Low-temperature electron paramagnetic resonance studies on natural clinchlore

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We present here a low temperature electron paramagnetic resonance studies on the natural monoclinic (IIb) clinochlore with the composition (Mg_{2.988} Al_{1.196} Fe_{1.6845} Mn_{0.026})_{5.8945} $(Si_{2.559} Al_{1.441})_4 O_{10} (OH)_8$, different temperatures (123-295 K). The population of spin levels (N) has been calculated for $g \approx 2.0$ and $g \approx 8.0$ resonance signals. EPR spectra of chlorite were also recorded at different temperatures in the 123-295 K range. The temperature was varied using a JES-UCT-2AX variable temperature controller. For low temperature measurements, nitrogen gas was evaporated from liquid nitrogen in a metal Dewar; the evaporation rate was controlled automatically. A temperature stability of ±1K was obtained by waiting for about 30 min at the set temperature before recording the spectrum at each temperature The room temperature spectrum exhibits two resonance signals centered at $g \approx 2.0$ and at $g \approx 8.0$.[1] The resonance signal at $g \approx 2.0$ shows a six line hyperfine structure (hfs) which is a characteristic of Mn²⁺ ions with a nuclear spin I = 5/2. Mn²⁺ ions belong to d⁵ configuration. In the case of d⁵ transition metal ions, it is known that axial distortion of octahedral symmetry gives rise to three Kramers doublets | ± 5/2, $\pm 3/2$ and $\pm 1/2$ It is observed that N increases with decreasing temperature. From EPR spectra, the spin-Hamiltonian parameters have been evaluated. The zero-field splitting (ZFS) parameter (D) is found to be decreasing with the increase of temperature in the temperature range 100 to 300 K, which is attributed to the thermally induced changes in the sitedistortions. The intensity of Fe³⁺ signal is also found to be temperature dependent and found to be similar to that of Mn^{2+} ions. The peak-to-peak width of the g ≈ 8.0 resonance signal is found to increase with decrease in temperature.

[1] Kumar G.N.H. *et al.*, (2009) *Phys. Chem. Minerals.* Doi 10.1007/s00269-009-0291-5 (in press)

In situ remediation: A noble approach for Arsenic contaminated groundwater

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A sustainable and economical technology that has been developed for the removal of metals from the groundwater is *in situ* bioprecipitation (ISBP) which consists of stimulating sulfate reducing bacteria to form insoluble metal sulfide precipitates. Stimulation of sulfate reducing bacteria is achieved by using substrates like lactate, acetate that provide reducing equivalents for reduction of sulfate and result in production of sulfides. The technology is proven for heavy metals like Zn and Cd but oxyanions like arsenate As(V) often present as co-contaminants at these metal contaminated sites (also geogenically) do get reduced as well into the mobile and toxic arsenite As(III) and represent a high risk for nearby receptors like drinking water wells.

Zero-valent iron (ZVI) is considered as a potential remediation agent due to multiple ZVI-metal interactions such as surface complexation, reduction, (co)precipitation and cementation. The anaerobic corrosion of ZVI causes the oxidation state to decrease and formation of hydrogen. The formed H_2 is a potential e-donor for sulphate reducing bacteria with a stoichiometric relation of 4mmolH₂/mmol of SO₄ reduced in autotrophic sulfate reduction.

The hydrogen generation potential was studied using different types of ZVI with particle sizes ranging between 70nm-300mm. The highest hydrogen production was observed with nano scale ZVI. Batch experiments are performed to stimulate SRB by the slow release of H_2 from nano and micro scale ZVI which can be used as an electron donor in microcosm tests. In these tests aquifer and groundwater containing metals (Zn,Cd), sulfate and oxyanions (arsenate/arsenite) are studied.

"This is a contribution of the AquaTRAIN MRTN (Contract No. MRTN-CT-2006-035420) funded under the European Commission Sixth Framework Programme (2002-2006) Marie Curie Actions, Human Resources & Mobility Activity Area – Research Training Networks"