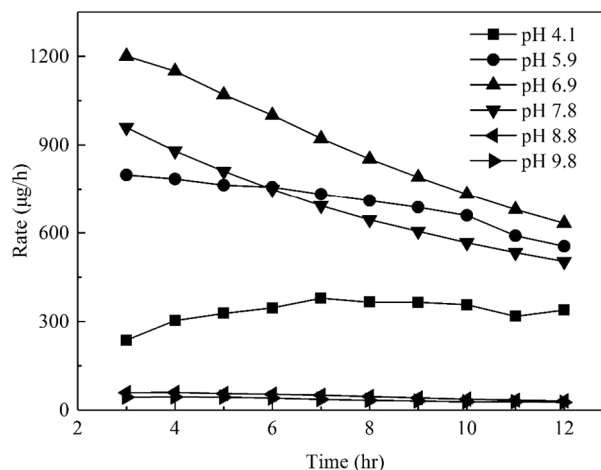


Fig. 2 – The release rate of vanadium (V) as a function of time at different pH values.

Therefore, more V was released from the dissolution of ultrafine grains in the first few hours. After rapid dissolution, the bulk mineral surface was exposed to aqueous solution and the mineral dissolution rate slowed, which then reduced the release rate of V. (2) The dissolved release behavior of the main coexisting elements (Fe or Ti) contained in the vanadium titanium magnetite mineral may also have affected the release rate of V with time. However, neither Fe nor Ti was detected in the solution (<0.01 mg/L detectable level) at studied pHs (4.1–9.8). This illustrated that the formation of surface complexes between dissolved V and iron or titanium (hydr)oxide may have delayed the release of V (Naeem et al., 2007). (3) The content of V in the mineral gradually decreased with time, resulting in a lower concentration of V in the solution as time went on. In view of the differences in the release rates at different times, the release rates of V for 3–12 hr were separately calculated and are discussed in the subsequent sections.

2.2. Effect of hydrogen ions on the release rate of V

2.2.1. Acid solution

Under relatively constant dissolved oxygen activity $\alpha(\text{O}_2) = 2.61 \times 10^{-4}$ mol/L, which corresponds to saturation with O_2 under atmospheric conditions, the average release rates of V at 3–12 hr increased from 4.62–6.64 $\mu\text{mol/hr}$ to 12.4–25.3 $\mu\text{mol/hr}$ when the pH increased from 4.1 to 6.9. Werner Stumm had emphasized that the pH-dependent surface charge of minerals is an important factor for their dissolution, with the minimum dissolution rates of minerals generally occurring at the pH_{PZC} (Stumm and Morgan, 1996). However, the pH_{PZC} of vanadium titanium magnetite mineral was measured as 6.3, so it did not follow the law. It is possible that some complex consequent reactions (i.e., adsorption or precipitation) after the dissolution of vanadium titanium magnetite mineral affected the release behavior of V. The logarithm of the release rate at 3–12 hr depended linearly on the logarithm of the hydrogen ion concentration (Fig. 3). From the slope of the fitting curves,

the average release rates of V at different times increased as $\alpha(\text{H}^+)^{0.099-0.265}$ with a correlation coefficient $R^2 > 0.963$, and the obtained activity coefficient of H^+ , α , at 3 hr was 2.7 times that at 12 hr, illustrating that the degree of dependence of the release rate on pH decreased with time.

2.2.2. Basic solution

Under the same conditions as above, the rate increased with decreasing hydrogen ion activity as $\alpha(\text{H}^+)^{-0.494} - (-0.527)$ with $R^2 > 0.807$ (Fig. 3). The absolute value of the activity coefficient of H^+ (α) was higher than that in the acidic solution, indicating that hydroxyl ion (OH^-) in the alkaline solution had a more significant effect on the release of V than hydrogen ion in the acidic solution. The average release rates sharply decreased from 9.86–18.8 $\mu\text{mol/hr}$ to 0.52–0.86 $\mu\text{mol/hr}$ when the pH increased from 7.9 to 9.8. The former rates are approximately 19–22 times greater than the latter. For $\text{pH} > 8$, there was almost no V release into the aqueous solution. Therefore, it seems that V is not as rapidly mobilized under harshly basic conditions as under relatively mild acidic and basic conditions (pH 5.9–7.9).

