Fast, selective and ecological ion-exchange materials for hydrometallurgy (FSE-IX)

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Abstract

In this project the plan is to combine in an optimal manner the good properties of inorganic ion-exchangers with ion-exchangers based on organic polymers. The resulting material will be a composite having either an inorganic ion-exchanger incorporated into an organic matrix or an inorganic matrix with organic functional groups. Furthermore, the aim is to utilize waste materials from mining industry, such as metal oxides, for the preparation of the new ion-exchangers. These synthesized materials will be tested in relevant hydrometallurgical applications.

During 2007 several manganese oxides with tunnel or layered structures have been prepared and studied as selective ion exchange materials. So far the main focus has been on a narrow-pore manganese dioxide, cryptomelane. In addition three other manganese oxides (hausmannite, birnessite and todorokite) have been prepared. These materials have been tested for the separation of metals like Ni, Co, Mn, and Zn from hydrometallurgical process solutions. In particular, attempts have been made to find an inexpensive oxidant for Mn(II) in the synthesis and to use authentic process streams as the Mn(II) source.

Preliminary tests have also been made to prepare composite materials, where the finely divided manganese oxides are embedded in a support material. Evaluation of various supporting methods and actual ion-exchange tests with the composite materials are the main objectives of the next project stage. As a reference for one possible application, the removal of Cu and Ni from zinc process solutions has been studied using silica-supported chelating adsorbents.

Results

A. Preparation and Characterization of Cryptomelane

Simulated hydrometallurgical process water containing about 1.2 g/L Mn and smaller amounts of Al, Ca, Fe, Mg; and Na (all < l00 mg/L) was used as the source for cryptomelane-type manganese oxide synthesis. Three out of five of the synthesised materials showed similar structural properties as a reference material synthesised from laboratory chemical. De Guzman's OMS cryptomelane was chosen as reference material due to its well-known structure and good ion-exchange properties. The three materials had low crystallinity (Fig. 1) but porous structure and high surface area (pore volume ~0.45 cm^3/g, ~90 m^2/g) that makes the materials well suited for ion exchange applications. Although part of the impurities of precursor followed manganese from the wastewater at the synthesis, the ion exchange properties of the materials were similar to the OMS material and high uptake of heavy metals, particularly nickel was observed.

As a result we were able to synthesis cryptomelane structured manganese oxide material from metallurgical wastewater simulant that has good ion exchange properties and potential for wide range of applications.

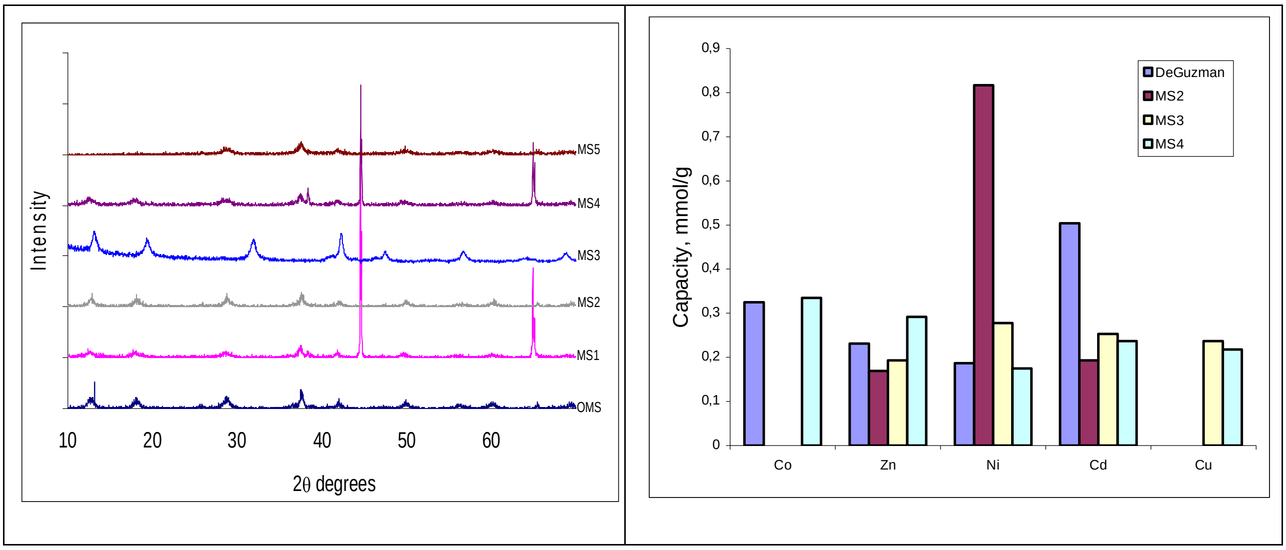

Figure 1 XRD analysis (a) and metal uptake capacities (b) for synthesized and reference cryptomelanes.

