

## Reduction of contaminant Tc(VII) by magnetite ( $\text{Fe}_3\text{O}_4$ ) and titanomagnetite ( $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ) nanoparticles

J. LIU<sup>\*1</sup>, C.I. PEARCE<sup>1</sup>, O. QAFOKU<sup>1</sup>, E. ARENHOLZ<sup>2</sup>, S. HEALD<sup>3</sup>, T. PERETYAZHKO<sup>1</sup> AND K.M. ROSSO<sup>1</sup>

<sup>1</sup>Pacific Northwest National Laboratory, Richland, WA 99354 USA (\* Correspondence: juan.liu@pnl.gov)

<sup>2</sup>Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

<sup>3</sup>Argonne National Laboratory, Argonne, IL 60439, USA

The radionuclide technetium is an important subsurface contaminant at many nuclear reprocessing sites, such as the Hanford site, Washington, USA. This research investigated reduction kinetics of the highly soluble pertechnetate anion  $[\text{Tc} (\text{VII})\text{O}_4^-]$  to sparingly soluble  $[\text{Tc} (\text{IV})\text{O}_2\cdot\text{H}_2\text{O}]$  by nanoscale mixed valent iron oxides. Magnetite ( $\text{Fe}_3\text{O}_4$ ) and Ti-substituted magnetite ( $\text{Ti}_x\text{Fe}_{3-x}\text{O}_4$ ) are common minerals in Hanford sediments. Nanoparticle forms with varying Ti content ( $0 < x \leq 0.5$ ) were synthesized using an aqueous solution protocol. The resulting magnetite ( $x = 0$ ) were  $\sim 12$  nm spherical nanoparticles, and titanomagnetite ( $0 < x \leq 0.5$ ), formed  $\sim 10$  nm spherical nanoparticles. X-ray diffraction (XRD) patterns show that the cell parameter increases with increasing Ti-doping up to  $x = 0.35$ , which indicates that, when present, titanium ions replaced iron ions in the crystal structure up to this amount. The distribution and ratio of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations were studied by X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). Lattice Fe (II) concentration increases systematically with increasing Ti doping when  $0 < x \leq 0.35$ , consistent with substitution as Ti (IV).

Tc (VII) reduction rates by the magnetite and titanomagnetite nanoparticles were measured in HEPES buffer solution at pH = 8. Titanomagnetite shows significantly higher reactivity than magnetite, and the higher levels of Ti-substitution yields a higher reduction rate and extent. No crystalline secondary phases were detected in the reaction products. The smaller cell parameters of the residual nanoparticle solids indicates that the structural Fe (II) was oxidized by Tc (VII). The collective measurements point to a picture of condition-sensitive dynamic exchange of reducing equivalents between bulk lattice Fe (II), more accessible surface-associated Fe (II), and solubilized Fe (II) that is dictated by the chemical potential of Fe (II) built into the solid, a property that in turn depends on the nature and content of aliovalent metal substitution impurities.

## Ore-forming fluid characteristics of the Hukeng tungsten deposit, Jiangxi Province, South China

JUN LIU<sup>1</sup>, HUISHOU YE<sup>2</sup>, GUIQING XIE<sup>2</sup> AND WEI ZHANG<sup>3</sup>

<sup>1</sup>The Civil Engineering School, Anhui University of Architecture, P.R. China (fzel@tom.com)

<sup>2</sup>Institute of Mineral Resources, Chinese Academy of Geological Sciences, P.R. China

<sup>3</sup>Geoscience and Resource School, China University of Geoscience, P.R. China

Hukeng tungsten deposit, located in Wugongshan metallogenic belt in central part of Jiangxi Province, South China, is one large scale quartz vein type wolframite deposit, which is in the south margin of Hukeng granite intrusion, covering the area of  $6 \text{ km}^2$ . The deposit can be divided into quartz-wolframite, quartz-fluorite-wolframite and quartz-pyrite-sphalerite-wolframite three metallogenic stages [1].

There are three dominant types of fluid inclusions related to metallogenesis in the Hukeng quartz vein wolframite deposit: liquid-rich inclusion, gas-rich inclusion and liquid-gas two-phase inclusion, in which liquid-gas two-phase inclusion occupies more than 90% of the whole.

The homogenization temperatures of fluid inclusions from quartz in three metallogenic stages vary from 200 to 300°C, with peak values between 220 and 240°C; and the salinities are from 0 to 10 wt% NaCl eq., with peak values between 6 and 8 wt% NaCl eq.; and the corresponding densities range from 0.7 to 1 g/cm<sup>3</sup>, with peak values between 0.8 and 0.9 g/cm<sup>3</sup>. These features represent that the fluids are medium temperature, low density and low salinity in the ore-forming fluids in the Hukeng tungsten deposit.

The analytic results get by Laser Raman Spectroscopy, indicate the fluids in different metallogenic stages of the deposit belong to  $\text{Na}^+-\text{K}^+-\text{Cl}^-\text{SO}_4^{2-}$  type, suggesting the fluids formed under relative reducing environment.

The H-O isotopic values show that the ore-forming fluids are predominated by magmatic water, mixed with minor amount of meteoric water. Moreover, the ore-forming fluids took place hydrogen and oxygen isotopic exchange with water from metamorphic rocks.

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[1] Liu. (2008) doctoral dissertation, China University of Geoscience, P.R. China, 76–78.