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Leaching characteristics of vanadium in mine tailings and soils near a vanadium titanomagnetite mining site

Jinyan Yang[a], Ya Tang[a], Kai Yang[a], Ashaki A. Rouff[b], Evert J. Elzinga[c], Jen-How Huang[d,*]

[a] *College of Architecture and Environment, Sichuan University, Chengdu 610065, People's Republic of China*
[b] *School of Earth and Environmental Sciences, Queens College City University of New York, 65-30 Kissena Boulevard, Flushing, NY 11367, USA*
[c] *Department of Earth & Environmental Sciences, Rutgers University, Newark, NJ, USA*
[d] *Institute of Environmental Geosciences, University of Basel, CH-4056 Basel, Switzerland*

HIGHLIGHTS

- Vanadium in the soil and mine tailings has low solubility.
- The leachability of vanadium in the mine tailings is lower than in the soil.
- Low risk of vanadium migrating from the soil and mine tailings into the surrounding environment.
- Drought and rewetting increase vanadium release from the soil and mine tailings.
- Soil leaching processes control vanadium transport in soils overlain with mine tailings.

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ABSTRACT

A series of column leaching experiments were performed to understand the leaching behaviour and the potential environmental risk of vanadium in a Panzhihua soil and vanadium titanomagnetite mine tailings. Results from sequential extraction experiments indicated that the mobility of vanadium in both the soil and the mine tailings was low, with <1% of the total vanadium readily mobilised. Column experiments revealed that only <0.1% of vanadium in the soil and mine tailing was leachable. The vanadium concentrations in the soil leachates did not vary considerably, but decreased with the leachate volume in the mine tailing leachates. This suggests that there was a smaller pool of leachable vanadium in the mine tailings compared to that in the soil. Drought and rewetting increased the vanadium concentrations in the soil and mine tailing leachates from 20 $\mu g\,L^{-1}$ to 50–90 $\mu g\,L^{-1}$, indicating the potential for high vanadium release following periods of drought. Experiments with soil columns overlain with 4, 8 and 20% volume mine tailings/volume soil exhibited very similar vanadium leaching behaviour. These results suggest that the transport of vanadium to the subsurface is controlled primarily by the leaching processes occurring in soils.

1. Introduction

Vanadium accounts for ~0.01% of the total mass of the Earth's crust [1], and is a ubiquitous element in the natural environment [2]. Naturally high vanadium levels can be found in rocks and minerals, ranging anywhere from 2 to 310 $mg\,kg^{-1}$. Global and European average soil vanadium concentrations are 90 and 60 $mg\,kg^{-1}$, respectively [2,3]. The major sources of vanadium in the surface environment are the combustion of fossil fuels and industrial wastes [4]. The relevance of anthropogenic vanadium in the environment has increased significantly in recent years due to an increased demand for vanadium in high-temperature industrial activities (e.g. steel-iron refining, electronics and dyeing). For example, in the refining industry the recovery of vanadium is only 60–70%, meaning that the remaining 30–40% of vanadium will be discharged into the environment via gas emissions, dust, waste water and slag [5]. Although environmental vanadium pollution does not pose an immediate threat to ecosystems on a global scale, high vanadium levels may cause local environmental hazards [5,6]. The presence of vanadium in environmental settings raises concerns due to its toxicological effects on human beings and animals [7,8].

Vanadium is a trace element essential to human beings and animals e.g. insulin-mimetic activity [9]. However, numerous reports have demonstrated the carcinogenicity and toxicity of vanadium at higher concentrations [10]. Vanadium has been recognised as a potentially dangerous pollutant in the same class as mercury, lead and arsenic [11]. In 1988, the United Nations Environment

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* Corresponding author. Tel.: +41 61 2670483; fax: +41 61 2670479.
E-mail address: jen-how.huang@unibas.ch (J.-H. Huang).

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Fig. 1. Location of the Panzhihua region within Sichuan Province, China.

Programme suggested categorising vanadium in the priority list of the environmental risk element sheet [12]. Vanadium is also listed on the United States Environment Protection Agency candidate contaminant list #2. The number of people affected by vanadium pollution is increasing, especially in the USA, South Africa, China and Russia [13]. China is one of the leading vanadium resource bases worldwide. The Chinese reserves of vanadium titanomagnetite amount to nearly 10 billion tonnes, ranking 3rd in the world after South Africa and Russia [14]. The Panzhihua region in Sichuan province in China is a major ore belt of vanadium titanomagnetite (Fig. 1), accounting for 11% of the world's reserves [14]. The economy of the Panzhihua region relies almost entirely on mining activities, which have been developed during the past half-century. Today, almost the entire Panzhihua region is polluted by vanadium [2]. In addition to refining emissions, vanadium also enters the local environment from solid wastes such as mine tailings, resulting in serious environmental problems [15]. The area for mine tailing disposal occupies 1 km^2 of land, with an effective capacity of 0.16 billion m^3 (Fig. 2a). Anti-infiltration measures have been implemented at the disposal sites, so that the wind-blown dispersal of vanadium from mine tailings during their processing and disposal is an important pathway for the introduction of vanadium into the environment (Fig. 2b).

