Controls on the formation and crystallization of Mg^{2+}-Fe^{3+}-SO_4^{2-} type layered double hydroxides

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Introduction

Layered double hydroxides (LDH) can play an important role in remediation of hazardous contaminants. Hydrotalcite-like (HTlc) LDH, also known as anionic clays, can be precipitated from numerous divalent (M^{2+}) and trivalent (M^{3+}) cations along with interlayer anions (A^{n-}) where the nature, M^{2+}/M^{3+} ratio and concentation of ions, hydrothermal conditions, aqueous pH can strongly control their formation and crystallization and, as such, their applicability to act as sorbents, catalysts, pharmaceuticals, etc. This study address such aspects using geochemical, spectroscopic, microscopic and diffractogram techniques.

Materials and Methods

HTlc formation was monitored using the coprecipitation synthesis method [1] at ambient temperature and pressure conditions and by varying the pH (7-13), M^{2+}/M^{3+} ratio (0.5-2.5), cation addition rate (2-100 ml h^{-1}), and cation concentrations (0.1-1.0 M) at a constant M^{2+}/M^{3+} ratio (1.0), while assessing the degree of crystallinity over 30 days at three temperatures (22, 65 and 95 °C) and two drying temperatures (100 and 200 °C). The resultant solid phases were studied using X-ray diffraction, Raman and ATR-Infrared spectroscopy, and SEM and thermogravimetric analysis.

Results and Discussion

Formation of HTlc was favored at pH ≥ 9 and $M^{2+}/M^{3+} \geq 0.75$ with both CO_3^{2-} and SO_4^{2-} as interlayer anions. The latttice parameters c and a determined at pH 13 and $M^{2+}/M^{3+}=2.5$ was ~23.5 Å and ~3.1 Å, respectively. Although HTlc formation was not greatly influenced by the reagent addition rate and M^{2+}-M^{3+} concentrations, slow addition appeared to inhibit development of $d_{(110)}$ plane representing poor 'a' crystallographic development, while slow addition and lower M^{2+}-M^{3+} concentrations facilitated slightly better crystallization. This may be explained by better nucleation and the lack of availability of elevated concentrations of cations [2].

The degree of crystallinity was observed to increase after ageing for 30 days at room temperature (RT, 22±2 °C), increasing the hydrothermal temperature to 95 °C within 1 day and increasing the drying temperature to 200 °C. The crystallization started lowering after 5 days and 1 day at 65 and 95 °C hydrothermal treatment, respectively.

Conclusions

Preliminary observations suggest increasing pH, M^{2+}/M^{3+} ratio, low M^{2+}-M^{3+} concentrations, and a slow mixing rate facilitate HTlc formation and enhance its crystallinity. Although HTlc is likely to develop crystallinity at RT upon prolonged exposure, elevated hydrothermal temperatures may adversely impact its structure.

[1] Cavani et al. (1991) *Catal Today* **11**, 173-301.
[2] Hickey et al. (2000) *J Mater Sci* **35**, 4347-4355.

Boron contamination at the McIntyre tailings, Timmins, Ontario

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Anomalous concentrations of soluble boron of uncertain origin occur in >40 year old mine tailings of the McIntyre-Hollinger mesothermal gold deposit. We seek to understand 1) the distribution and movement of B in the tailings and 2) sources of soluble B including: the wall-rock of the mineralization, the gangue minerals, and anthropogenic borax that might have been used to smelt the gold ore.

To explore the distribution of boron within an area of about 100,000 m^2, eight boreholes (e.g. H1) were drilled manually to a depth of ~9 m and sampled at ~0.15 or ~1 m intervals. The samples were leached with deionized water at a sediment:water ratio of 1:3 and the filtered leachate was analyzed by ion chromatography. Boron is distributed heterogeneously with depth and distance from the edge of the tailings dam (Fig. 1). Boron contents correlate positively with the ≤38 μm grain size fraction, indicating that absorbtion onto silt-clay particles and/or low permeability result in B build-up. Tailings near surface and at the margin of the dams are coarser and depleted in B. Ephemeral, efflorescent hydrous Mg-borate found along the dam edge is consistent with an outflow of B along paths of high permeability.

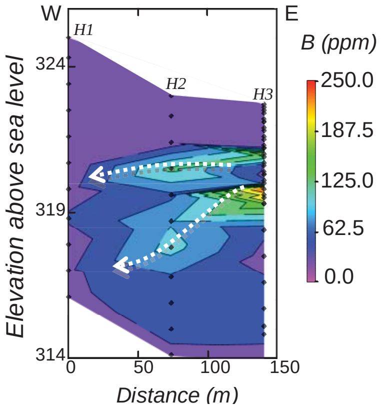

Figure 1: W-E cross-section of B (ppm) distribution and proposed discharge paths to edge of the dam ~20 m west of H1.

The unusual B contents in the McIntyre tailings might originate from altered basaltic wall-rock with B contents <3000 ppm. However, the erratic character of the anomaly suggests that the release of B from the disposal of crushed, borax-fluxed slag into the tailings is also possible. Fresh tourmaline in the tailings sediment and relatively soluble gangue minerals (anhydrite, calcite, siderite, etc.) with <6 ppm B (via laser ablation ICP-MS) cannot account for the amount of soluble B encountered.