

THE SORPTION PROPERTIES OF TOBERMORITE MODIFIED WITH Na⁺ AND Al³⁺ IONS

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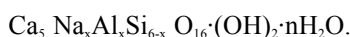
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The effect of Al₂O₃ and NaOH on the formation of 1.13 nm - tobermorite under hydrothermal conditions and ion exchange capacity of tobermorites with and without Al³⁺ as well as with double [Na⁺ + Al³⁺] substitution in relation to heavy metal ions (Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) under static and dynamic conditions were studied. Ion exchange capacity of crystalline 1.13 nm tobermorite and that of Al - substituted tobermorites are insignificant. Insertion of Na⁺ ions into the crystalline lattice of tobermorite increases ten times ion exchange capacity of the sorbent. The ion exchange capacity of [Na⁺ + Al³⁺] - substituted tobermorite is 279 mg Cu²⁺, 230 mg Ni²⁺ and 206 mg Zn²⁺ per gram of the sorbent. The dynamic activity of this compound is highest for Ni²⁺ and Zn²⁺ ions, average for Cu²⁺ and lowest for Co²⁺ ions. Ion exchange capacity of the [Na⁺ + Al³⁺] - substituted tobermorite is only slightly related to the addition of NaOH and Al₂O₃.

INTRODUCTION

The minerals of calcium silicate hydrates group are found in nature. In addition, they are formed during the hydrothermal processes, such as under the evaporation of silica bricks, aerated concrete, or thermal insulating materials [1-3]. The quantity of the new formed product, their phase composition and structure crucially affect their exploitation properties. Therefore, calcium silicates have always been of great importance in the chemistry of binding materials. This interest has grown considerably during recent years.

S. Komarneni et. al [4, 5] have found that calcium silicate hydrates, the first minerals of tobermorite group have good sorption properties. The tobermorite ion exchange capacity increased when Al³⁺ and Na⁺ ions are inserted into tobermorite crystal lattice in an isomorphous way. The chemical formula of such [Na⁺ + Al³⁺] - substituted tobermorite is:



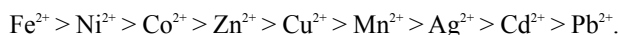
These compounds are a new family of inorganic cations exchangers [4].

Tobermorites ion exchange capacity depends on its chemical composition as well as on the structure of crystalline lattice. Naturally occurring and synthetic unsubstituted tobermorites are noted for their low ion exchange capacity. This is predetermined by the fact that Ca²⁺ ions in these compounds are inserted between separate layers and connected by a strong chemical

bond with the oxygen atoms [3]. Extraneous ions may interfere only if this bond is broken up. Al substituted tobermorites have similar properties. Si⁴⁺ ions in their crystal lattice are replaced by Al³⁺ ions.

However, the situation is changing when Na⁺ ions are inserted into an Al substituted tobermorite crystal lattice. Al³⁺ ions are isomorphously substituted for Si⁴⁺ ions in tetrahedral sites and alkali metal ions, such as Na⁺ are placed in the interlayer and compensate the deficient charge. Na⁺ are very mobile and easily pass into solution being replaced by other ions with higher oxidation degree.

[Na⁺ + Al³⁺] - substituted tobermorites were firstly used for Co²⁺ and Mg²⁺ sorption from aqueous solutions [6, 7]. Recently, it was determined that this compound sorbs divalent ions of heavy metals [8]. The authors proposed the following order of cations according to their ability to participate in exchange reactions with tobermorite:



[Na⁺ + Al³⁺] - substituted tobermorites also show selectivity for some cations, firstly for Cs⁺ and Rb⁺ [9, 10, 11]. Recent data have indicated that this compound is selective to Sr²⁺ ion [12]. Moreover, Fe³⁺ ion may interfere into the tobermorite crystal lattice during ion exchange reaction. Such modified tobermorites may be used as a catalyst in various technologically important chemical reactions [13].

Thus tobermorites is another family of cation exchangers in addition to clay minerals and zeolites. The cation exchange and selectivity properties of substituted tobermorites fall between those of clays and zeolites [14]. Unlike clay minerals and zeolites, the new group of cation exchangers is expected to be thermodynamically stable in cement and concrete with a similar chemical composition. Therefore, the new cation exchangers will be suitable for inexpensive solidification in cement after use, for example, in decontamination of cesium from low-level nuclear wastes [15,16].

However, all these studies lack more detailed data on the relation of tobermorite ion exchange capacity to the quantity of Al^{3+} or $[\text{Na}^+ + \text{Al}^{3+}]$ ions in the lattice. No data have been published on the sorptive properties of tobermorite under dynamic conditions, i.e. in a stream of water.

