



Ion-exchange properties of $Zn_4(OH)_6(SO_4) \cdot 2.5H_2O$

Йонообменни свойства на $Zn_4(OH)_6(SO_4) \cdot 2.5H_2O$

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Introduction

In the process of detailed examination of the mutual transformations of zinc hydroxy-salts, a stable phase with powder diffraction pattern not described in the ICDD database was obtained. There are two main reactions for obtaining the new phase: (i) during reaction of both Zn-hydroxy nitrates with sulfate solutions and Zn-hydroxy sulfates (osakaite, namuwite, gordaite) with nitrate solutions and (ii) reaction between Zn hydroxy-sulfates and NaI or KI solutions. The obtained new phase was characterized by a greater value of $d_{001} = 17.84 \text{ \AA}$ comparing to that of other Zn hydroxy sulfate compounds. The chemical formula $Zn_4(OH)_6SO_4 \cdot 2-2.25H_2O$, calculated from the chemical and thermal analyses (Stanimirova et al., 2018) suggests that this new phase is probably a part of the group of zinc hydroxy-salts with similar composition $Zn_4(OH)_6SO_4 \cdot nH_2O$ ($n=5$ osakaite; $n=4$ namuwite, $n=3$ leinsteinite). This type of minerals is built of octahedral-tetrahedral layers and provides many useful ion exchange and sorption properties (Newman, Jones, 1999; Marangoni et al., 2009; Hongo et al., 2010; Hussein et al., 2012; Stanimirova, 2019).

The aim of the present study is to check the possibilities for ion exchange of this new zinc-hydroxy-sulfate-hydrate phase.

Experimental

Initial material: New zinc hydroxy sulfate hydrate phase, $Zn_4(OH)_6SO_4 \cdot 2-2.25H_2O$ was obtained by mixing of 0.5 g of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and 50 ml of 1M Na_2SO_4 for 48h at room temperature and pH of the solution between 5–7.

Ion-exchange properties were investigated by mixing of 0.2 g $Zn_4(OH)_6(SO_4) \cdot 2.5H_2O$ with 20 ml water solution of NaCl, $CaCl_2$ or $SrCl_2$ with different concentrations (0.5M, 1M, or 2M) for different time (24h, 48h and 72h) at room temperature. The pH of the solutions varied in the range 6–8. The products were washed with distilled water and dried at room temperature.

Method: The phase composition of the initial sample and the products was studied by powder X-ray diffractometer D2 Phaser Bruker AXS with Cu-K α radiation in steps of $0.02^\circ \text{ s}^{-1}$.

Results and Discussion

The XRD pattern of the initial sample and the obtained phases from the final transformation processes are presented on Fig. 1. The treatment of the new zinc hydroxy sulfate phase with NaCl results on the formation of gordaite, as the reaction completed in 72 hours. The behavior of the phase is similar to that of the mineral namuwite ($Zn_4(OH)_6(SO_4) \cdot 4H_2O$), which is another confirmation of the affiliation of the phase to the family of zinc hydroxy sulfate mineral representatives. The transformation process is based on the replacement of the water molecule from the apical position of the zinc tetrahedron in the hydroxide layer with Cl^- ion, while the resulting negative charge is compensated by Na^+ – water complexes in the interlayer space (Stanimirova, 2019). The similarity of the studied phase with these representatives is the fact that in the process of transformation in the system the appearance of namuwite is observed (Fig. 1).

The behavior of the new phase at treatment with chloride solutions of divalent cations (Ca^{2+} and Sr^{2+})

is again similar to that of the mineral namuwite: the treatment with 1M CaCl_2 leads to the formation of „Ca-gordaitite” for 24 hours, while the treatment with 0.5 M SrCl_2 leads to the appearance of strontium form of the gordaitite and traces of the celestine (SrSO_4). At a higher concentration of SrCl_2 , the

celestine is formed by Sr^{2+} cations and all available SO_4^{2-} groups, while the other components in the system lead to the formation of a simonkolleite, $\text{Zn}_5(\text{OH})_8\text{Cl}_2$.

The main difference that can be noted in the behavior of the new phase compared to that of the na-