2.3. Effect of dissolved oxygen on the V release rate

For these experiments, the temperature (293.15 K) and pH were kept constant at 4.1 or 8.8 and the concentration of dissolved oxygen was varied by applying partial pressures of O_2 corresponding to 5%, 10%, 21%, 40%, 60% and 80% of the atmospheric pressure. The $\alpha(\text{O}_2)$ was calculated using the known partial pressure over the influent solution and the temperature dependence of Henry's constant for O_2 (Clegg and Brimblecombe, 1990). The rates were fitted to fractional orders of $\alpha(\text{O}_2)$ (Fig. 4). When the feed solution was equilibrated with gas mixtures containing more than 40% O_2 , a decreasing trend in the reaction rate was observed at pH 4.1. This suggests that oxygen adsorption on the mineral surface may be a limiting step and that the surface becomes saturated at a certain partial pressure of O_2 above the influent

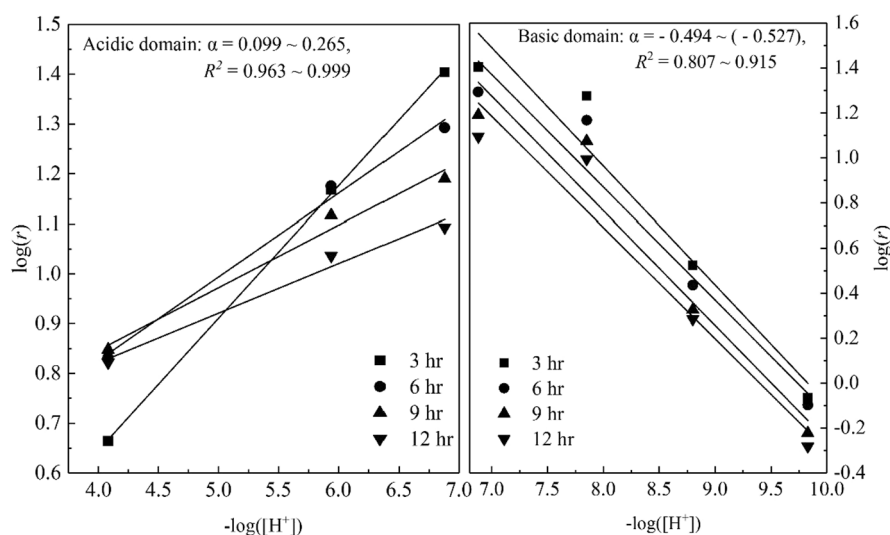


Fig. 3 – Logarithm of the rate vs. logarithm of hydrogen ion activity at $T = 293.15$ K and $\alpha(\text{O}_2) = 2.61 \times 10^{-4}$ mol/L. The reaction orders with respect to the hydrogen ion activity are 0.099–0.265 in an acidic solution and -0.494 – (-0.527) in a basic solution.