Heavy metals are widely produced by wide branches of industry, e.g. galvanization, paint, leather, glass, battery metal. Moreover, development of new effective sorbents is essential for improving wastewater purification.

The aim of this work was to estimate the influence of the quantity of Al^{3+} or $[\text{Na}^+ + \text{Al}^{3+}]$ ions in the crystal lattice of the 1.13 nm tobermorite to its ion exchange capacity in relation to heavy metal ions under static and dynamic conditions. In addition, the effect of Al_2O_3 and NaOH on the process of 1.13 nm tobermorite formation under hydrothermal conditions was studied.

EXPERIMENTAL

Materials used in this research were: fine grind reagent $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (loss on ignition - 23.5 %, specific surface area $S_a = 1350 \text{ m}^2/\text{kg}$ by Blain); amorphous Al_2O_3 , obtained by heating $\text{Al}(\text{OH})_3$ for five hours at 550°C temperature ($S_a = 505 \text{ m}^2/\text{kg}$); calcium oxide ($\text{CaO}_{\text{free}} = 98 \%$, $S_a = 548 \text{ m}^2/\text{kg}$) obtained by calcination of calcium carbonate at 1000°C temperature for three hours. Solutions of NaOH , CuSO_4 , NiSO_4 , ZnSO_4 , and CoSO_4 have also been applied.

The X-ray diffraction analysis was performed using DRON - 6 diffractometer, with scanning in a 2θ angle range $4-60^\circ$ with Ni - filtered CuK_α radiation. A thermal analyzer DuPont 990 was applied for differential scanning calorimetry (DSC) studies; with the heating rate $10^\circ\text{C}/\text{min}$. The specific surface area of the raw materials was determined by the Blain method [17]. The concentration of heavy metal ions in the solutions was determined by the atomic emission spectroscopy using a SpectraMetrics Perkin Elmer 503 instrument.

The molar ratios of initial mixtures were: $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.83$ and $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0; 0.025; 0.050$ or 0.075 , respectively. Some of them were

supplemented with 5%, 10% or 20 % of Na_2O (as NaOH) of the dry matter mass.

Water and 33.5% NaOH solution was added to dry, thoroughly homogenized mixtures (the water/solid ratio of the suspension $W/S = 10$) and stirred. The synthesis of calcium silicate hydrates was carried out in a rotating autoclave A - 08 (16 rpm) in the medium of saturated steam pressure at the temperature of 175°C , duration of isothermal curing was 16 or 24 hours. The product of the synthesis was filtered, rinsed with ethyl alcohol to prevent carbonation of material, dried at the temperature of $105^\circ\text{C} \pm 5$, and granules with size of 1 - 0.4 mm were prepared.

Cation exchange experiments under static conditions were conducted as follows: 0.5 g of the tobermorite was equilibrated for different periods in glass vials with 200 ml solution containing 100, 500 and 1000 mg/l CoSO_4 , CuSO_4 , NiSO_4 , or ZnSO_4 at room temperature without shaking. The solution and the solid phase in the glass vials were separated by filtration after different periods of equilibration (5 - 1500 min). The solutions were analyzed for metal ions by atomic emission spectroscopy.

A glass column with 10.8 mm internal diameter and 220 mm length was used for ion exchange experiments under dynamic conditions. It was filled up with three layers: 20 mm layer of glass granules (0.2 - 1 mm), 30 mm layer of sorbent, and 20 mm layer of glass granules. The layers were sealed with each other as well as from the top and the bottom by a mesh sieve. 1 g of a sorbent was used.

The solution with heavy metal ions flew in the vial from the bottom to the top; flow speed was constant and equal to 2 ml/min. The concentration of heavy metal ions in the periodically taken samples was determined by the atomic emission spectroscopy. The pH of solutions was neutral or close to neutral.

RESULTS AND DISCUSSION

Sorption of cobalt ions by Al^{3+} modified tobermorites

Changing the duration and temperature of the synthesis very often leads to the formation of mixtures C-S-H(I) with tobermorite. The products presented below were synthesized at 175°C to estimate the ion exchange capacity and to study the effect of Al^{3+} insertion in the sorbent structure.

- 1) C-S-H(I) (molar ratio of the mixture $\text{CaO}/\text{SiO}_2 = 0.83$, duration of synthesis $\tau = 2 \text{ h}$);
- 2) 1.13 nm tobermorite ($\text{CaO}/\text{SiO}_2 = 0.83$; $\tau = 16 \text{ h}$);
- 3) Al-substituted tobermorites ($\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.83$ and $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025; 0.05; 0.075$; $\tau = 24 \text{ h}$).

