Release kinetics of vanadium from vanadium (III, IV and V) oxides: Effect of pH, temperature and oxide dose

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ABSTRACT

Batch experiments were performed to derive the rate laws for the proton-promoted dissolution of the main vanadium (III, IV and V) oxides at pH 3.1–10.0. The release rates of vanadium are closely related to the aqueous pH, and several obvious differences were observed in the release behavior of vanadium from the dissolution of V2O5 and vanadium(III, IV) oxides. In the first 2 hr, the release rates of vanadium from V2O3 were \( r = 1.14 \times [H^+]^{0.269} \) at pH 3.0–6.0 and \( r = 0.016 \times [H^+]^{-0.048} \) at pH 6.0–10.0; the release rates from VO2 were \( r = 0.362 \times [H^+]^{0.129} \) at pH 3.0–6.0 and \( r = 0.017 \times [H^+]^{-0.097} \) at pH 6.0–10.0; and the release rates from V2O5 were \( r = 0.131 \times [H^+]^{-0.104} \) at pH 3.1–10.0. The release rates of vanadium from the three oxides increased with increasing temperature, and the effect of temperature was different at pH 3.8, pH 6.0 and pH 7.7. The activation energies of vanadium (III, IV and V) oxides (33.4–87.5 kJ/mol) were determined at pH 3.8, pH 6.0 and pH 7.7, showing that the release of vanadium from dissolution of vanadium oxides follows a surface-controlled reaction mechanism. The release rates of vanadium increased with increasing vanadium oxides dose, albeit not proportionally. This study, as part of a broader study of the release behavior of vanadium, can help to elucidate the pollution problem of vanadium and to clarify the fate of vanadium in the environment.

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Introduction

Vanadium (V) has been suggested to be a potentially dangerous pollutant that is in the same class as mercury (Hg), lead (Pb) and arsenic (As) (Moskalyk and Alfantazi, 2003); the United Nations Environment Program has categorized V on the priority list of environmental risk elements (Naeem et al., 2007; Huang et al., 2015). Over the last few decades, the V level has been significantly rising in the biosphere and will be of great concern in the future (Ringelband and Hehl, 2000). There are large-scale V pollution in many regions worldwide, which is largely attributable to mining activities and anthropogenic influences. For example, the concentrations of dissolved V reached up to 30–220 mg/L in Wyoming River, U.S.A, which was commonly in association with mining activities (Schroeder, 1970; Shiller and Boyle, 1987). The soils directly used by humans were found to contain much higher V levels (1510–3600 mg/kg) than the average V concentration (10–220 mg/kg dry mass) in different soils (Jiao et al., 2009; Poledniok and Buhl, 2003; Teng et al., 2006, 2011; Maluszynski, 2007). Despite the growing economic
importance of V and its status as an emerging contaminant, the processes that control the release and mobilization of V in the environment have been much less studied compared to other trace elements, e.g., As, Pb and Hg (Huang, 2014; Selin, 2009; Smedley and Kinniburgh, 2002). The problem with evaluating V in the environment is confounded by the limited understanding of V biogeochemistry relative to the other 3d transition elements. Therefore, there is a real need to develop a better understanding of the geochemistry of V, beginning with its release from predominant sources.

Weathering, atmospheric dry and wet deposition, and mining have been recognized as the main pathways for V to enter the environment (Morrell et al., 1986). Through dissolution of vanadium minerals, waste rocks, industrial dust and other vanadium products, dissolved V enters the soil and waters, which has an important adverse impact on the food chain. Although there have been some reports on the content of V in the soil and local surface and underground water, the release behavior of V from important sources, i.e., V-containing minerals and products, remains unknown (Hamada, 1998; Huang et al., 2015; Shiller and Mao, 2000; Soldí et al., 1996; Teng et al., 2006, 2011; Wright and Belitz, 2010). The release kinetics and mechanisms of V from the dissolution of typical minerals were studied in parallel. As a part of a broader study on the release behavior of V, this study will focus on the release of V from synthetic products (V2O5, VO2 and V2O3).