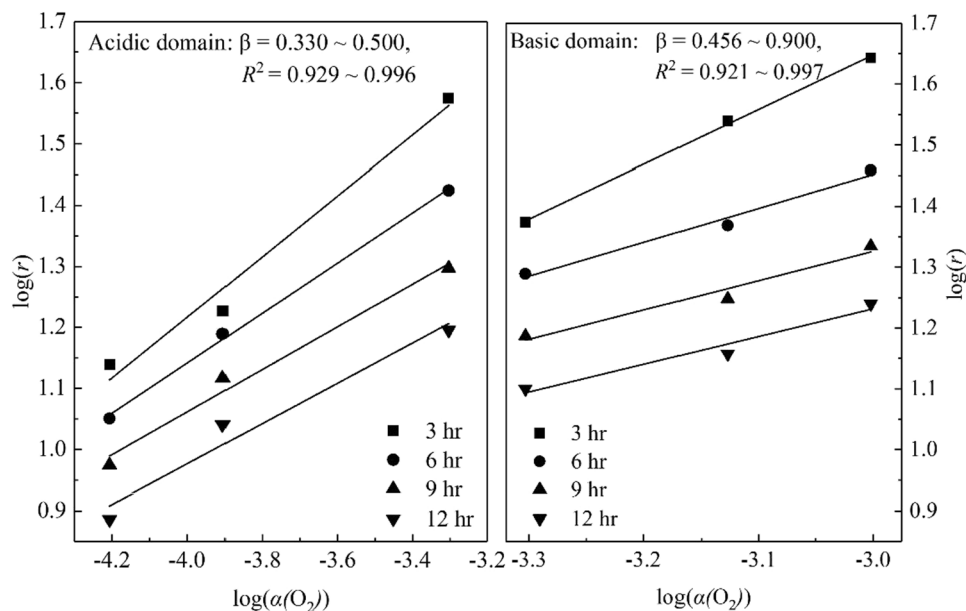


Fig. 4 – Logarithm of the rate vs. logarithm of dissolved oxygen activity at $T = 293.15$ K. The reaction orders with respect to dissolved oxygen activity are 0.330–0.500 in an acidic solution and 0.456–0.900 in a basic solution.

solution. Therefore, an alternative form of the rate law is given by Eq. (3):

$$r = k' \alpha(\text{H}^+)^{\alpha} \frac{K \alpha(\text{O}_2)}{1 + K \alpha(\text{O}_2)} \quad (3)$$

where, the rate is proportional to the surface coverage of oxygen on the mineral surface represented by the Langmuir isotherm (Langmuir, 1916). K then represents the equilibrium constant for the adsorption of oxygen on the solid surface. Eq. (3) can be rearranged into Eq. (4):

$$\frac{\alpha(\text{O}_2)}{r} = \frac{1}{k' \alpha(\text{H}^+)^{\alpha} K} + \frac{\alpha(\text{O}_2)}{k' \alpha(\text{H}^+)^{\alpha}} \quad (4)$$

The plots of $\alpha(\text{O}_2)/r$ vs. $\alpha(\text{O}_2)$ are linear (Fig. 5). Using the regression parameters, k' and K can be obtained.

2.3.1. Acid solution (pH 4.1)

The release rate of V increased from 7.7–13.76 to 15.67–37.56 $\mu\text{mol/hr}$ with increasing oxygen when $\alpha(\text{O}_2) \leq 4.97 \times 10^{-4}$ mol/L, while, with the further increase of $\alpha(\text{O}_2)$ ($> 4.97 \times 10^{-4}$ mol/L), a decrease in the reaction rate was observed (11.07–25.39 $\mu\text{mol/hr}$) from 15.67–37.56 $\mu\text{mol/hr}$ at $\alpha(\text{O}_2) = 4.97 \times 10^{-4}$ mol/L. The relationship between the release rate of V and activity of dissolved oxygen [$\alpha(\text{O}_2)$] from 6.22×10^{-5} to 4.97×10^{-4} mol/L was fitted, as shown in Fig. 4. From the slope of the regression line, the dependence