As expected, after the first two hours of hydrothermal synthesis only semi-crystalline calcium silicate hydrate (I) is formed from the CaO and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ mixture (figure 1a, curve 1; d-spacing 0.305, 0.280 and 0.183 nm). The 1.13 nm tobermorite (figure 1a, curve 2; d-spacing 1.14, 0.308 and 0.297 nm) is formed by synthesis prolonged to 16 hours together with calcium silicate hydrate (I).

A small amount of Al_2O_3 in the initial mixture ($\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025$) increases the crystallinity of 1.13 nm tobermorite, which becomes a single product of the synthesis (figure 1a, curve 3). With increasing aluminum addition (the molar ratios $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.05$ and 0.075 respectively), the quantity of tobermorite diminishes, semi-crystalline calcium silicate hydrate (I) remains, and calcium aluminum silicate hydrate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ is formed. The endothermic effect at 330°C (figure 1b, curves 4, 5) is typical in the DSC curves.

The products of synthesis can be arranged in the following sequence of falling crystallinity of tobermorite according to Taylor [17, 18]:

Al-substituted tobermorite ($\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025$) \rightarrow 1.13 nm tobermorite \rightarrow Al-substituted tobermorites of similar degree of crystallinity (with $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.050$ and 0.075) \rightarrow calcium silicate hydrate (I).

In figure 2 the sorption rate of Co^{2+} by a semi-crystalline mineral calcium silicate hydrate (I) of the tobermorite group is shown. The initial Co^{2+} ion concentration in solution 100 mg/l decreased below 1 mg/l in 24

hours. The capacity of this sorbent depends on the duration of the process as well as on the initial Co^{2+} ion concentration in the solution. The amount of sorbed Co^{2+} ions increased from 1.35 mg/g to 13.34 mg/g when initial concentration increased from 100 mg/l to 1000 mg/l. Such a good sorption capacity of calcium silicate hydrate (I) can be attributed to its semi-crystalline structure: the Ca-O bond is weak [16] and external ions can easily penetrate to the interlayer space.

The sorption capacity of 1.13 nm tobermorite is lower than that of calcium silicate hydrate (I). It is a well-crystallized compound with Ca^{2+} ions distributed between the layers of its crystal lattice. The Ca-O bond is strong and Co^{2+} ions can enter to the lattice only by destroying this bond. The process is particularly slow even when the initial Co^{2+} ion concentration in the solution is high.

Al-substituted tobermorites, in particular those synthesized from mixtures of a molar ratio $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.075$, show a lower sorption capacity most probably because the negative charge in this compound is compensated by divalent Ca^{2+} ions instead of monovalent cations, just like in the structure of unsubstituted tobermorite.

The tobermorite ion exchange capacity is almost independent on the quantity of Al_2O_3 added. However, our previous works [7, 19] have demonstrated that with the larger quantity of Al^{3+} in the initial mixture of more semi-crystalline calcium silicate hydrate (I) remains in the product of synthesis. The data of X-ray diffraction analysis presented here prove these results (figure 1a).