It is known that V exists in oxidation states that range from 2+ to 5+, and 3+, 4+, and 5+ are the most common oxidation states. Vanadium pentoxide (V2O5) is the most important synthesized vanadium compound, and it is used in many industrial processes, especially for producing additives for steel manufacture, such as ferrovanadium. Approximately 80% of the world’s produced V is being used as an additive in the steel industry (Imtiaz et al., 2015). Vanadium trioxide (V2O3) and dioxide (VO2) are reduction products of V2O5 that also have diverse applications, extending from catalysts to pigments and battery industries (Huang et al., 2015; Manning et al., 2004). In their metallurgical and in-use processes, they may enter soils and waters through atmospheric deposition or the disposal of wastes near industrial establishments. Although the vanadium (III, IV and V) oxides are the main vanadium products, only thermodynamic data are available for them, and there is little information on their dissolution kinetics (Assem and Levy, 2009; Post and Robins, 1976).

It is known that there are more than 60 reaction equilibria and more than 20 vanadium species in the V-H2O system, and the vanadium species vary with the concentration of V, pH and Eh (Post and Robins, 1976). The dissolution of V2O5, V2O4 and VO2 may formally be regarded as the mobilization of dissolved V (Eqs. (1)–(3)). Clearly, the aqueous pH has a significant effect on the dissolution of vanadium (III, IV and V) oxides.

\[
\begin{align*}
V_2O_3 + 4 H^+ &= 2 VOH^{2+} + H_2O \quad (1) \\
V_2O_4 + 4 H^+ &= 2 VO^{2+} + 2 H_2O \quad (2) \\
V_2O_5 + 2 H^+ &= 2 VO_2^+ + H_2O \quad (3)
\end{align*}
\]

Dissolved V(III) species only exist under anoxic conditions and at pH < 10, where they become unstable relative to V(V) species. The vanadyl ion (VO2+) is stable at pH < 4.5 or in anoxic environments. V(V) species predominate in oxic environments at low pH values and in both oxic and anoxic environments at pH > 8. Increased pH may cause condensation of VO2 to V10O286–. Usually, the dissolution of vanadium oxides is accompanied by redox reactions between dissolved V(III), V(IV) and V(V) under environmental conditions. Because this process is extremely complex, the transformation of V chemical forms and valences will not be considered in this study. Only total dissolved V in aqueous solutions from the dissolution of V2O5, V2O4 and V2O3 was measured and discussed.

The aim of the present work is to study the release of V from vanadium-containing products and to establish kinetic rate laws that are applicable under environmentally relevant conditions (pH 3.1–10.0). The effects of the oxide dosage and temperature (over the range 25–50°C) on the release rate of V were studied.

1. Materials and methods

1.1. Vanadium (III, IV and V) oxides

Standard powders of vanadium trioxide (V2O3) and vanadium (IV) oxide (VO2) with purity higher than 99% were purchased from Alfa Aesar (Shanghai, China). Their specific surface areas were 3.007 and 0.528 m2/g, respectively. Vanadium pentoxide (V2O5) with purity higher than 99.9% was purchased from Shandong Xiya Chemical Industry Co. Ltd. (China). Its specific surface area was 4.187 m2/g. X-ray diffraction graphs of the three oxides (Fig. 1) reveal pure vanadium (III, IV and V) oxides in the crystalline phase and different crystal lattice structures, which may result in different dissolution behaviors.

