Sorption of Cobalt and Nickel by Biogenic Birnessite

JASQUELIN PEÑA¹*, ANNA A. SIMANOVA¹, JOHN R. BARGAR³, AND GARRISON SPOSITO²

(*correspondence: jasquelin.pena@unil.ch)

¹University of Lausanne, Switzerland, jasquelin.pena@unil.ch, (anna.simanova@unil.ch⁾

²Lawrence Berkeley National Laboratory, Berkeley, USA (gsposito@berkeley.edu)

³Stanford Synchrotron Radiation Lightsource, Menlo Park, USA (horger@slag.stonford.edu)

USA,(bargar@slac.stanford.edu)

Birnessite minerals (layer-type MnO₂) produced by bacteria and fungi participate in important biogeochemical processes, particularly trace metal scavenging. Biogenic birnessite, which is enmeshed in a matrix of bacterial cells and extracellular polymeric substances (biomass), has nanoparticulate dimensions and significant structural disorder created by Mn(IV) vacancies. Trace metals tend to adsorb at vacancy sites or become incorporated into the MnO₂ sheet. Thus, the additional sorption sites presented to the solution by the biomass and the mineral particle edges may have a lower affinity for metals than the vacancy sites. In this study we use extended X-ray absorption fine structure (EXAFS) spectroscopy to investigate the mechanisms of Co and Ni sorption in slurries containing Co, Ni and Co + Ni at pH 6 to determine whether metal ions partition to non-vacancy binding sites in the presence of a competing metal. We expect that Co binds strongly to vacancy sites, out-competing Ni, and thus forcing Ni to bind to particle edges or biomass.

In Co-only and Co + Ni samples, we observed similar sorption mechanisms: significant incorporation of Co into the MnO₂ sheet as Co(III) and adsorption at vacancy sites as Co(II). In addition, the fraction of adsorbed Co(II) increased with surface loading. Time-resolved Co K-edge EXAFS spectra acquired from a biomass-free MnO₂ suspension (δ-MnO₂) suggest that adsorbed Co(II) precedes Co(III) incorporation. In contrast to Co sorption, Ni sorption in the Co+Ni samples differed significantly from the Ni-only samples [1]. In the presence of Co, Ni sorption at vacancy sites was markedly reduced, with Ni partitioning to the biomass and birnessite particle edges. Our results indicate that Co uptake into biogenic MnO₂ effectively reduces the proportion of vacancy sites available for Ni sorption, whereas Co uptake is not impacted by Ni sorption. This research is relevant to polluted environments where the attenuation and bioavailability of competing metals may be determined by their affinity to the available sorption sites.

[1] Pena, J., Kwon, K. D., Refson, K., Bargar, J. R., Sposito, G. (2010) *Geochim. Cosmochim. Acta* 74, 3076-3089.

The study on the solubility of the vanadium system focused on Panzhihua, China

 $\begin{array}{c} \textbf{Y}. \textbf{PENG}^{1,2}, \textbf{Y}. \textbf{ZENG}^{1,2*}, \textbf{J}. \textbf{J}. \textbf{LI}^1, \textbf{S}. \textbf{FENG}^{1,2}\\ \textbf{AND} \textbf{X}. \textbf{D}. \textbf{YU}^1 \end{array}$

¹College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu, 610059, P. R. China;

²Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu, 610059, P. R. China

(* correspondence: zengyster@gmail.com)

In recent years, the interest of the relationship between microelement and human health increased. Vanadium absence may have negative effects, and it also can be toxic if exposure occurs at high enough levels. It has strong transfer ability in environment. This ability related to the solubility of vanadium in soil solution.

Panzhihua, Sichuan is an important production base of vanadium and titanium magnetite. The vanadium storage is 64% of the total vanadium in China. The vanadium mining and smelting accelerated the vanadium diffusion in soil and water. It causes special environmental problems of vanadium in Panzhihua. Different surface soil in the region, the average mass fraction of vanadium is over 100×10^{6} ,[1] far exceeding the background values of Chinese soil vanadium 86×10^{6} .[2] The amount of vanadium in the soil surrounding smelter is 16.5 times of contrast values. The amount of vanadium in the plant samples is 6.6 times of contrast values.[3]

The solubility of vanadium in soil solution is effected by coexisting ions in soil, such as potassium, sodium, phosphorus and so on. In order to investigate the relationship of solubility between vanadium and the other co-existing ion in soil, the phase equilibria of the quinary system NaVO₃ + $KVO_3 + NaH_2PO_4 + KH_2PO_4 + (NH_2)_2CO + H_2O$ and its five quaternary sub-systems were studied at 298 K with isothermal dissoluble method. According to the experimental results, the crystallization form of metavanadate is polyoxovanadate in the weakly acid system. The dissolution and migration of vanadium in aqueous solution has negative correlation with H₂PO₄⁻ and (NH₂)₂CO. The exisiting of K⁺ has little effect on the solubility of vanadium. This suggest that in similar soil environment, the solubility of vanadium was restrained by the increase of H2PO4 and (NH2)2CO, which can affect the transfer ability of vanadium.

The Research Fund from the Sichuan Provincial Education Department (11ZZ009).

Teng, Tuo & Ni. (2003) Chinese Journal of Geochemistry, 22, 253-262.
Wei, Chen & Zheng. (1991) Environmental Science, 12, 12-19.
Wang & Wei. (1995) Element Chemistry of Soil Environment, 231-241.