S1 of S3

Supplementary Materials: Coprecipitation of Co²⁺, Ni²⁺ and Zn²⁺ with Mn(III/IV) oxides formed in metal-rich mine waters

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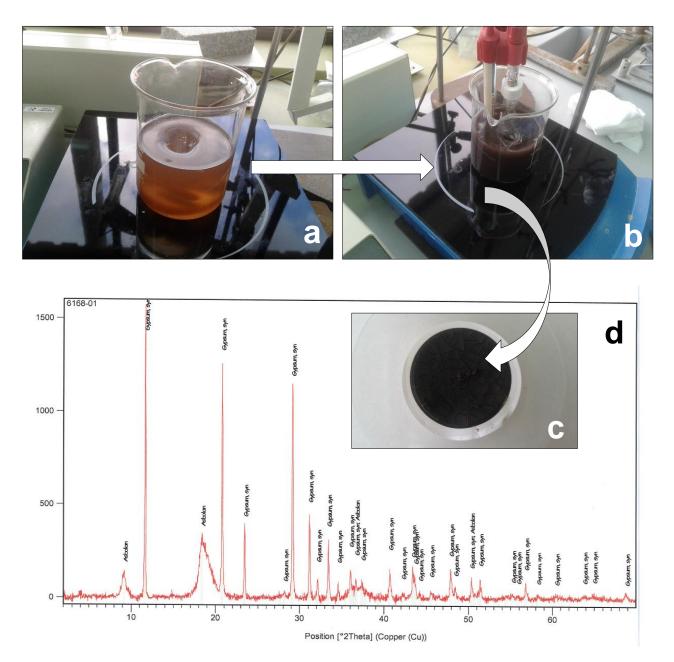
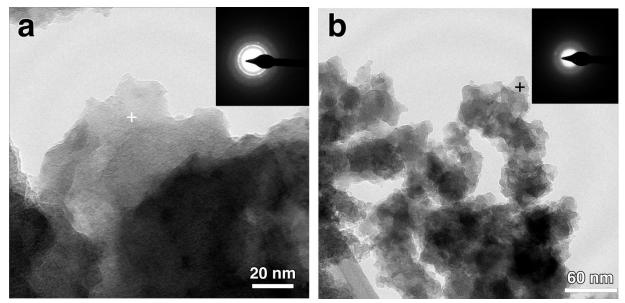


Figure S1. Synthesis of Mn oxides by oxidation of disolved Mn(II) in metal-rich mine water: (**a**) Brown solution at the begining of the oxidation experiment in stirring unit; (**b**) black suspension produced after prolonged Mn(II) oxidation during several weeks; (**c**) black precipitate recovered by vacuum-filtration of the suspended Mn oxides; (**d**) corresponding XRD pattern for a Mn precipitate obtained in the experiment with water from La Zarza (see also Figure 3c-d for SEM images).

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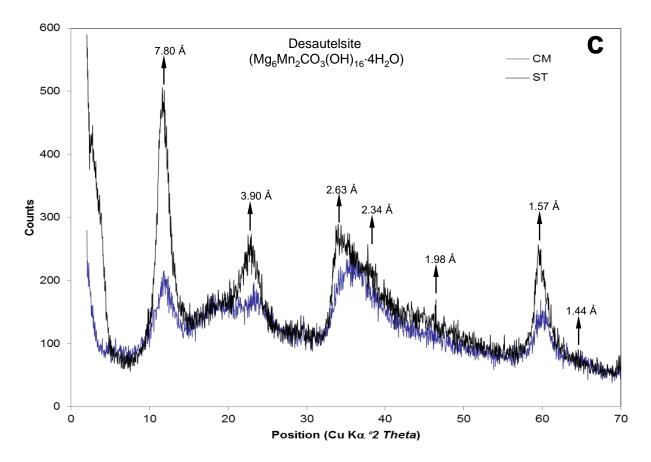


Figure S2. (a-b) TEM images of nanometric precipitates containing Mn, Mg and Zn obtained by neutralization of metal-rich acidic mine water from Cueva de la Mora (a) and San Telmo (b) mines (the insets show the electron diffraction patterns obtained for the points indicated with cross symbols). These precipitates were formed between pH 9.0 and 10.0 and contained abundant desautelsite $(Mg_6Mn_2CO_3(OH)_{16}\cdot 4H_2O)$. (c) XRD patterns obtained for these precipitates, showing the major peaks of desautelsite. Reprinted from [1] with kind permission from The Royal Mineralogical Society of Great Britain and Northern Ireland.

[1] Sánchez-España J; Yusta I. Low-crystallinity products of trace metal precipitation in neutralized pit lake waters without ferric and aluminous adsorbent: Geochemical modelling and mineralogical analyses. *Mineral. Mag.* **2015**, 79, 781–798.

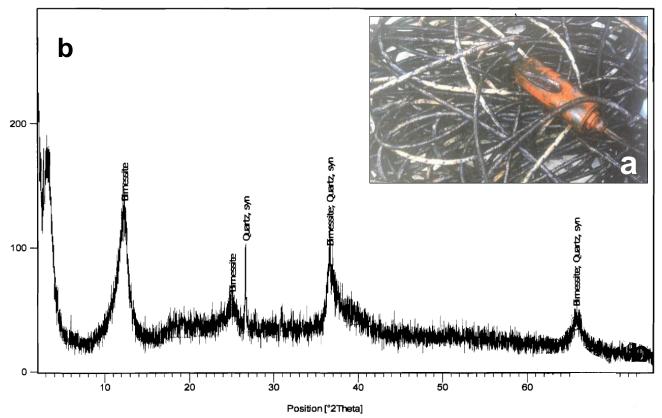


Figure S3. (a) Detail of Mn oxides coating mooring ropes in the Reocín mine pit lake; these Mn oxides were periodically sampled and analyzed during 2008 to 2010; (b) Example of XRD pattern for one of these samples, which was dominated by birnessite, along with some detrital quartz (Qtz). Reprinted from [2].

[2] López-Pamo, E.; Sánchez-España, J.; Santofimia, E.; Reyes, J.; Martín-Rubí, J.A. Limnología físico-química del lago formado durante la inundación de la Corta de Reocín, Cantabria (Marzo 2008-Febrero 2009). Instituto Geológico y Minero de España (IGME), Ministerio de Ciencia e Innovación: Madrid, Spain, 2009. Unpublished Report; p. 116.