1.2. Dissolution experiment for vanadium oxides

The release rates of vanadium from the dissolution of vanadium oxides were measured in a batch of 250-mL HDPE bottles. In each experiment, the solutions with initial volume equal to 200 mL and accurately weighed vanadium (III, IV and V)
oxides (equivalent 2 mmol/L V) were introduced into the batch reactor. Then, the mixed solution was shaken using a thermostatic oscillator at 170 r/min. At certain intervals over 72 hr, 1 mL of aqueous solution was collected using disposable PP/PE syringes (Zhiyu medical Equipment Co., Ltd., Shanghai, China) that were fitted with CME 0.45 μm hydrophilic syringe filters (Jinteng Laboratory Equipment Co., Ltd., Tianjin, China). Feed solutions at pH 3.1–4.9 were adjusted using diluted hydrochloric acid; the solutions with a pH between 6.0 and 8.0 were adjusted with the addition of different ratios of 2-(N-Morpholino)-ethane sulfonic acid (MES) and sodium hydroxide. The basic solutions (pH 7.7–10.0) were mixtures of sodium carbonate and sodium bicarbonate in varying proportions, and the levels of the two salts were chosen to give a total ionic strength of 0.05 mol/L. The ionic strength of the feed solutions at pH 3.1–7.7 was adjusted to 0.05 mol/L with sodium chloride. To determine the activation energies of vanadium oxides, experiments were repeated at different temperatures (25, 35 and 50°C) at selected pH values (3.8, 6.0 and 7.7). For dose-dependent experiments, the vanadium (III, IV and V) oxides equivalent to 2, 20 and 100 mmol/L V were added to 200 mL of aqueous solution with pH 6.0. The pH of the solutions was measured at the beginning and at the end of the experiments. Almost no drift in pH was observed within experimental error; thus, only the initial pH value was reported for each experiment. All mentioned reagents were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. (Beijing, China). All reagents were analytically pure grade or better.

1.3. Estimation of the release rate of V

For the sake of contrastive analysis among different vanadium oxides, the release rates of V were calculated from the mobilized level of total V in the solution with time (Eq. (4)) based on the dissolution reactions of vanadium (III, IV and V) oxides (Eqs. (1)–(3)). The release level (mmol/m²) of Vtot in all experiments was normalized with respect to the specific surface area of the vanadium (III, IV and V) oxides.

\[ r = \frac{d[V_{\text{tot}}]}{dt} = k t \]  

(4)

1.4. Analytical methods

The total V determination was performed with inductively coupled plasma optical emission spectroscopy (NexION300, PerkinElmer Inc., USA) with a detection limit of 10 μg/L. Of each sample, 3 replicates were used. The relative standard deviation for each sample was <1.0%. Some aqueous samples were diluted with Milli-Q water to fit in the working range (0–20 mg/L). The specific BET-surface area was determined by multiple-point N₂ adsorption using a Quantachrome Autosorb-iQ surface area measuring apparatus (Boynton Beach, FL, USA). The qualitative crystalline phases of three oxides were analyzed using X-ray diffraction (XRD) (X pert pro MPD, PANalytical B. V., Holland). Conditions: Cu Kα radiation, 40 kV and 40 mA, 2 theta range 10–60° with a scan rate step of 0.05°/sec, using an X’Celerator detector. The determinations of the zero points of charge (pHzpc) of the three vanadium oxides were performed with the immersion technique (Bourikas et al., 2003). With this technique, 200 mL of aqueous solutions of 0.05 mol/L NaNO₃ electrolyte with varying pH level (2–10) was prepared, and 0.1 g of each oxide was added to the above solutions. The aqueous suspensions were equilibrated for 20 hr to reach an equilibrium pH value. The pH of each suspension was then measured by a digital pH meter. The absolute values of the pH changes, δpH, were then determined from the difference between the initial pH and equalized pH of the suspension. The pzc was identified as the pH at which the minimum δpH was obtained.

2. Results and discussion

2.1. pH-dependent release rate of V

The mobilized levels of V from the three vanadium oxides, at different pH values, were plotted against time (Fig. 2a–c). For vanadium(III) and (IV) oxides, the released V monotonically increased with time. That is because relatively small amounts of V were released from the dissolution of vanadium(III) and (IV) oxides within 72 hr, which was far from the saturation level of V in the aqueous solutions. For V₂O₅, however, due to its high solubility, the saturation level of V was reached after 12 hr; thus, in the first 12 hr, the release V level monotonically increased with time and then reached a plateau, corresponding to the dissolution equilibrium after 12 hr. Furthermore, for the three vanadium oxides, in the first 2 hr, the average V release levels were higher than those at 2–72 hr. Therefore, to facilitate the analysis, the release rates of V were obtained by piecewise fitting (Table 1) (the correlation coefficients, R², range from 0.84 to 0.99 with an average of 0.90). In addition, an obvious pH-dependent trend was found for the release amount of V. The release rate that is dependent on [H⁺] can be expressed by Eq. (5):

\[ r = \frac{d[V_{\text{tot}}]}{dt} = k'(\text{[H}^+\text{]}^\alpha) \]  

