THE SORPTION PROPERTIES OF GYROLITE FOR COPPER IONS

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The sorption properties of synthetic pure gyrolite (CaO/SiO_2 = 0.66; 96 h; 200°C) for copper ions has been examined. It has been proved that stability and cation exchange capacity of gyrolite depend on concentration of copper ions in the $Cu(NO_3)_2$ solution. It should be emphasized that crystal structure of gyrolite is quite stable only in the solution when initial amount of Cu^{2+} ions is 1 g/l and its cation exchange capacity is equal to 54.32 mg Cu^{2+}/g after 360 min of sorption at 25°C. In the solutions with higher initial concentrations $c_{Cu^{2+}}$ = 5.0; 10.0; 20.0 g/l, the cation exchange reaction proceed intensively at the beginning of the adsorption process. The amount of adsorbed Cu^{2+} ions in the crystals lattice of gyrolite after 15 min is equal to: 94 mg Cu^{2+}/g, when $c_{Cu^{2+}}$ = 5.0 g/l; 580 mg Cu^{2+}/g, when $c_{Cu^{2+}}$ = 10.0 g/l; 1480 mg Cu^{2+}/g, when $c_{Cu^{2+}}$ = 20.0 g/l. Meanwhile, partial replacement ($Ca^{2+} \leftrightarrow Cu^{2+}$) led to amorphization of the gyrolite crystals (lattice) and stimulate the formation of new compounds: gerhardite, gyrolite gel and C–S–H(I). The products of sorption were characterized by X-ray diffraction analysis, simultaneous thermal analysis and Fourier-transform infrared spectroscopy.

INTRODUCTION

Many types of inorganic materials act as cation exchangers, e.g. clay minerals, hydroxyapatities, layered zirconium phosphate, frame work alumosilicates and etc. [1-6]. Meanwhile, there are a huge number of environmental contaminants associated with industry: organic compounds, heavy metals, gases, and acids. These waste products will generally need to be identified according to the industrial process in question, neutralized or rendered less harmful and finally disposed of into the surrounding land, air or watercourses. It is urgent to develop new effective sorption materials in order to achieve better purification of the effluent. For example, heavy metals are widely produced by various branches of industry, e.g. galvanization, paint, leather, glass. Most of the heavy metals may have a carcinogenic, mutagenic effect. Moreover, development of new effective sorbents is essential for improving wastewater purification.

S. Komarneni et al. have reported that calcium silicate hydrates prepared under hydrothermal treatment act as cation exchanger with some metal cations with Ca^{2+} or Si^{4+} in their lattice structure [7-10].

The cation exchange reactions and selectivity properties of substituted tobermorites were widely explored in the previous works [2, 6-15]. It was found out that these compounds can be used in the cation exchange reaction instead of clay minerals or zeolites. Substituted tobermorites can be used in the cation exchange reaction of many metals atoms which cation exchange capacity vary in this sequence: $Pb^{2+} < Cd^{2+} < Ag^{2+} < Mn^{2+} < Cu^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+} < Fe^{2+}$ [14]. The new group of cation exchangers unlike clay minerals and zeolites is expected to be thermodynamically stable in cement and concrete, because they have 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.

However, gyrolite has been analyzed considerably less [16-19]. One of the reasons why properties of gyrolite are not analyzed in detail is that the synthesis of this compound is more complex and it is still rarely applied in practice. As it results from some published works it is suitable for water cleaning from heavy metal ions [20] and it is known for its selectivity to DNA clearage [21].