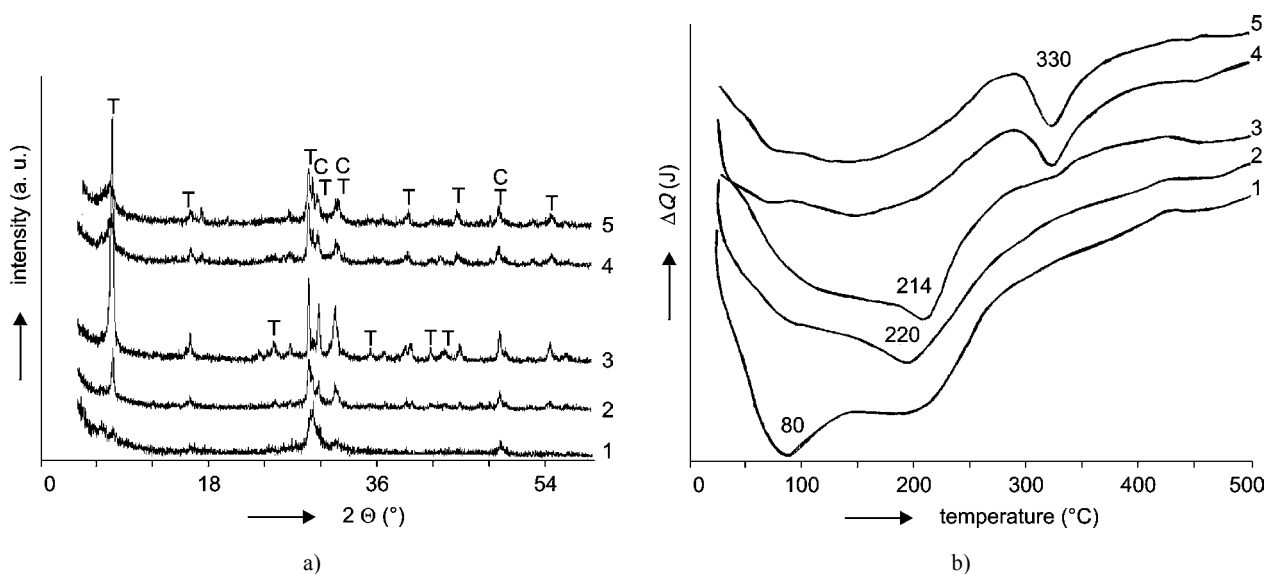


Figure 1. X-ray diffraction patterns a) and DSC curves b) of the products synthesized at 175°C . The molar ratios of initial mixtures and the duration of isothermal curing: 1 - $\text{CaO}/\text{SiO}_2 = 0.83$, $\tau = 2$ h; 2 - $\text{CaO}/\text{SiO}_2 = 0.83$, $\tau = 16$ h; 3-5- $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.83$, $\tau = 24$ h; $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025$ (3); $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.05$ (4); $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.075$ (5).

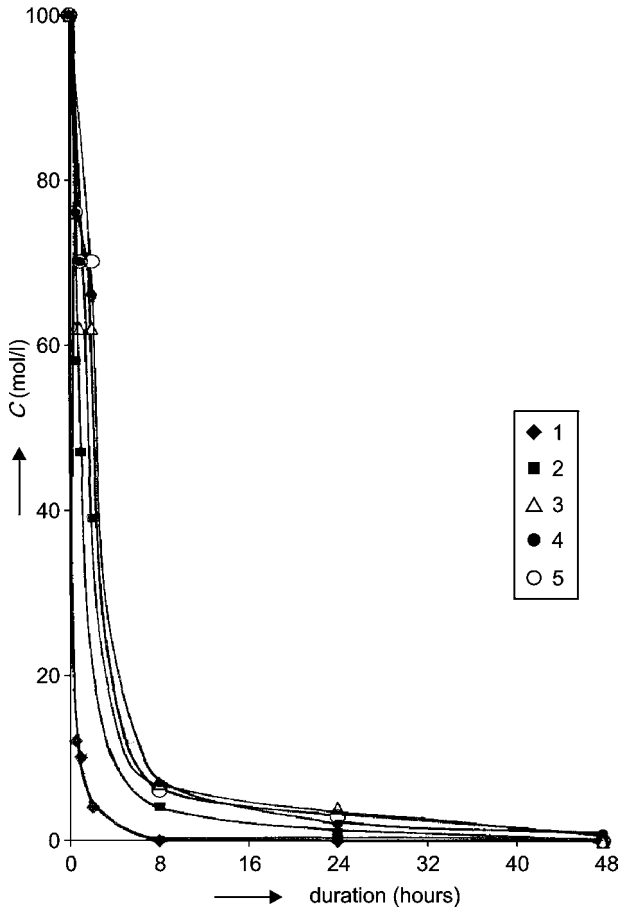


Figure 2. Kinetic sorption of cobalt ion by calcium silicate hydrates. The initial Co^{2+} ion concentration is 100 mg/l: 1 - calcium silicate hydrate (I); 2 - 1.13 nm tobermorite; 3 - 5 - Al-substituted tobermorites: $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025$ (3); $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.05$ (4); $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.075$ (5).