(5)

The logarithm of the rate, expressed in mmol/(m²·hr), was plotted against the logarithm of the hydrogen ion concentration (Fig. 3a and b); next, α and k’ were obtained from the slope and intercept of the fitting curves, respectively.

2.1.1. Release rate of V from the dissolution of V₂O₅

In general, acidic conditions are beneficial to the release of V from the dissolution of V₂O₅. There was a negative effect of pH on the release of V from the dissolution of VO₂ under neutral and alkaline pH conditions. In the first 2 hr, the maximum and minimum release rates were observed at pH = 3.1, \( r = 1.65 \times 10^{-2} \text{ mmol/(m}^2\text{·hr)} \) and at pH = 6.0, \( r = 3.08 \times 10^{-2} \text{ mmol/(m}^2\text{·hr)} \), respectively. Additionally, at pH 3.0–6.0, the release rate of V monotonically decreased from \( 1.65 \times 10^{-1} \) to \( 3.08 \times 10^{-2} \text{ mmol/(m}^2\text{·hr)} \) with increasing pH, while at pH 6.0–10.0, the rate monotonically increased from \( 3.08 \times 10^{-2} \) to \( 5.15 \times 10^{-2} \text{ mmol/(m}^2\text{·hr)} \). From Fig. 3a, k and α were obtained as \( k' = 1.14 \) and \( α = 0.269 \) for pH 3.0–6.0 (R² = 0.937) and \( k' = 0.016 \) and \( α = -0.048 \) for pH 6.0–10.0 (R² = 0.866). At 2–72 hr, the same pH-dependent trend was observed, and the maximum and minimum release rates were still at
pH = 3.1 and pH = 6.0, respectively. However, the release rates at all pH values \((9.55 \times 10^{-4} - 1.85 \times 10^{-2} \text{ mmol/(m}^2\cdot\text{hr})\) were only 1/32–1/6 of the release rates in the first 2 hr \((3.08 \times 10^{-2} - 1.65 \times 10^{-1} \text{ mmol/(m}^2\cdot\text{hr})\)). From Fig. 3b, \(k'\) and \(a\) are obtained as \(k' = 0.549\) and \(a = 0.434\) for pH 3.0–6.0 \((R^2 = 0.856)\) and \(k' = 4.24 \times 10^{-4}\) and \(a = -0.054\) for pH 6.0–10.0 \((R^2 = 0.840)\).

In general, under acidic conditions, the release rates were significantly affected by the aqueous pH and, ultimately, the \(\text{H}^+\) concentration. The results are consistent with the theory on proton-promoted dissolution of other oxides and silicates (Sposito, 2004).

2.1.2. Release rate of V from the dissolution of VO\(_2\)

The data for the release rate of V from dissolving VO\(_2\) were analyzed in the same way as described above. Generally, a similar pH-dependent trend for VO\(_2\) was found, and most of the rates at the corresponding pH values had the same order of magnitude (Table 1). It can be seen from Fig. 2b that strong acidic (pH 3.1) and basic (pH 10.0) conditions are beneficial to the release of V from the dissolution of VO\(_2\). In other words, there was a negative effect of pH on the release of V from the dissolution of VO\(_2\) under nearly neutral pH conditions. In the first 2 hr, there was a small difference in the release rate of V at pH 3.1 \((1.53 \times 10^{-1} \text{ mmol/(m}^2\cdot\text{hr})\) and pH 10.0 \((1.68 \times 10^{-1} \text{ mmol/(m}^2\cdot\text{hr})\). The minimum release rate was still observed at pH = 6.0, \(r = 5.96 \times 10^{-2} \text{ mmol/(m}^2\cdot\text{hr})\). From Fig. 3a, \(k'\) and \(a\) are obtained as \(k' = 0.362\) and \(a = 0.129\) for pH 3.0–6.0 \((R^2 = 0.914)\) and \(k' = 0.017\) and \(a = -0.097\) for pH 6.0–10.0 \((R^2 = 0.865)\). Compared with the corresponding \(k'\) and \(a\) in the V\(_2\)O\(_3\) experiments, it can be found that the degree of pH dependence increased under basic conditions, while it decreased under acidic conditions.