It is presumable that gyrolite can adsorb more atoms of metals to compare with 1.13 nm tobermorite, because the crystal structure of this compound is built up by the stacking of SiO_4 tetrahedral sheets (S_1, S_2, and $\bar{S}_2$, where S_2 and $\bar{S}_2$ are symmetry-related units) and CaO_6 octahedral sheets (O and $\bar{O}$, which are symmetry-related units) [22]. The Si–O_4 - tetrahedra in the silicate sheets are linked by sharing three oxygens to give a pseudo-hexagonal sheet structure with tetrahedra in six-membered rings. Each unit cell contains three distinct silicate sheets two of which (S_2 and $\bar{S}_2$) are symmetrically equivalent with the six-membered rings having four tetrahedra pointing one way and two the other; the third sheet (S_1) has alternate tetrahedra six-membered rings pointing in opposite directions. These sheets are linked by layers of Ca–(O,OH) polyhedra to built up a "complex layer" perpendicular to c axis; additional Ca atoms and H_2O molecules occupy the interlayers between these units giving a unit cell with a 2.2 nm repeat along *c* [22]. Meanwhile, tobermorite crystal structure gave smaller unit cell with a 1.13 nm and it is a rather stable compound because the standard Gibbs energy of it's formation from raw materials is $\Delta_f G^0_{298}$ = -10766.3 kJ/mol (gyrolite - $\Delta_f G^0_{298}$ = -4387.3 kJ/mol).

The aim of this paper was to explore cation exchange capacity of gyrolite for Cu^{2+} ions and to evaluate its application as a new effective sorption material. A proposed cation exchange reaction mechanism is presented.

EXPERIMENTAL

Pure gyrolite was synthesized after 96 hours at 200°C temperature from a stoichiometric composition (CaO/SiO_2 = 0.66) of calcium oxide (CaO was produced by burning calcium oxide at 950°C for 0.5 hours, specific surface area Sa = 548 m^2/kg by Blaine) and fine-grained $SiO_2 \cdot nH_2O$ (ignition losses 21.43 %, S_a = 1560 m^2/kg) mixture. Dry primary mixture was mixed with water in the vessels of stainless steel (water/solid ratio of the suspension W/S = 10.0). The product was filtered off, dried at the temperature of 50 ± 5°C and sieved through sieve with a mesh width of 80 µm. These synthesis conditions were chosen according to previously published data [24].

Ion exchange experiments were carried out at 25°C temperature in the thermostatic absorber Grant SUB14 by stirring 1 g of gyrolite in 100 ml of $Cu(NO_3)_2$ aqueous solution containing 1; 5; 10; 20 g/l of Cu^{2+} ions for 360 min. The percentage of exchange was determined on the basis of concentration variation of the cations in solution and in the calcium silicate hydrates using a Perkin-Elmer Analyst 4000 spectrometer. The value of pH was taken by Hanna instrument (Hi 9321, microprocessor pH meter).

The X-ray powder diffraction (XRD) data were collected with DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2-60° (2θ) in steps of 2θ = 0.02°.

Simultaneous thermal analysis (STA: differential scanning calorimetry-DSC and thermogravimetry-TG) was also employed for measuring the thermal stability and phase transformation of synthesized products at a heating rate of 15°C/min, the temperature ranged from 30°C up to 1000°C under air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used.

FT-IR spectra have been carried out with the help of a Perkin Elmer FT-IR Spectrum X system. Specimen were prepared by mixing 1 mg of the sample with 200 mg of KBr. The spectral analysis was performed in the range of 4000-400 cm^{-1} with spectral resolution of 1 cm^{-1}.

The specific surface area of the raw materials was determined by the Blaine's method with air permeability apparatus (Model 7201, Toni Technik Baustoffpruf-systeme GmbH).