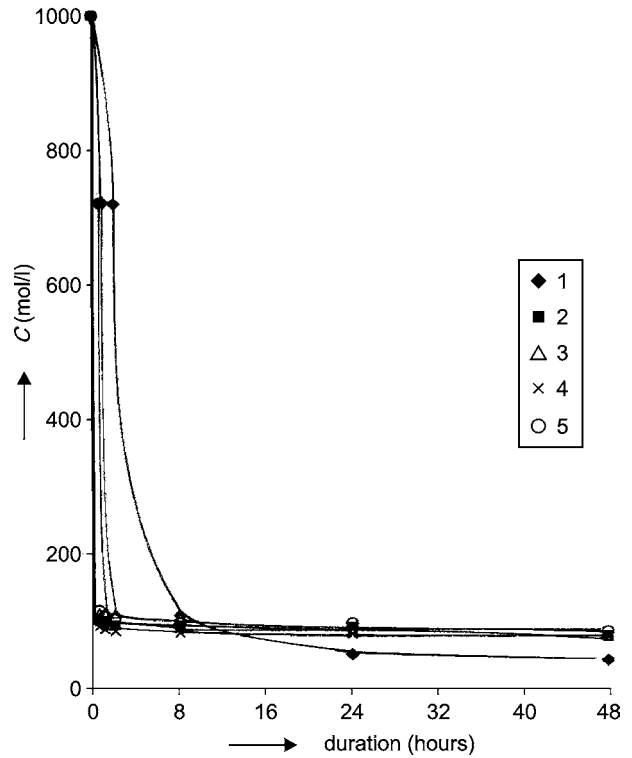


Figure 4. Kinetic sorption of cobalt ion by tobermorites. 1 - 4 $[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorites cured at 175°C for 24 h. The molar ratios of the initial mixtures: $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.83$, $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025$. The amount of added Na_2O (as NaOH): 1 - 5%; 2 - 10%; 3 - 15%; 4 - 20%; 5 - pure 1.13 nm tobermorite. The initial Co^{2+} ion concentration is 1000 mg/l.

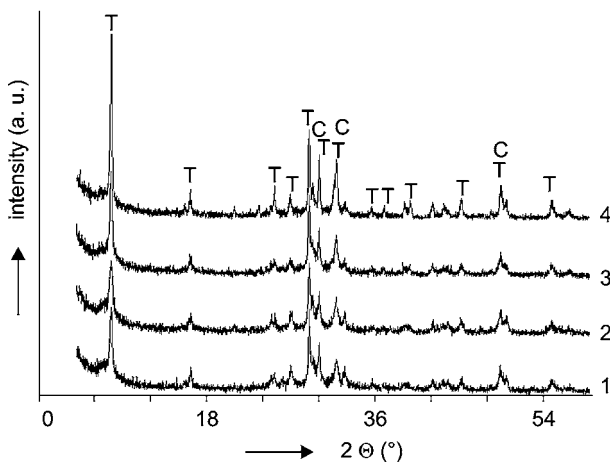


Figure 3. The X-ray diffraction patterns of $[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorites cured at 175°C for 24 h. The molar ratios of initial mixtures: $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.83$, $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025$. The amount of added Na_2O (as NaOH), %: 1 - 20; 2 - 15; 3 - 10; 4 - 5.

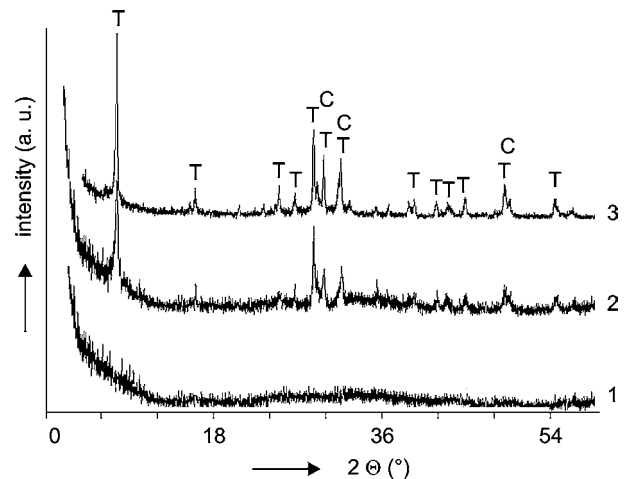


Figure 5. X-ray diffraction patterns of $[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorite cured at 175°C for 24 h. The molar ratios of initial mixture: $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.83$, $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025$, 5% addition of Na_2O (as NaOH). 1 - after 48 h of sorption; 2 - after 2 h of sorption; 3 - before sorption.

In comparison to tobermorite, ion exchange capacity of pure calcium silicate hydrate (I) is several times higher. It implies that Al^{3+} ions penetrating between different layers of calcium silicate hydrate (I) decreases the sorption properties of this compound.

Thus both pure and Al substituted tobermorites have not exhibited significant ion exchange capacities. Application of such sorbents is disadvantageous because it is by far easier and cheaper to synthesize semi-crystalline calcium silicate hydrate of calcium silicate hydrate (I) type having better sorption properties.

Synthesis of tobermorites with double $[\text{Na}^+ + \text{Al}^{3+}]$ - substitution and their sorption properties in relation to Co^{2+} ions

It is known that Al^{3+} ions penetrate into the crystal lattice of 1.13 nm tobermorite and replace Si^{4+} ions. Thus, in this structure a surplus negative charge is formed. In other sorbents like in zeolites and clays such charge is usually compensated by monovalent cations participating in the ion exchange with higher valency cations in the solution.

However, there are no data showing the relation between the sorption capacity of tobermorite and the amount of $[\text{Na}^+ + \text{Al}^{3+}]$ ions incorporated in their lattice. In this part of investigation tobermorites with different amount of $[\text{Na}^+ + \text{Al}^{3+}]$ were synthesized and their sorption properties in relation to Co^{2+} ions were investigated.