At 2–72 hr, strongly acidic conditions (pH 3.1) were more beneficial to the release of V from VO\(_2\) than basic conditions (pH 10.0), and there was a big difference between the release rates of V at pH 3.1 \((1.87 \times 10^{-2} \text{ mmol/(m}^2\cdot\text{hr})\) and pH 10.0 \((4.75 \times 10^{-3} \text{ mmol/(m}^2\cdot\text{hr})\). The minimum release rate was still observed at pH = 6.0, \(r = 3.83 \times 10^{-4} \text{ mmol/(m}^2\cdot\text{hr})\). The general release rates at all pH values were much lower \((3.38 \times 10^{-4} - 1.87 \times 10^{-2} \text{ mmol/(m}^2\cdot\text{hr})\) than those in the first 2 hr \((5.96 \times 10^{-2} - 1.68 \times 10^{-1} \text{ mmol/(m}^2\cdot\text{hr})\), especially at pH 6.0. From Fig. 3b, \(k'\) and \(a\) are obtained as \(k' = 0.262\) and \(a = 0.422\) for pH 3.0–6.0 \((R^2 = 0.873)\) and \(k' = 1.46 \times 10^{-4}\) and \(a = -0.168\) for pH 6.0–10.0 \((R^2 = 0.841)\). Compared with the corresponding \(k'\) and \(a\) in the first 2 hr, the general degree of dependence on pH increased under acidic conditions, while it decreased in basic conditions. In general, proton-promoted release of V was also observed in the dissolution of VO\(_2\), especially under acidic conditions.

| Table 1 - pH-dependent release rates of vanadium from dissolving vanadium (III, IV and V) oxides. |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                 | pH 3.1         | pH 3.8         | pH 4.9         | pH 6.0         | pH 7.1         | pH 7.7         |
| Release rate for 0–2 hr (mmol/(m\(^2\)·hr)) |                |                |                |                |                |                |
| \(V_2O_3\)      | 1.65 \times 10^{-1} | 1.22 \times 10^{-1} | 4.32 \times 10^{-2} | 3.08 \times 10^{-2} | 3.50 \times 10^{-2} | 3.85 \times 10^{-2} | 3.76 \times 10^{-2} | 5.15 \times 10^{-2} |
| \(VO_2\)        | 1.52 \times 10^{-1} | 1.04 \times 10^{-1} | 9.22 \times 10^{-2} | 5.96 \times 10^{-2} | 9.49 \times 10^{-2} | 1.03 \times 10^{-1} | 1.10 \times 10^{-1} | 1.68 \times 10^{-1} |
| \(V_2O_3\)      | 3.97 \times 10^{-1} | 3.18 \times 10^{-1} | 4.16 \times 10^{-1} | 4.85 \times 10^{-1} | 4.75 \times 10^{-1} | 5.49 \times 10^{-1} | 5.17 \times 10^{-1} | 1.70 \times 10^{-1} |
| Release rate for 2–72 hr (mmol/(m\(^2\)·hr)) |                |                |                |                |                |                |
| \(V_2O_3\)      | 1.85 \times 10^{-2} | 1.39 \times 10^{-2} | 7.01 \times 10^{-3} | 9.55 \times 10^{-4} | 9.21 \times 10^{-4} | 1.19 \times 10^{-3} | 1.23 \times 10^{-3} | 1.56 \times 10^{-3} |
| \(VO_2\)        | 1.87 \times 10^{-2} | 3.88 \times 10^{-3} | 2.42 \times 10^{-3} | 8.38 \times 10^{-4} | 3.34 \times 10^{-3} | 4.62 \times 10^{-3} | 5.31 \times 10^{-3} | 4.75 \times 10^{-3} |
| \(V_2O_3\) (2–8 hr) | 1.34 \times 10^{-1} | 1.81 \times 10^{-1} | 1.54 \times 10^{-1} | 1.40 \times 10^{-1} | 1.67 \times 10^{-1} | 2.08 \times 10^{-1} | 6.26 \times 10^{-2} | 6.98 \times 10^{-2} |
| \(V_2O_3\) (12–72 hr) | 1.27 \times 10^{-2} | 1.43 \times 10^{-2} | 1.04 \times 10^{-2} | 7.30 \times 10^{-3} | 5.95 \times 10^{-3} | 4.71 \times 10^{-3} | 3.97 \times 10^{-3} | 1.02 \times 10^{-2} |
2.1.3. Release rate of V from the dissolution of V₂O₅