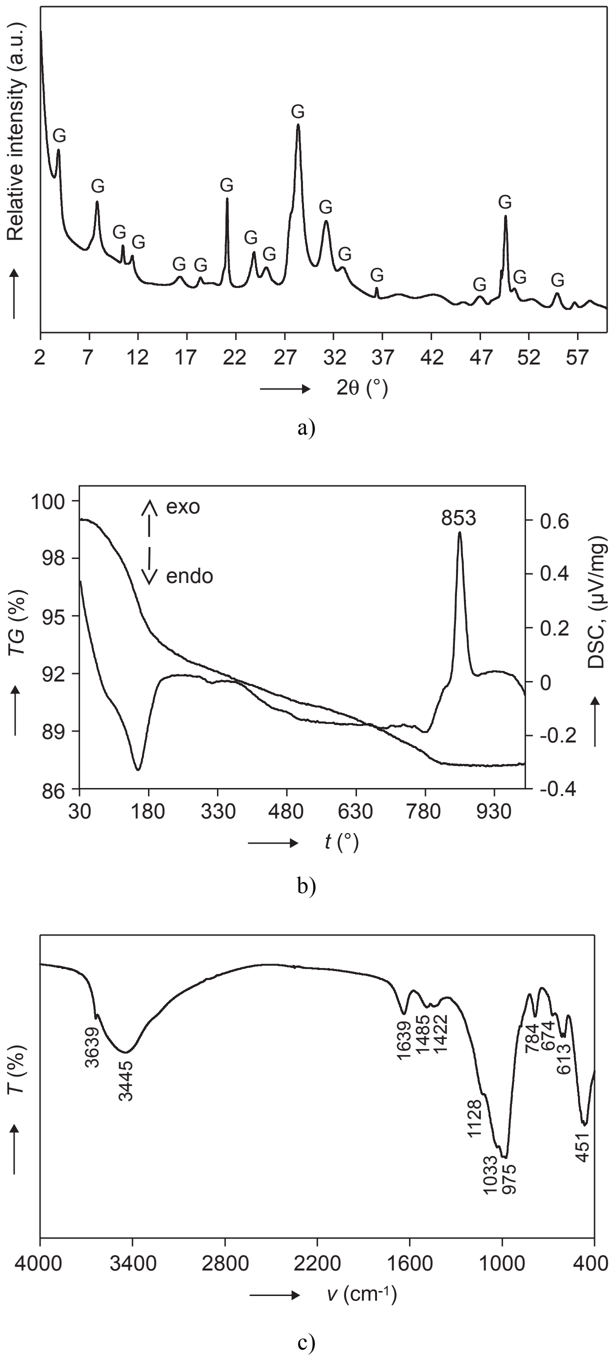
RESULTS AND DISCUSSION

Synthetic pure gyrolite was characterized by XRD, STA, FT-IR spectroscopy methods (Figure 1). First of all, the formation of pure gyrolite was confirmed by X-ray diffraction analysis: the most characteristic peak (*d*-spacing-2.2 nm) of gyrolite which is not characteristic to other calcium silicate hydrates is identified. Moreover, in the X-ray diffraction patterns the peaks were determined with *d*-spacing - 1.1262; 0.8371; 0.4197; 0.3732; 0.3511; 0.2803; 0.2141 nm, which are also typical for gyrolite (Figure 1a).

The results of XRD were confirmed by others analysis too. On the DSC curve only two thermal effects characteristic to gyrolite are visible: broad endothermic peak in the temperature range of 137-143°C is related to the loss of physisorbed and interlayer water from the crystal structure of gyrolite and the second exothermic peak at 853°C is associated with recrystallization of this compound into wollastonite (Figure 1b). The shape of absorption bands of FT-IR spectrum, its multiplicity and width also are specific to gyrolite (Figure 1c) [19, 23].

The results of ion exchange experiments showed that stability and cation exchange capacity of gyrolite depend on concentration of copper ions in the $Cu(NO_3)_2$ solution. The cation exchange reaction proceed intensively at the beginning of the adsorption process. The amount of adsorbed Cu^{2+} ions in the crystals lattice of gyrolite after 15 min is equal to 28.72 mg Cu^{2+}/g when the initial amount of Cu^{2+} ions in the solution is 1 g/l (Figure 2, curve 1). Prolonging the duration of the sorption process the reaction rate greatly decreases and after 6 h the amount of Cu^{2+} ions incorporated into gyrolite crystal structure increase only twice (54.32 mg Cu^{2+}/g). The cation exchange capacity of gyrolite is almost two times larger than that of tobermorite [24].