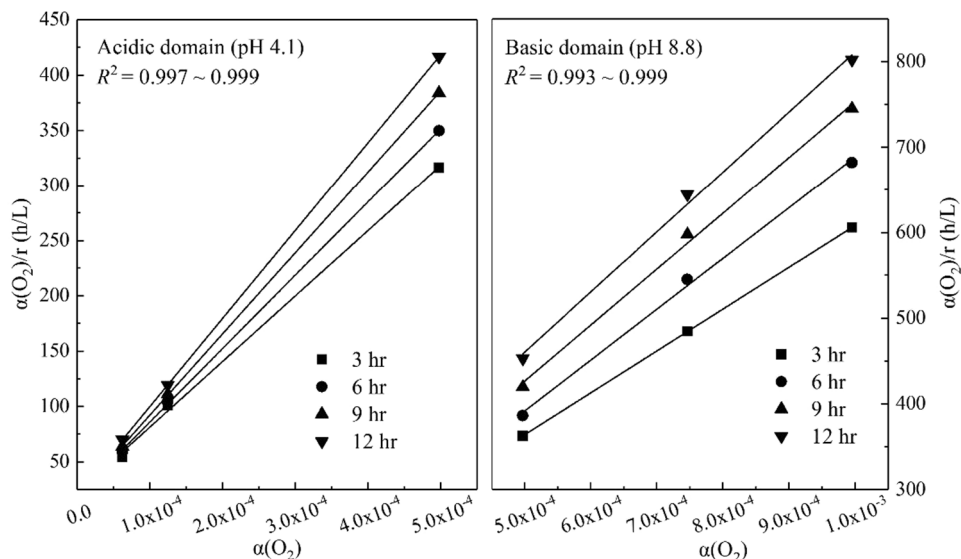


Fig. 5 – Langmuir plots: dissolved oxygen activity over rate vs. dissolved oxygen activity at $T = 293.15$ K. $k' = 3.2 \times 10^{-6}$ – 1.7×10^{-5} and $K = (2.7$ – $3.9) \times 10^4$ mol/L in an acidic solution and $k' = (2.0$ – $2.5) \times 10^{-11}$ and $K = (4.1$ – $6.5) \times 10^3$ mol/L in a basic solution.

on $\alpha(\text{O}_2)^{0.330-0.500}$ can be calculated ($R^2 > 0.929$). Combining the regressions in Figs. 2 and 3, the rate constants 9.9×10^{-5} – 2.9×10^{-3} were obtained. The parameters in Eq. (4) obtained from Fig. 5 are as follows: $k' = 3.2 \times 10^{-6}$ – 1.7×10^{-5} and $K = 2.7 \times 10^4$ – 3.9×10^4 mol/L. According to Eq. (4), the rate asymptotically tends to 15.67–37.56 $\mu\text{mol/hr}$ with increasing oxygen activity. Furthermore, 70%–80% of this rate is achieved at $\alpha(\text{O}_2) = 2.61 \times 10^{-4}$ mol/L, corresponding to a partial pressure of 1.0 atm. The Langmuir adsorption of dissolved oxygen appears to be a plausible explanation for the leveling of the rate at $\alpha(\text{O}_2) > 4.97 \times 10^{-4}$ mol/L. A similar saturation effect was observed in the oxygen dependence of the dissolution rates of arsenopyrite and stibnite, and the equilibrium constant K for adsorption of oxygen is the same magnitude as for arsenopyrite and stibnite ($K = 1 \times 10^4$ mol/L and 2.22×10^4 mol/L, respectively) (Asta et al., 2010; Biver and Shoty, 2012).

2.3.2. Basic solution (pH 8.8)

At a pH of 8.8, four experiments were performed in which the activity of dissolved oxygen was varied from 2.61×10^{-4} mol/L (21% O_2) to 9.95×10^{-4} mol/L (80% O_2). Correspondingly, the V release rate increased from 0.61–1.15 $\mu\text{mol/hr}$ to 17.38–43.94 $\mu\text{mol/hr}$. From the slope of the regression line in Fig. 4, the dependence on $\alpha(\text{O}_2)^{0.456-0.900}$ was calculated ($R^2 > 0.921$). Remarkably, the degree of dependence of the release rate on $\alpha(\text{O}_2)$ is larger than that in acidic solution. The Langmuir parameter from Fig. 5 is $k' = 2.0 \times 10^{-11}$ – 2.5×10^{-11} , and the adsorption equilibrium constant is $K = 4.1 \times 10^3$ – 6.5×10^3 mol/L. The rate according to the Langmuir form of the rate law asymptotically tends to 17.38–43.94 $\mu\text{mol/L}$. Additionally, 80%–83% of this value is achieved at $\alpha(\text{O}_2) = 7.46 \times 10^{-4}$ mol/L, corresponding to a partial pressure of 2.86 atm. Therefore, saturation is predicted to occur at a higher oxygen pressure than in acidic solution, and the adsorption constant K only has $1/(6.0-6.7)$ of its value in acidic solution, while the rate constant k' is approximately two orders of magnitude smaller than that in acidic solution.