From Fig. 2c, it can be observed that there are obvious differences in the release behavior of V between V₂O₅ and vanadium (III, IV) oxides. (1) The dissolution equilibrium of V₂O₅ was rapidly reached at all pH values. (2) Strongly basic conditions (pH 9.0 and 10.0) were beneficial to the release of V from the dissolution of V₂O₅. In other words, there was a negative effect of pH on the release of V from the dissolution of V₂O₅ under acidic and neutral pH conditions. (3) The release rates of V from V₂O₅ were higher than the release rates from vanadium (III, IV) oxides.

In detail, in the first 2 hr, the maximum and minimum release rates were observed at pH = 10.0, \( r = 1.83 \text{ mmol/(m}^2\cdot\text{hr)} \) and pH = 3.8, \( r = 3.18 \times 10^{-1} \text{ mmol/(m}^2\cdot\text{hr)} \), respectively. In general, at pH 3.0–10.0, the release rates of V monotonically increased from 3.18 \times 10^{-1} to 1.83 mmol/(m²·hr) with increasing pH. At 2–8 hr, an obvious decrease in the release rates at pH 9.0 (6.26 \times 10^{-2} mmol/(m²·hr)) and 10.0 (6.98 \times 10^{-2} mmol/(m²·hr)) was observed compared with the results in the first 2 hr. Only a slight decrease in the release rates was observed at pH 3.1–7.7. From Fig. 3a, \( k' \) and \( \alpha \) are obtained as \( k' = 0.131 \) and \( \alpha = -0.104 \) for pH 3.1–10.0 \( (R^2 = 0.837) \), illustrating that the effect of the pH on the release rate of V from V₂O₅ is more important than for vanadium (III, IV) oxides.

At 12–72 hr, a reverse pH-dependent trend was observed compared with the first 8 hr. At pH 3.1–9.0, the release rates of V monotonically decreased from 1.27 \times 10^{-2} to 3.97 \times 10^{-3} mmol/(m²·hr) with increasing pH. The maximum and minimum release rates were observed at pH = 9.0, \( r = 1.27 \times 10^{-2} \text{ mmol/(m}^2\cdot\text{hr)} \) and at pH = 9.0, \( r = 3.97 \times 10^{-3} \text{ mmol/(m}^2\cdot\text{hr)} \), respectively. The general release rates at all pH values were much lower (1.27 \times 10^{-2}–3.97 \times 10^{-3} mmol/(m²·hr)) than those in the first 2 hr (3.18 \times 10^{-1}–1.83 mmol/(m²·hr)), especially at pH 9.0 and 10.0. From Fig. 3b, \( k' \) and \( \alpha \) are obtained as \( k' = 0.029 \) and \( \alpha = 0.099 \) for pH 3.0–9.0 \( (R^2 = 0.956) \) and \( k' = 8.14 \times 10^{-7} \) and \( \alpha = -0.410 \) for pH 9.0–10.0 \( (R^2 = 1) \), which illustrate that the pH has a small effect on the release of V when the dissolution of V₂O₅ has reached an equilibrium state.