It should be noticed that in the solution of 5 g Cu^{2+}/l, the cation exchange capacity of adsorbent increases up to 144.81 mg Cu^{2+}/g after 6 hours (Figure 2b). Unexpected results were obtained with 10 g Cu^{2+}/l: at first 15 min the adsorbed amount of Cu^{2+} ions is equal to 580 mg Cu^{2+}/g, but extending the duration of the reaction the copper ions are desorbed from the crystal lattice of gyrolite (Table 1). The same phenomenon was found by using 20 g Cu^{2+}/l solution.

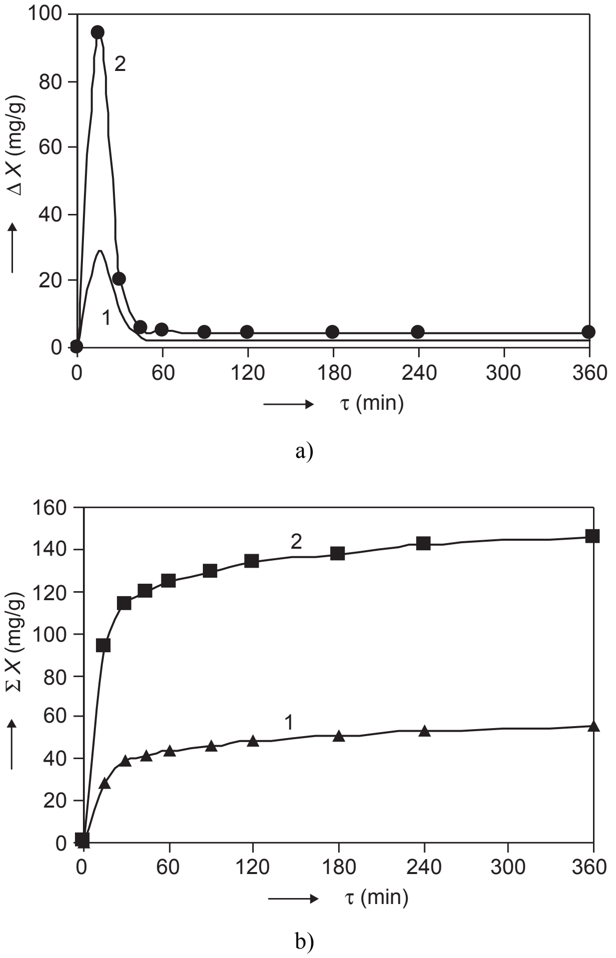


a)

b)

c)

Figure 1. X-ray diffraction pattern (a), DSC-TG curve (b) and FT-IR spectrum (c) of pure gyrolite. Duration of hydrothermal synthesis at 200°C is equal to 96 h. Indices: G - gyrolite.



a)

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Figure 2. Diferential (a) and integral (b) kinetic curves of Cu^{2+} ions adsorption from $Cu(NO_3)_2$ solution when initial concentration Cu^{2+} ions are 1.0 g/l (curve 1) and 5.0 g/l (curve 2) at 25°C.

Table 1. Adsorbed amount of Cu^{2+} ions.

Cu^{2+} concentration in the solution (g/l)	Absorbed amount of Cu^{2+} ions (mg/g), duration of sorption at 25°C				
	15 min	30 min	360 min		
	Calculated according to variation of concentration			Determined in the adsorbent	Average
1	28.72	39.24	55.42	53.22	54.32
5	94.00	100.00	146.25	143.36	144.81
10	580.00	0	0	0	0
20	1480.00	0	0	0	0

The main reason is *pH*-value of the initial cation metal solutions, which varied with the concentration of salt. *pH*-value of solution decreases when concentration both of Cu^{2+} ions and NO_3^- ions increase in the solution. Hovewer, *pH*-value of solution rapidly increases when gyrolite was mixed with solution. This change is attributed to the degree of release of Ca^{2+} ions from the structure of the gyrolite solid in solution during the reaction.