The addition 5% of Na_2O in the initial mixture leads to the formation of tobermorite of higher crystallinity. Higher addition (up to 20% Na_2O) brings amorphous structure of Al-substituted tobermorite. It is attributed to rather significant alkaline pH when Na^+ ions are in a liquid phase. Consequently, the solubility of $\text{Ca}(\text{OH})_2$ in a liquid phase decreased and the total concentration of calcium ions is lower. These conditions are favorable to the primary formation of calcium silicate hydrate of low - base. Even on addition of 20% Na_2O , pectolite or other sodium silicate has not been identified in the products of synthesis.

$[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorite sorbs a larger quantity of Co^{2+} cations in half an hour and the equilibrium was attained sooner (figure 4). The sorption capacity is only slightly related to the NaOH addition.

Pure tobermorite sorbents, Al-substituted ones as well as the semi-crystalline calcium silicate hydrate (I) show lower ion exchange capacity, as compared to crystalline $[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorites. The exchange kinetics in these substituted tobermorite sorbents is fast and the change is irreversible.

The major reason for an increase in sorption capacity is the fact that the excess negative charge in the structure of tobermorite is compensated by Na^+ cations

participating in the ion exchange with the higher valency Co^{2+} cations presented in the solution. Thus, participation of alkaline metals but not Ca^{2+} ions does promote cation exchange.

Ion exchange led to a loss of crystallinity of tobermorite. Most Ca^{2+} ions as well as $[\text{Na}^+ + \text{Al}^{3+}]$ ions presented in tobermorites can be replaced by Co^{2+} ions. The sorbent becomes amorphous during these reactions. X-ray diffraction analysis (figure 5, curve 2) shows that the process of amorphization begins even on partial substitution of Co^{2+} ions for Ca^{2+} ones. Full exchange led to amorphization of tobermorite (figure 5, curve 1). The crystalline structure will become amorphous when all Co^{2+} ions are substituted for Ca^{2+} after 48 h.

Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} ions sorption by substituted tobermorite under static and dynamic conditions

$[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorite containing 5% Na_2O was chosen for further experiments. Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} ions sorption under dynamic conditions was also studied. Interestingly, the structure of tobermorites can resemble either clay minerals or zeolites depending on their chemical composition and the nature of synthesis, i.e. the structure of tobermorite can be flexible (normal) in the case of clay minerals or rigid (anomalous) in the case of zeolites [14]. Tobermorites with basal interplanar distance decreasing from 1.13 nm to 0.93 nm during dehydration process are commonly called normal and those having basic reflection constant are called anomalous [20]. Both natural and synthetic zeolites show very high ion exchange capacity and are one of the most widely used sorbents.

The thermal type of tobermorite of the above composition (5 % Na_2O) was determined after heating at temperature 300°C. Interplanar distance remained stable (1.13 nm), although the material had lost most of its water content (figure 6, curve 2). Anomalous tobermorite with Al^{3+} and Na^+ ions inserted into a crystal lattice was synthesized during hydrothermal synthesis at 175°C.

When the sorption is carried out under static conditions (figure 7), the concentration of heavy metals in solutions decreases twice for Cu^{2+} ions in 35 minutes, for Zn^{2+} and Co^{2+} ions after 40 minutes and for Ni^{2+} ions as late as after 120 minutes at initial concentrations of heavy metal ions 100 mg/l. At the initial sorption stage, copper was sorbed more quickly by $[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorite, when compared with cobalt, zinc, and nickel.

However, all investigated solutions are almost completely cleaned from heavy metals (figure 7) if duration of the process is extended to 1440 minutes.

Therefore, it is impossible to eliminate Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺ ions from water under static conditions (initial C₀ = 100 mg/l) up to concentrations, permissible for effluent discharge to sewerage system, using the modified tobermorite sorbents.

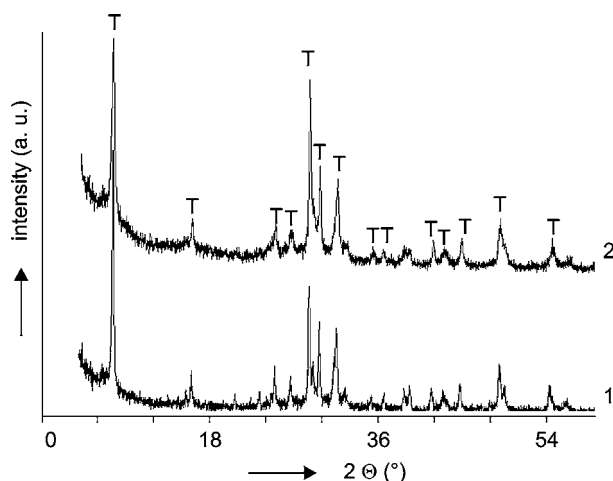


Figure 6. X-ray diffraction patterns of [Na⁺ + Al³⁺] - substituted tobermorites cured at 175°C for 24 h. 1 - 1,13 nm tobermorite; 2 - the same after 2 h of heating at 300°C.