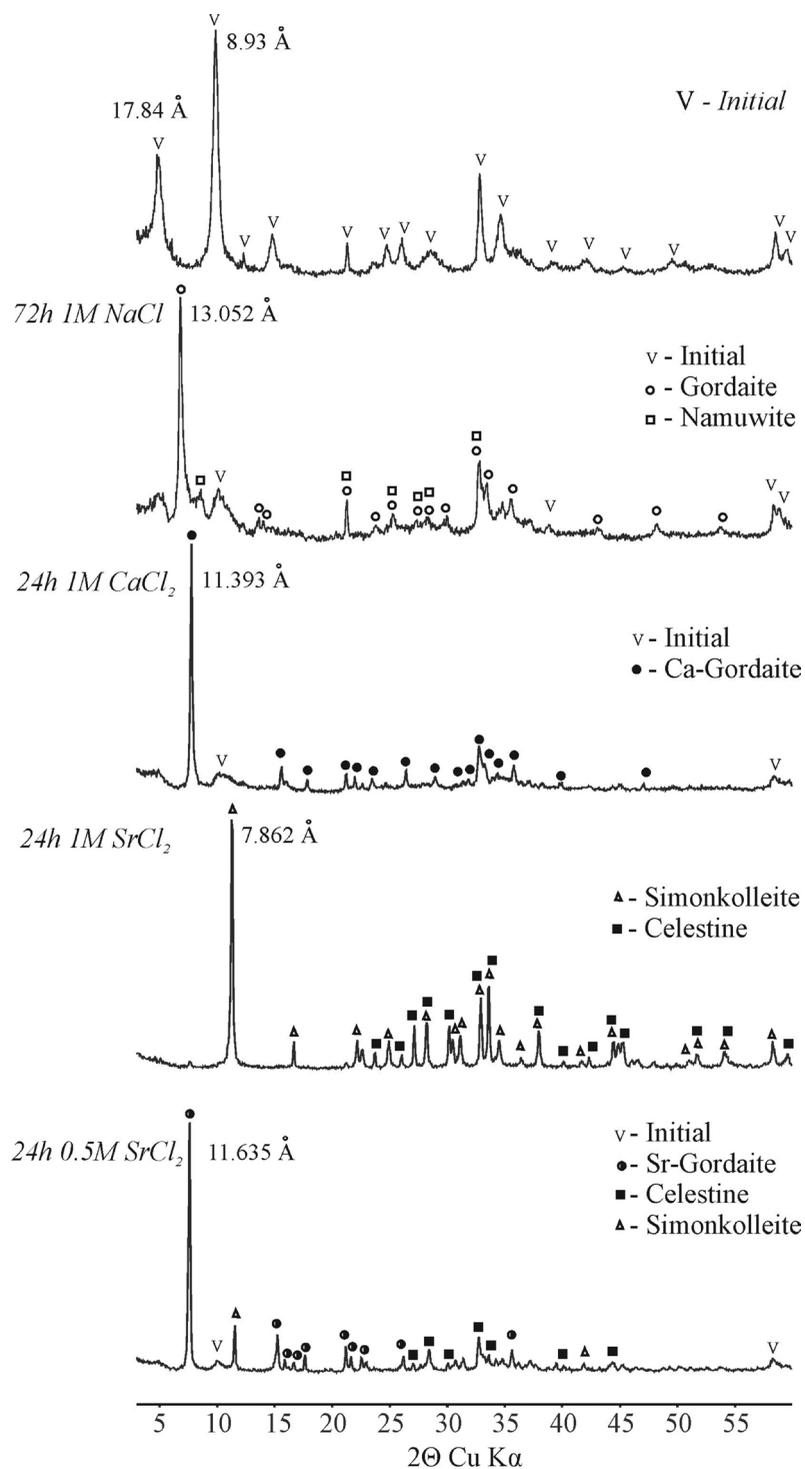


Fig. 1. XRD patterns of the initial and the products of the exchange reactions

muwite is the time to reach the final products. The kinetics of the namuwite transformation reaction is almost constant for a number of cations (Na^+ , K^+ , NH_4^+ , Ca^{2+} and Sr^{2+}) (Stanimirova, 2019), while the rate of transformation of the new phase into the various cationic forms of the gordaite clearly depends on the type of cation in solution. The obtaining of M^{2+} -gordaite (Ca or Sr-form) through ion exchange reaction proceeds much faster than the obtaining of the Na-form of the gordaite mineral. Despite the fact that the value of $d_{001} = 17.84 \text{ \AA}$, the interlayer space of the structure of the new phase is apparently more closed. This suggestion is supported both by the calculated smaller amount of water molecules and by the observed rates of formation of the various cationic forms of gordaite during treatment with chloride solutions. Two complexes of $[\text{Na}(\text{H}_2\text{O})_6]^+$ are presented in the gordaite structure, which caused an opening of the interlayer space with 2.56 \AA in comparison to that in the namuwite. The higher ionic potential of both Ca^{2+} and Sr^{2+} in comparison to that of Na^+ cation provokes their coordination with $9\text{H}_2\text{O}$ molecules. However, in the M^{2+} -gordaites, due to the presence of only one cation-water complex, the interlayer space opens by about $0.5\text{--}1 \text{ \AA}$. Obviously, the more closed interlayer space of the new phase requires more time to open in the process of ion exchange with hydrated Na^+ compared to the intercalation of Ca^{2+} or Sr^{2+} .

In conclusion, it could be summarized that the new phase has exchange properties potentials, like other zinc hydroxy sulfate hydrates composed of

octahedral-tetrahedral layers. The results obtained for the kinetics of ion-exchange reactions are additional useful data for the solving of the structure of the new zinc-hydroxy-sulfate-hydrate phase in the future.

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