Thus, it should be emphasized that gyrolite is quite stable in the solution when initial amount of Cu^{2+} ions is 1 g/l and its stability decreases in the solutions with lower *pH* values. In order to identify the stability of gyrolite and a new phases of the solids, the products of sorption were characterized with numerous instrumental analysis methods.

The X-ray powder diffraction results show that the cation exchange reactions leads to a partial loss of crystallinity of gyrolite as can be deduced from the decrease of the relative intensities of *d*-spacing of gyrolite (Figure 1a) and Cu-substituted gyrolite (Figure 3). In the products new compounds were identified: gyrolite gel (*d*-spacing - 1.13, 0.421, 0.363, 0.312, 0.298 nm), C–S–H(I) (*d*-spacing - 1.13, 0.363, 0.312, 0.183 nm) and gerhardite (*d*-spacing - 0.697, 0.346,

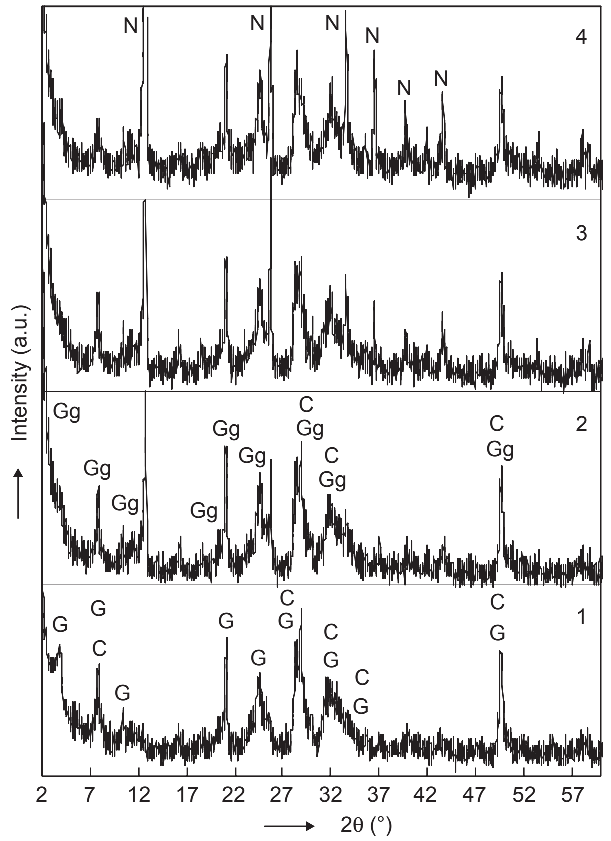
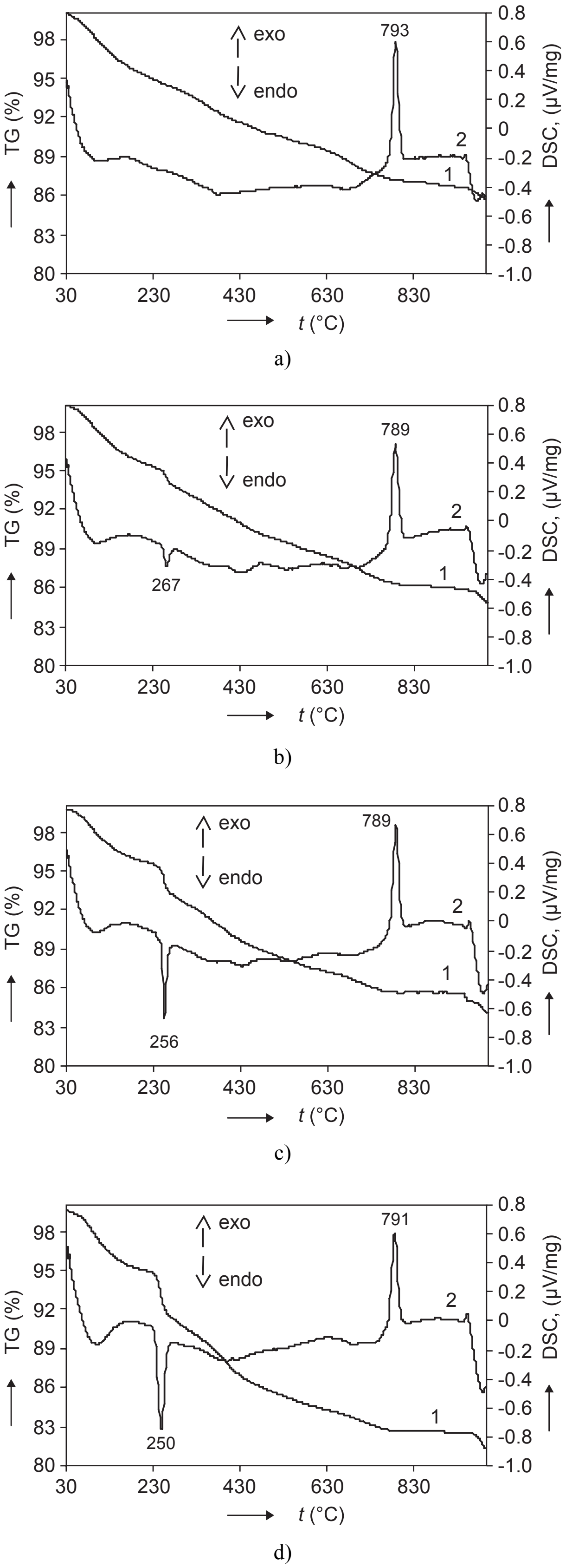