2.4. Effect of temperature on the V release rate

The effect of temperature was studied over the range of 293.15–313.15 K. In general, the release rate of V increased markedly with increasing temperature. For the release rate at 3 hr, when the temperature increased from 293.15 to 313.15 K, the rate increased from 4.6 to 18.3 $\mu\text{mol/hr}$ at pH 4.1 and from 1.2 to 55.1 $\mu\text{mol/hr}$ at pH 8.8. This illustrated that more V will enter the environment in summer. The rate constants (Table 1) at different temperatures were computed from Eq. (2), and then $\ln(k)$ vs. $1/T$ was plotted (Fig. 6). However, there was a nonlinear relation ($R^2 = 0.130$ – 0.258) between $\ln(k)$ and $1/T$ at pH 4.1, and weak linear relation ($R^2 = 0.590$ – 0.670)

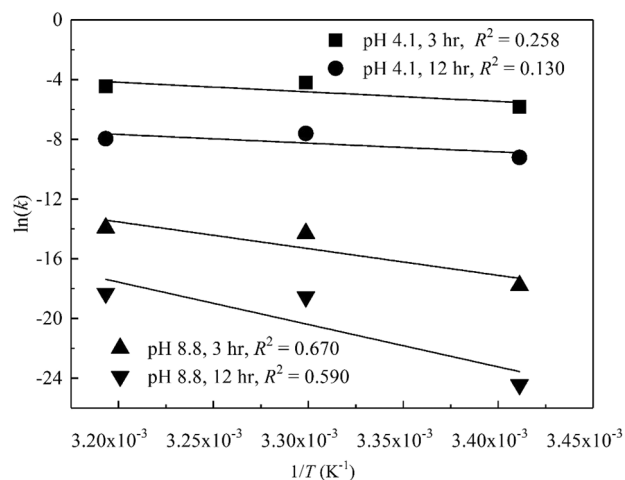


Fig. 6 – Arrhenius plots [$\ln(k)$ vs. $1/T$] for the temperature range of 293.15–313.15 K and $\alpha(\text{O}_2) = 2.61 \times 10^{-4}$ mol/L. The activation energy is estimated to 148–235 kJ/mol in a basic solution.

at pH 8.8. Thus, from the slopes of the fitting lines, $-E_A/R$, the activation energy (E_A) at pH 8.8 was roughly computed as 148–235 kJ/mol based on the Arrhenius equation. The activation energy in basic solution reported here is larger than that for orpiment dissolution (59.1 ± 0.4 kJ/mol) and for realgar dissolution (64.2 ± 9.8 kJ/mol) (Lengke and Tempel, 2002, 2003), and much greater than the value that is generally given (approximately 20 kJ/mol) for chemical reaction rates controlled by diffusion (Lasaga, 1984). The above results indicate that the dissolution release of V is controlled by a surface reaction mechanism.

2.5. Effect of foreign ions on the release rate of V

Experiments were performed at pH 6.9 and temperature of 298.15 K as well as 21% O_2 saturation under atmospheric pressure. The addition of Na^+ , Ca^{2+} , Mg^{2+} , K^+ , NO_3^- , Cl^- , SO_4^{2-} and CO_3^{2-} promoted the release of V (Fig. 7). Of note, 5 mmol/L of the above ions increased the release rate of V by a factor of approximately 1.2–1.6, and 50 mmol/L of the above ions only increased the rate by 1.2–1.9 times compared with the control groups. This illustrated that an increase in the foreign ion concentration of an order of magnitude did not significantly increase the release rate of V. Because V usually occurs in the +5 oxidation state in aqueous solution, which can be categorized as the cationic species VO_2^+ , neutral species $\text{VO}(\text{OH})_3$ and anionic species $\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}$, $\text{V}_{10}\text{O}_{27}(\text{OH})_3^{5-}$, $\text{V}_{10}\text{O}_{28}^{6-}$, $\text{VO}_2(\text{OH})^{2-}$, $\text{VO}_3(\text{OH})^{2-}$, VO_4^{3-} , $\text{V}_2\text{O}_6(\text{OH})^{3-}$, $\text{V}_2\text{O}_7^{4-}$, $\text{V}_3\text{O}_9^{3-}$, and $\text{V}_4\text{O}_{12}^{4-}$, competitive adsorption between added anions and cations

Table 1 – Rate constant k of the dissolution reaction as a function of the temperature in acidic (pH 4.1) and basic (pH 8.8) solutions.

