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Synthesis and anion exchange properties of a Zn/Ni double hydroxide salt with a guarinoite structure

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ABSTRACT

In this study, the first route to synthesize a compound with the guarinoite structure $(Zn,Co,Ni)_6(SO_4)(OH,Cl)_{10}\cdot 5H_2O$ is reported. Zn/Ni guarinoite is obtained from the reaction of $NiSO_4\cdot 7H_2O$ with solid ZnO in aqueous solution. The resulting green Zn/Ni guarinoite ($(Zn_{3.52}Ni_{1.63})(SO_4)_{1.33}(OH_{7.64})\cdot 4.67H_2O$) was characterized by X-ray diffraction, infrared spectrometry, UV–Visible spectrometry and thermal analysis. It is shown that its structure is similar to the one described for the layered Zn sulfate hydroxide hydrate, i.e. brucite layers with $\frac{1}{4}$ empty octahedra presenting tetrahedrally coordinated divalent atoms above and below the empty octahedra. Ni atoms are located in the octahedra and zinc atoms in tetrahedra and octahedra. In this structure the exchangeable anions are located at the apex of tetrahedra. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations show that the Zn/Ni guarinoite is composed of aggregates of hexagonal plates of several hundreds of nanometers. Due to its interest for industrial or environmental applications, the exchange of sulfate groups by carbonates has been investigated. Results show a limited exchange and a higher affinity of the Zn/Ni guarinoite for sulfates compared to carbonates.

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1. Introduction

Guarinoite ($(ZnCoNi)_6(SO_4)(OH,Cl)_{10}\cdot 5H_2O$) is a mineral that has been discovered in 1993 in the Cap Garonne mine (Var, France). This mine has been worked for copper and lead, but is mostly known to have provided numerous new mineral species such as Perroudite $Hg_5Ag_4S_5(Cl,I,Br)_4$ [1], Geminite $Cu_2As_2O_7\cdot 3H_2O$ [2], Camerolaite $Cu_4Al_2[HSbO_4,SO_4](OH)_{10}(CO_3)\cdot 2H_2O$ [3], Deloryite $Cu_4(UO_2)(MoO_4)_2(OH)_6$ [4], Capgaronite HgS.Ag(Cl,Br,I) [5], Theresemagnanite $(CoZnNi)_6(SO_4)(OH,Cl)_{10}\cdot 8H_2O$ [6], Zdenekite $NaPbCu_5(AsO_4)_4Cl\cdot 5H_2O$ [7], Mahnertite (Na,Ca)-$Cu_3(AsO_4)_2Cl\cdot 4H_2O$ [8], Iltisite HgSAg(Cl,Br) [9], or Pushcharovskite $Cu(AsO_3\cdot OH)\cdot H_2O$ [10].

Sarp [6] has described guarinoite as bright to deep pink aggregates or rounded aggregates made up of thin hexagonal crystals (space group: $P63$, $P63/m$, or $P6322$, with $a = 8.344$ and $c = 21.59$ Å).

Guarinoite is related to the group of hydroxide salts presenting a layered structure. Several different structures are represented in this group. The first one is derived from the structure of brucite $Mg(OH)_2$, where Mg^{2+} cations are occupying the centers of OH^- octahedra joined by their edges to form infinite layers, and where the layers are linked by hydrogen bonds between hydroxyl groups at octahedral vertices. This structure is well represented by the layered double hydroxides (LDHs) family ($[M(II)_{1-x}M(III)_x(OH)_2]\ [A^{n-}]_{x/n}\cdot mH_2O$) where some M^{3+} cations are replacing a part of the M^{2+} cations, thus generating positively charged brucite-like layers that are counterbalanced by anions (A^{n-}) located between the layers [11,12]. These compounds are largely studied as they find many industrial applications such as catalysts, catalyst supports or precursors, anion exchangers, or part of heterostructured nanohybrids [13–16].

The two other structures are represented by basic hydroxides or the double hydroxide salts family (DHS, also known as hydroxyl double salts or hydroxy double salts), in which a part of the divalent cations is not replaced by trivalent cations as in LDHs but is replaced by another divalent cation. The first one is also derived from the structure of brucite, where some OH^- groups are replaced by another anion. The general formula of this family could be written as $(M^{II}_{2-x}M'^{II}_x)(OH)_{2-y}A^{n-}_{y/n}\cdot mH_2O$, where M^{II} and M'^{II} are divalent metal cations such as Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, …

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and A^{n-} an anion such as NO_3^-, Cl^-, SO_4^{2-}, CO_3^{2-}, … [17,18]. Such compounds have been studied, as the anion exchange for large organic species (i.e. aliphatic chain anions) coordinating the metal ion has allowed to tune the interlayer spacing, and thus their magnetic properties [19–23].

The second one is related to the structure of zinc hydroxide nitrate [24,25]. It can be regarded as a variation of a hypothetical $Zn(OH)_2$ structure in the C6 or CdI_2-type group. One quarter of the zinc atoms are removed from the octahedral interstices of the layers. Each filled octahedron shares its edges with two unoccupied and four occupied octahedra. The resulting layer is negatively charged: $[Zn_3^{oct}(OH)_8]^{2-}$. Tetrahedrally coordinated zinc atoms are located above and below the empty octahedron. Three corners of the tetrahedron are occupied by hydroxide ions belonging to the layer described above, the fourth by a water molecule, or another anion [25–27]. Guarinoite and many other Zn/Ni or Zn/Co hydroxide salts belong to this last group.