Figure 3. X-ray diffraction patterns of gyrolite after adsorption process (25°C, 360 min), when concentration Cu^{2+} ions, g/l: 1-1.0; 2 - 5.0; 3 - 10.0; 4 - 20.0. Indices: G - gyrolite, Gg - gyrolite gel, C - C–S–H (I), N - gerhardite.



a)

b)

c)

d)

Figure 4. TG (1) and DSC (2) curves of gyrolite after adsorption process (25°C, 360 min), when concentration Cu^{2+} ions, g/l: 1 - 1.0; 2 - 5.0; 3 - 10.0; 4 - 20.0.

0.267, 0.246, 0.226, 0.207 nm) (Figure 3). The formation of the latter compoud ($Cu_2(OH)_3NO_3$) comfirmed endotermic peak at 250 - 267°C in the DSC curve (Figure 4b-d). Also, exothermic peak at 789°C shows the formation of semi-crystalline calcium silicate hydrates (C–S–H(I), gyrolite gel). Moreover, the recrystallization process of these compounds to wollastonite proceed at lower temperature, approximately 70°C, to compare with pure gyrolite (Figure 1b, Figure 4).

All the above presented data were confirmed by the method of FT-IR spectroscopy, which can be used to distinguish gyrolite from others calcium silicate hydrates [23].

The most intense absorption bands of gyrolite slightly decrease, especially those located at 3638, 3464, 1032, 612, 595 and 464 cm^{-1} upon reactions with Cu^{2+} (Figure 5). The positions of some these (3638, 3464, 1032 cm^{-1}) are slightly shifted may be attributed to some modification in the structure, due to $Ca^{2+}\leftrightarrow Cu^{2+}$ exchange. Presence of very weak sharp band at about 3638 cm^{-1} confirms the presence of OH^- groups which are bound in the structure; while the presence of broad band located at 3464 and weak one at 1638 cm^{-1} may due to the physically adsorbed water. Also, FT-IR spectroscopy data show that after chemisorption process intensity of absorption bands characteristic to gerhardite at about 1421, 1385 and 1344 cm^{-1} are largest, when concentration of Cu^{2+} is 20 g/l (Figure 5). Generally FT-IR spectra data supports and agree with the results obtained from XRD patterns and thermal analysis.