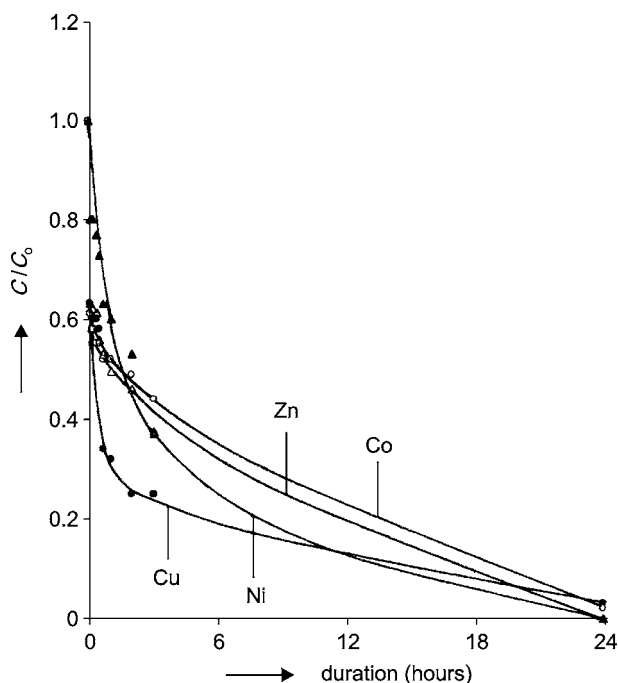


Figure 7. The kinetic curves of Co²⁺, Zn²⁺, Cu²⁺ and Ni²⁺ ion sorption by [Na⁺ + Al³⁺] - substituted tobermorite under static conditions in single component solutions. Initial concentrations (mg/l): Zn²⁺ - 135.7; Co²⁺ - 89.8; Cu²⁺ - 78.6; Ni²⁺ - 94.7. (C₀ - initial concentration, C' - final concentration).

Sorption capacity (quantity of sorbed metal ions per g of the sorbent) of the modified tobermorite sorbent is ten times bigger than of the modified clay sorbent in the experiments under static conditions. Sorption capacity of the modified clay in respect to nickel, copper and zinc ions is equal to 1.45; 1.76; 0.83 meq/g, respectively [22]. In this work the sorption capacity of [Na⁺ + Al³⁺] - substituted tobermorite for the same cations is equal to 7.84, 8.77, 6.29 meq/g, i.e. almost ten times bigger than of the sorbent produced by heating up to the clay.

Under dynamic sorption conditions, Co²⁺ ions are the first to penetrate the filter and Ni²⁺ ions are the last (figure 8). Dynamic sorbent activity, showing the quantity sorbed by the sorbent from the beginning of the process till the time when the trace of heavy metal ions is noted in the flow streaming from the vial is calculated if the experiment is led under dynamic conditions. The sorbent activity depends on physical, chemical properties of a sorbent as well as on sorption type.

Sorbent granules of 1 - 0.4 mm fraction size have been used in this work. The following time interval passed before the ions penetrated the sorption vial: 150 min for Ni²⁺ ions, 120 min for Cu²⁺ ions (figure 8), 30 min. for Co²⁺ ions and 150 min for Zn²⁺ ions. During this time, 1 g of sorbent adsorbed 2.72 mg of Co²⁺ ions, 15.42 mg of Zn²⁺ ions, 8.30 mg of Cu²⁺ ions and 15.63 mg of Ni²⁺ ions. The highest dynamic activity of the sorbent was found for Ni²⁺ and Zn²⁺ ions, average for Cu²⁺, and the lowest for Co²⁺ ions.