Most of these compounds have exhibited anion exchange properties [13,17,28–32]. These properties can find many applications. One of the most promising applications is remediation. Indeed many pollutants, from natural or anthropogenic origin, due to high concentrations in water, have disastrous environmental and health implications, such as nitrates [33], fluorides [34] or arsenates [35]. The most studied family of layered hydroxides, i.e. layered double hydroxides, has shown an important limitation for such applications due to their high affinity for carbonates compared to most of the other anions [13]. So, due to the abundance of carbonates in nature, it remains a subject of great interest for environmental applications to find anion exchangers with a low affinity for carbonates.

Many different synthesis routes have been used to obtain these compounds: the most usual synthesis method to obtain such compounds is coprecipitation [12,36], but other routes such as "chimie douce" [37,38] or reaction of a metal salt with a metal oxide or hydroxide [25,28,39–42] have also been used.

As far as the authors know there has been no report on the synthesis of guarinoite in the literature. A few papers have already been published on Zn/Ni hydroxides with different anions [27–29,31,43–47] but none of the synthesized compounds by these authors do present the guarinoite structure.

The aim of this paper is to report a synthesis route for Zn/Ni guarinoite and investigate whether this compound is presenting anion exchange properties.

2. Material and methods

Zn/Ni guarinoite was prepared by a chemical reaction using $NiSO_4 \cdot 7H_2O$ (Prolabo 99%) solution and ZnO powder (Prolabo 99.5%). ZnO powder of 2 g was added to 50 ml of 0.64 M $NiSO_4 \cdot 7H_2O$ aqueous solution (Ni/Zn mole ratio = 1.25) under vigorous stirring at room temperature for 2 h. Then stirring was stopped and the precipitate was aged at room temperature for 1 day. The slurry was centrifuged at 4000 rpm for 5 min (Jouan CR412). The supernatant was eliminated and the sample was dried in a furnace at 40 °C for 24 h.

The anion exchange properties were investigated by mixing 2 g of the synthesized Zn/Ni guarinoite with 100 ml of 0.1 M Na_2CO_3 solution. The mole amount of CO_3^{2-} added was nearly 3 times that of the sulfate content of guarinoite. After equilibrating during 1 day at room temperature, the solid was separated by centrifugation and dried in a furnace at 40 °C for 24 h.

Chemical compositions (Zn and Ni concentrations) have been determined by atomic absorption with a Varian AA 200 after dissolution of the solids by an acid solution composed of HNO_3, HF and $HClO_4$.

Sulfate and carbonate concentrations were determined by measurements of S and C with a Horiba carbon/sulfur analyzer EMIA-820 V.

Powder X-ray diffraction (XRD) patterns have been performed on a Siemens D5000 diffractometer using Co$K\alpha$ radiation operating at 40 kV and 30 mA at room temperature. The scans have been recorded from 4° to 84° (2θ) with a step of 0.02° and a counting time of 1 s per step.

For in-situ temperature study, diffraction data were collected in a conventional Bragg–Brentano configuration with a Vantec-1 linear detector on a X-ray Bruker D8 Advance (Cu$K\alpha_{1,2}$ radiation—40 kV and 40 mA). The diffractometer was equipped with an Anton Paar oven chamber (model HTK1200N) based on a Kanthal® resistive heating attachment for temperature up to 1200 °C. The slits used were 0.3° for the beam and 2.5° Soller for the axial divergence. The diffraction patterns have been recorded between 10° and 70° (2θ) with a step of 0.0164° (2θ). Data acquisition time was 15 min per scan. The heating rate was 10 °C min^{-1} in air and a delay time of 15 min was used to stabilize the sample temperature. Choice of the experimental temperatures was based on the DTA curve to characterize the phenomena observed. The sample temperature has been calibrated using known phase transitions and the thermal expansion of alumina. Peaks have been attributed to the corresponding crystalline phases using ICDD database (PDF-2).

DTA/TG measurements were recorded by a Setaram 92 using platinum crucibles. The powdered samples were analyzed using a heating rate of 10 °C min^{-1} in air (0.5 l h^{-1}).

Infrared spectra were obtained with an attenuated total reflection (ATR) device (Golden Gate) on a Bruker Equinox IFS-55 infrared spectrometer. For each spectrum 20 scans were performed from 4000 to 550 cm^{-1}.

The scanning electron microscopy (SEM) observations have been performed on samples previously sputter-coated with a thin layer of carbon, using a Jeol 6100 coupled with an energy dispersive spectrometer (Kevex Quantum) for chemical analysis, at 25 kV.

The transmission electron microscopy (TEM) observations have been performed at 200 kV (Philips CM20 with a CCD Gatan camera). The TEM samples were prepared by dispersing the powder products in alcohol by ultrasonic treatment, dropping them onto a porous carbon film supported on a copper grid, and then drying them in air.

UV–Visible spectra were obtained on compacted powder sample with an integrating sphere device (Labsphere) on a Perkin Elmer lambda 20 UV–Vis spectrometer. The spectra have been performed in the range of 200–1100 nm with a scan speed of 240 nm min^{-1} at room temperature.

3. Results and discussion

3.1. Structural and thermal characterization

The powder resulting from the synthesis process is a pale green powder. This is far different from the pink color described by Sarp [6] for natural guarinoite. However, this pink color is due to the presence of cobalt ions within the natural guarinoite which are absent from the synthesized compound. Indeed, Zn/Ni double hydroxide salts were described as green powders [27,28,31,44,45] and pale green films [29].

Fig. 1a shows the X-ray diffraction pattern of the synthesized green powder. The diffraction peaks correspond to that of the hexagonal guarinoite mineral with the chemical formula $(Zn,Co,Ni)_6(SO_4)(OH,Cl)_{10} \cdot 5H_2O$ (JCPDS 46-1276). Indexed peaks

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