2.1.4. Correlation between the release rate and pHzpc of vanadium oxides

Many theoretical models of oxide and silicate dissolution have verified that at a pH corresponding to the pHzpc of the dissolving solid, minimum dissolution rates of minerals are observed (Stumm and Morgan, 1996). However, this does not seem to hold for the dissolution of vanadium oxides. In the studied pH values, the pHzpc of vanadium (III, IV and V) oxides is estimated to be approximately 2.2 or less, but this does not correspond to the minimum release rate of V from the three vanadium oxides. For vanadium (III and IV) oxides, the minimum release rate was at pH 6.0. For V₂O₅, the minimum release rate (0–8 hr) was at pH 3.8. Therefore, for...
respectively. For VO2, the corresponding release rates increased from 2.01 × 10^2 mmol/(m²·hr) to 8.68 × 10^2 mmol/(m²·hr) (Table 2) were obtained from piecewise fitting. The release rate constants increased with increasing temperature, and the effect of the temperature was different at pH 3.8, pH 6.0 and pH 7.7. The natural logarithm of the rate constant vs. inverse absolute temperature under acid and basic conditions. The plots for natural logarithm of the rate constant vs. inverse absolute temperature of VO2, V2O3 at pH 3.8, 38.0 and 87.5 kJ/mol (R² = 0.76-0.99) and for V2O5 are 48.0, 76.3 and 97.6 kJ/mol (R² = 0.76-0.99). The activation energies of V2O3 at pH 3.8, pH 6.0 and pH 7.4 were investigated. The release rates of V from three oxides at pH 3.8, pH 6.0 and pH 7.7, the natural logarithm of the rate constant vs. inverse absolute temperature was plotted in Fig. 5a–c. The activation energies of V2O3 at pH 3.8, pH 6.0 and pH 7.7 were obtained from the fits. The release rate constants for V2O3 are 8.3 × 10^-2, 1.35 × 10^-2 and 7.43 × 10^-2 mmol/(m²·hr), respectively. For VO2, the corresponding release rates increased from 1.11 × 10^-2 mmol/(m²·hr) to 8.68 × 10^-2 mmol/(m²·hr) to 2.97 × 10^-2 mmol/(m²·hr). For V2O5, the corresponding release rates increased from 1.11 × 10^-2 mmol/(m²·hr) to 8.68 × 10^-2 mmol/(m²·hr) to 2.97 × 10^-2 mmol/(m²·hr). Therefore, there are two rate constants for every dose, which were obtained from piecewise fitting. The release rate constants are k1 = 0.38, 0.80 and 1.27 mmol/(m²·hr) and k2 = 6.7 × 10^-3, 2.6 × 10^-2 and 3.2 × 10^-2 mmol/(m²·hr) for 2, 20 and 100 mmol/L V. In addition, for the three vanadium oxides at pH 3.8, pH 6.0 and pH 7.7, the natural logarithm of the rate constant vs. inverse absolute temperature is plotted in Fig. 5a–c. The activation energies of V2O3 at pH 3.8, 13.9 and 28.6 kJ/mol (R² = 0.76-0.99) and for V2O5 are 48.0, 76.3 and 97.5 kJ/mol (R² = 0.76-0.99). These activation energies are greater than the values (20 kJ/mol or less) that is generally given for chemical reaction rates controlled by diffusion (Lasaga, 1984); therefore, the release of V from the dissolution of vanadium oxides is recognized as a surface-controlled reaction mechanism.

