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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. Among the four influencing factors, pH and temperature are especially important for the V release rate. However, different pH-dependent trends were observed in acidic and basic solutions. 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: $r = k'\alpha(\mathrm{H}^+)^{\alpha}\frac{K\alpha(\mathrm{O}_2)}{1+K\alpha(\mathrm{O}_2)}$ where, $\alpha = 0.099–0.265$, $k' = 3.2 \times 10^{-6}–1.7 \times 10^{-5}$, $K = 2.7 \times 10^{4}–3.9 \times 10^{4}$ mol/L in acid solution (pH 4.1), and $\alpha = -0.494 - (-0.527)$, $k' = 2.0 \times 10^{4}–2.5 \times 10^{-11}$, and $K = 4.1 \times 10^{3}–6.5 \times 10^{3}$ 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.

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 μg/L or less, but the value increases to approximately 70 μg/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 μg/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 μg/L, while in the control sites, the values were only 10–30 μg/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; Połedniok 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 ($Fe(V,Ti)_3O_4$) 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 μg/L) and moderate (25 to 49 μg/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 ($(Fe_{2.5}Ti_{0.5})_{1.04}O_4$, 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 MΩ/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.

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