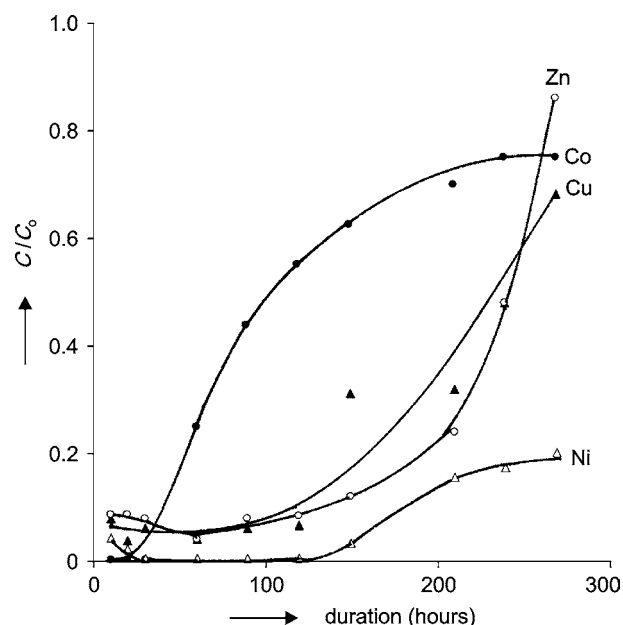


Figure 8. The kinetic curves of Co²⁺, Zn²⁺, Cu²⁺ and Ni²⁺ ion sorption by [Na⁺ + Al³⁺] - substituted tobermorite under dynamic conditions. Initial concentrations (mg/l): Zn²⁺ - 51.4; Co²⁺ - 45.3; Cu²⁺ - 34.6; Ni²⁺ - 52.1.

In addition, it is possible to calculate the amount of ions sorbed before the ions penetrated the column with the known sorbent quantity (1 g), solution flow rate (2 ml/min), and the initial concentration of sorbed ions. Theoretical sorption capacity is $1 \text{ g} \cdot 12.5 \text{ meq/g} = 12.5 \text{ meq/g} = 368 \text{ mg Co}^{2+}$ ions. The penetration of the sorbent is affected only slightly by the ion type and corresponds to only about 0.7 % of the assumed sorption capacity for Co^{2+} ions, 2.97 % for Cu^{2+} ions, 6.8 % for Ni^{2+} ions and 7.49 % for Zn^{2+} ions.

CONCLUSIONS

1. Semi-crystalline mineral calcium silicate hydrate (I) of the tobermorite group effectively eliminates Co^{2+} ions from a solutions as Ca-O bond in its structure is weak and external ions can easily penetrate into the interlayer space. The initial Co^{2+} ion concentration in the solution 100 mg/l or 500 mg/l was decreased below 1 mg/l in 24 h.
2. Ion exchange capacities of crystalline 1.13 nm tobermorite and Al-substituted tobermorites are insignificant. Consequently, they are inappropriate for cleaning water with heavy metal ions.
3. Insertion of Na^+ ions into the crystalline lattice of tobermorite increases ten times the ion exchange capacity, which is higher than that of clays and close to sorption capacity of zeolites.
4. The $[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorite begins to amorphize with a partial exchange of Ca^{2+} ions by Co^{2+} . Increasing amount of sorbed Co^{2+} brings higher degree of crystallinity of the tobermorite structure.
5. The modified tobermorite sorbent decreases the initial concentrations of Zn^{2+} , Cu^{2+} , Ni^{2+} and Co^{2+} ions (initial concentration $C_0 = 100 \text{ mg/l}$) to the limit being permissible for waste water cleaning.
6. The ion exchange capacity of $[\text{Na}^+ + \text{Al}^{3+}]$ - substituted tobermorite is 279 mg of Cu^{2+} , 230 mg of Ni^{2+} and 206 mg of Zn^{2+} per gram of the sorbent.
7. The dynamic activity of this compound is highest for Ni^{2+} and Zn^{2+} ions, average for Cu^{2+} and lowest for Co^{2+} .

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SORPČNÍ VLASTNOSTI TOBERMORITU MODIFIKOVANÉHO IONTY Na^+ A Al^{3+}

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Tématem příspěvku je vliv Al_2O_3 a NaOH na tvorbu 1,13-ti nm tobermoritu v hydrotermálních podmínkách a iontově- výměnná kapacita tobermoritu jak čistého tak substituovaného Al^{3+} a $[\text{Na}^+ + \text{Al}^{3+}]$ k těžkým kovům (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}) ve statických a dynamických podmínkách. Iontově- výměnná kapacita krystalického 1,13-ti nm tobermoritu a Al-substituovaného tobermoritu je nevýznamná. Inerce iontů Na^+ do krystalové mřížky tobermoritu zvyšuje jeho iontově- výměnnou kapacitu desetinásobně. Iontově výměnná kapacita Na^+ , Al^{3+} -substituovaného tobermoritu je 279 mg Cu^{2+} , 230 mg Ni^{2+} a 206 mg Zn^{2+} na gram sorbentu. Dynamická aktivita Na^+ , Al^{3+} -substituovaného tobermoritu je jen mírně ovlivněna přidávkou NaOH a Al_2O_3 .