### 2.3. Effect of the vanadium oxide dose on the V release rate

The release rates of V from dissolution of different doses of vanadium oxide were studied at pH 6.0. The release rates of V increased with increasing oxide dose, albeit not proportionally (Fig. 6). For V2O3, the rate constants were 8.21 × 10^-4, 7.25 × 10^-2 and 1.68 × 10^-1 mmol/(m²·hr) when the corresponding added oxide levels were equivalent to 2, 20 and 100 mmol/L V. When the dose increased by one order of magnitude, the release rate increased by approximately two orders of magnitude. For VO2, when the dose increased to the equivalent of 100 mmol/L V, the curves began to plateau, corresponding to the attainment of dissolution equilibrium after 12 hr. Therefore, the release rate constant (1.68 × 10^-1 mmol/(m²·hr)) was calculated for 0–12 hr. In general, with increasing VO2 dose from the equivalent of 2 to 20 and 100 mmol/L V, the release rate of V proportionately increased from 3.88 × 10^-2 to 4.15 × 10^-2 and 1.68 × 10^-1 mmol/(m²·hr). For V2O5, at the equivalent of 2 mmol/L V, there was a plateau corresponding to the dissolution equilibrium formed after 4 hr, while at 20 and 100 mmol/L V, the plateau formed after 12 hr. Therefore, there are two rate constants for every dose, which were obtained from piecewise fitting. The release rate constants are k1 = 0.38, 0.80 and 1.27 mmol/(m²·hr) and k2 = 6.7 × 10^-3, 2.6 × 10^-2 and 3.2 × 10^-2 mmol/(m²·hr) for 2, 20 and 100 mmol/L V.

Table 2 – Temperature-dependent release rates of vanadium from dissolving vanadium (III, IV and V) oxides for 0–8 hr (unit: mmol/(m²·hr))

<table>
<thead>
<tr>
<th>pH</th>
<th>V2O3</th>
<th>VO2</th>
<th>V2O5</th>
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<tr>
<td></td>
<td>pH 3.8</td>
<td>pH 6.0</td>
<td>pH 7.4</td>
</tr>
<tr>
<td>298.15 K</td>
<td>2.01 × 10⁻²</td>
<td>0.266 × 10⁻²</td>
<td>0.632 × 10⁻²</td>
</tr>
<tr>
<td>308.15 K</td>
<td>2.27 × 10⁻²</td>
<td>0.793 × 10⁻²</td>
<td>1.35 × 10⁻²</td>
</tr>
<tr>
<td>323.15 K</td>
<td>8.68 × 10⁻²</td>
<td>2.97 × 10⁻²</td>
<td>7.43 × 10⁻²</td>
</tr>
</tbody>
</table>

Fig. 5 – Plots for natural logarithm of the rate constant vs. inverse absolute temperature under acid and basic conditions. The activation energies of vanadium (III, IV and V) oxides can be calculated from the slope of the fitting curves.
V, respectively. The increases in the rate constants are proportionately much less than the corresponding increases in the dose.

3. Conclusions

The dissolution of vanadium (III, IV and V) oxides is an important release source of V, especially the dissolution of V₂O₅. The aqueous pH, temperature and dose of vanadium oxides play important roles in the release rates of V from the dissolution of vanadium (III, IV and V) oxides. A similar proton-promoted release behavior of V is concluded from V₂O₃ and VO₂. In general, acidic solution is more beneficial to the release of V than basic solution. However, for V₂O₅, strongly basic conditions (pH 9.0 and 10.0) are beneficial to the release of V. Additionally, at pH 3.1–10.0, the release rates of V in the V₂O₅–H₂O system are higher than the rates in the vanadium (III, IV) oxides-H₂O system. These results indicate that the risk grade of V₂O₅ is much higher than that of vanadium (III, IV) oxides, which should be emphasized in prevention and control measures for production and uses.

The release rates of V from the three oxides increased with increasing temperature or oxide dose, indicating that the pollution level of V may be aggravated in the summer. The rate laws for the proton-promoted release of V over the pH range of 3.1–10.0 were derived. The release rates of V at the studied environmental conditions were also obtained. The release level of V under certain conditions can be estimated by considering the V release rate, revealing the V pollution status in a local area as well as improving knowledge on the environmental geochemical cycle and fate of V.

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