Vanadium occurs naturally in soils as a trace element originating from the weathering of bedrock. It is frequently found in soil minerals in the tetravalent and trivalent oxidation states, incorporated as VO^{2+} and V^{3+} lattice components, which are considered to be relatively stable and do not participate in vanadium transformation reactions in soils [16,17]. Anthropogenic inputs from the burning of fossil fuels and mining activities may lead to soil vanadium enrichment [2,18]. This added vanadium is usually associated with organic matter, clay, Al and Fe oxides, and compared to natural sources, is mobile and bioavailable in soils [19]. In the soil solution, vanadium speciation is predominately pentavalent, whereas tetravalent vanadium is much less common [20]. Soils in the Panzhihua region contain elevated concentrations of vanadium, up to 940 mg kg^{-1} [2]. The soil vanadium concentrations are greatest in soils impacted by smelting and mining, and are lower in agricultural and urban soils. Teng et al. [2] performed sequential extractions using acetic acid, hydroxylammonium chloride and hydrogen peroxide extractants, and found that most soil vanadium in Panzhihua is present in the residual fraction. Quantitative information concerning the mobility and leachability of vanadium in soils and mine tailings, particularly under hydrodynamic conditions, is rare. Moreover, the potential for vanadium transfer from the mining wastes to the adjacent environmental compartments (e.g. soils) is rarely investigated. Thus the objectives of this study were to (1) characterise the vanadium mobility and leaching behaviour in Panzhihua soils, mine tailings and soils overlain with mine tailings; (2) assess the potential vanadium transfer from mine tailings to the underlying soils; and (3) investigate the influence of drought and rewetting on the vanadium mobilisation from soils and mine tailings. This information is important for the accurate assessment of vanadium release from soils and mine tailings induced by rainfall events. It also allows a more precise determination of the environmental risk posed by vanadium containing soils and mine tailings, and for the design of appropriate remediation measures. Because the current state of knowledge concerning the geochemical and thermodynamic behaviour of vanadium to date is very limited, the exact modelling of vanadium leaching in soils and mine tailings for detailed interpretation is still not feasible. This study aims to provide insight into the processes affecting the release of vanadium from soils and mine tailings, which can ultimately help to define the kinetics and thermodynamics governing the geochemical behaviour of vanadium in the environment.

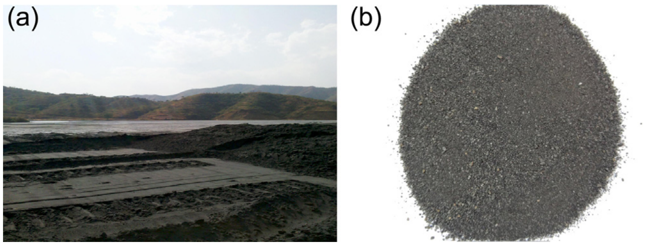

Fig. 2. (a) Disposal site of mine tailings near the Panzhihua mining site and (b) representative sample of the mine tailing materials used in this study.

2. Methods and materials

2.1. Site description and soil and mine tailing sampling

The sampling site is located in the Panzhihua region, Sichuan province, SW-China, at an elevation of 1200 m above sea level at 26°05′–27°21′ N; 101°08′–102°15′ E (Fig. 1). It is situated in the north temperate zone, with a large temperature difference between day and night. The average annual temperature is around 19.7–20.5 °C with long hours of sunshine (2300–2700 h a^{-1}) and strong solar radiation (578–628 kJ cm^{-2}) [2]. Rainfall occurs predominantly from June to October at an average annual rate of 860 mm. The mine tailings were collected directly from the disposal site (Fig. 2a) and air-dried for use. A soil with a relatively low vanadium content was sampled from an agricultural site, using a corer (ø 7.5 cm) to 20-cm depth to obtain a 1-kg mixture of 3 samples taken within a distance of 2–5 m of each other. The soil was oxic and well-drained, and contained no minerals that occur under reducing conditions (e.g. sulphides). The sample was homogenised, sieved to 2 mm and air-dried prior to sequential extraction and leaching experiments. Field-moist samples were used for pH measurements using a pH electrode in a 1:2.5 soil and mine tailing/water ratio. Organic carbon contents were calculated from analyses using the Walkley–Black technique [21], assuming that the content of sulphide phases in our well-drained soil was negligible. However, the organic carbon in the mine tailings may be overestimated due to the presence of magnetite. The characteristics of the soil and mine tailings are shown in Table 1. The soil contained 83.95% sand, 9.51% silt and 6.54% clay as determined by the hydrometer method [22].

2.2. Sequential extraction

Sequential vanadium extraction in the soil and mine tailings was performed based on the schemes proposed by Wenzel et al. [23] and Tessier et al. [24], as the BCR method has been extensively applied to determine vanadium fractionation in Panzhihua soils by Teng et al. [2]. The extraction sequence of Wenzel et al.