The cryptomelane studies were carried out mostly at UH. A master's thesis on this topic is nearly finished and one scientific article is under preparation.

B. Synthesis and Characterization of Other Manganese Oxides

The conventional cryptomelane synthesis is based on oxidation of Mn(II) by permanganate ions and, therefore, processes using less expensive chemicals are desirable. One key objective was thus to optimize the reagent used in oxidation so that the production costs could be minimized. It has been found that Mn(II) can be oxidized to the target oxidation state using oxygen or even air in highly alkaline solutions. At these conditions the primary product is a layered manganese oxide, birnessite, which can be transformed by ion-exchange and hydrothermal treatments to the tunnel structures.

Depending on the template ion and the process conditions, both narrow-pore cryptomelane and wide-pore todorokite can be obtained.

Oxidation of Mn(II) at less alkaline conditions yields hausmannite-type oxides. These materials do not have tunnel structures, but they still have distinct ion-exchange properties and adsorb efficiently transient metals, like Cu and Ni.

A synthetic $MnSO_4$ solution was used as the manganese source. The oxides were characterized by elemental analysis (ICP-OES, SEM-EDAX), by structural and spectral analysis (XRD, FTIR) and by physico-chemical means (pH and redox titrations). Further characterization methods included thermal analysis as well as particle size and pore volume measurements.

The tendency of manganese oxides to reduce and dissolve at acidic conditions and in the presence of easily oxidizing materials (Fe^{II}, Co^{II} or organic substances) limits their use in some applications. The acid resistance of the synthetized oxides has been measured in order to elucidate the dissolution mechanisms. The highly oxidized and highly crystalline materials were found to be more stable than the lower oxides.

These studies were mainly carried out at LUT and a scientific article is under preparation in co-operation with UH.

In part A we showed that the manganese oxide could be prepared without previous solution purification. Nevertheless, we also studied at LUT an alternative route by utilizing solvent extraction to recover manganese from the mixed-metal feed and then to produce pure $MnSO_4$ solution as an intermediate. Results from this sub-project were reported in a conference presentation [1].

C. Hydrometallurgical Separations with Silica-Based Chelating Adsorbents

Removal of impurity metals, notably copper, nickel and cobalt, from concentrated zinc solutions is one possible application for the manganese oxide ion-exchangers. As a reference, this case was studied using commercially available silica-supported chelating adsorbents and the results have been reported in manuscript [2].

Impact of the study

The research group is in frequent contact with mining companies. This enables us to be aware of the composition of the potential process streams. The opening the Talvivaara nickel mine in Sotkamo could be an important source of e.g. manganese but also other materials.

On the other hand the knowledge accumulated in this FA project is without delay communicated to industry through the cooperating researchers. Parallel to this FA funded project we had during 2007 the following cooperation projects funded by industry: 1) Recovery of minor metals with anion exchangers from Talvivaara solution (J.Tamminen and E.Paatero, LUT 2007); 2) Recovery of metals from chloride solutions (with Norilsk Nickel Harjavalta Oy by N. Kaakkolammi, Master's Thesis, LUT 2007); 3) Utilizing of gypsum formed in mining industry (with Talvivaara Project Oy by K. Pussinen Master's Thesis, in preparation); and 4) Recovery of germanium with ion-exchange (with OMG Kokkola Chemicals, by J. Heinonen, Masters's Thesis in progress)

Progress of the research

The project has proceeded as scheduled in the original application. However, some reorganization of the topics was found appropriate. More resources were allocated in preparation and characterization of the manganese oxides (task D), and this has been the main topic also at LUT. Studies on functionalization of TiO_2 and other oxides (task C) have thus been postponed to later stages and only an extensive literary survey has been made so far (task A). Based on a preliminary study on ZrO_2 as a support was omitted from the future plan due to price and stability.

Publications

1. J. Pakarinen, E. Paatero, Recovery of Manganese from Mixed Metal Solutions by Solvent Extraction with Organophosphorus Extractants, Conference in St. Petersburg State Mining Institute, 25-27.4.2007 (Oral presentation + article in press).
2. K. Sirola, M. Laatikainen, M. Lahtinen and E. Paatero, Separation of Copper and Nickel from Concentrated $ZnSO_4$ Solutions with Silica-Supported Chelating Adsorbents (Submitted to Sep. Purif. Technol., 2007).