T(K)	r (pH 4.1)	r (pH 8.8)	k (pH 4.1)	k (pH 8.8)
293.15	2.5–4.6	0–1.2	$1.9.9 \times 10^{-5}$ – 2.9×10^{-3}	2.5×10^{-11} – 1.9×10^{-8}
303.15	12.8–23.8	12.4–38.1	5.0×10^{-4} – 1.5×10^{-2}	8.8×10^{-9} – 6.2×10^{-7}
313.15	8.9–18.3	15.7–55.1	3.5×10^{-4} – 1.2×10^{-2}	1.1×10^{-9} – 8.9×10^{-7}

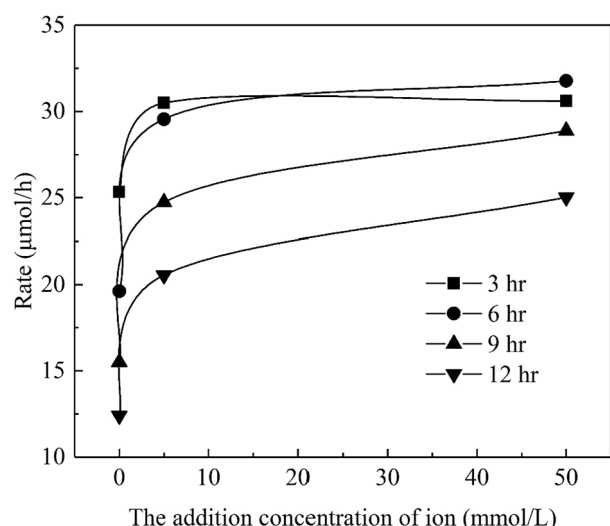


Fig. 7 – The effect of ions on the release rate of V at $T = 293.15\text{ K}$ and $\alpha(\text{O}_2) = 2.61 \times 10^{-4}\text{ mol/L}$.

as well as various species of V might have occurred at the mineral surface, decreasing the adsorption of V on the surface of minerals and promoting the release of V (Costa, 2015; Naeem et al., 2007).

2.6. Effect of coexisting components on the release rate of V

The solubility of V_2O_5 is 0.8 g in 100 mL of aqueous solution at 293.15 K (Assem and Levy, 2009). However, there was at most 48 mg/L V in the solution in all experiments, which is much less than 4058 mg/L (the concentration of V at the theoretical solubility of V_2O_5). One reason may be because their chemical structure, surface characteristics, physicochemical characteristics and coexisting components are different. The other may be ascribed to the effect of coexisting components in the natural mineral sample. The adsorption of dissolved V on the surface of Fe oxides, TiO_2 and Al_2O_3 was considered to be an important inhibitor of V release. Naeem et al. (2007) studied the removal of V with TiO_2 -based and iron-based adsorbents, illustrating that the maximum adsorption capacity was 100 mg V/g adsorbent under acidic conditions and 20 mg V/g adsorbent under basic conditions. Based on the above values, 1000 and 200 mg/L V could be adsorbed by coexisting Fe and TiO_2 under acidic and basic conditions, respectively. Additionally, Al_2O_3 and anatase TiO_2 had excellent adsorption ability for V at pH 3–9 (Wehrli and Stumm, 1988a, 1988b). In addition, $\text{Ca}(\text{VO}_3)_2$ and $\text{Mg}(\text{VO}_3)_2$ precipitates due to interaction between dissolved V and CaO/MgO under basic conditions may be another explanation (Li et al., 2014).

3. Conclusions

The release behavior of V is greatly affected by the studied conditions: pH, dissolved oxygen, temperature and addition of foreign ions. Release rate equations of V from the dissolution of vanadium titano-magnetite under acidic and basic conditions were established. The rate is proportional to fractional

powers of the hydrogen ion and dissolved oxygen activities. The dependence on dissolved oxygen may also be described by the Langmuir adsorption of oxygen on the vanadium titano-magnetite surface, which has the advantage of explaining the observed saturation rate under acidic solutions. Similarly, saturation is predicted to occur in basic solutions at a much higher partial pressure of oxygen. The reaction temperature is another important factor that affects V release. The activation energy was found to be in the range for surface-controlled dissolution mechanisms in acidic and basic solutions. The addition of various ions was found to promote the release of V. Moreover, the release level of V under certain conditions can be estimated by considering the V release rate, providing information on the V pollution status in local areas as well as the environmental geochemical cycle and fate of V.

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