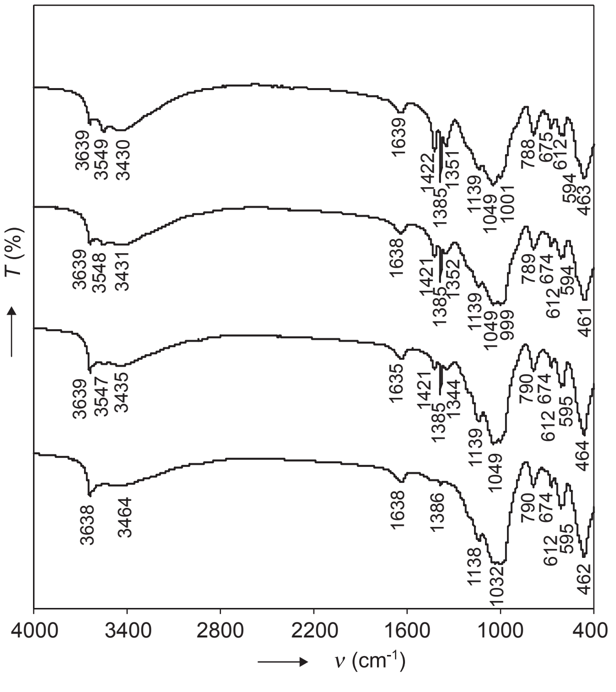
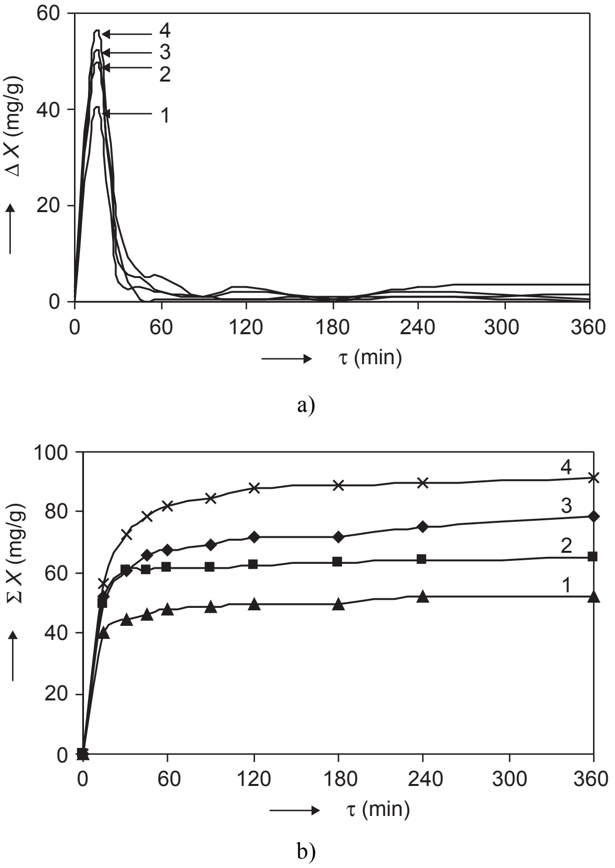


Figure 5. FT-IR spectra of gyrolite after adsorption process (25°C, 360 min), when concentration Cu^{2+} ions, g/l: 1 -1.0; 2 - 5.0; 3 - 10.0; 4 - 20.0.

It was determined that gyrolite acts as a chemisorbent but not like usual sorbent because during cation exchange reactions proceed only partial exchange ($Ca^{2+}\leftrightarrow Cu^{2+}$), e. g. in these reactions the exchange of $Ca^{2+}\leftrightarrow Cu^{2+}$ was found to be non-stoichiometric (Figure 6).

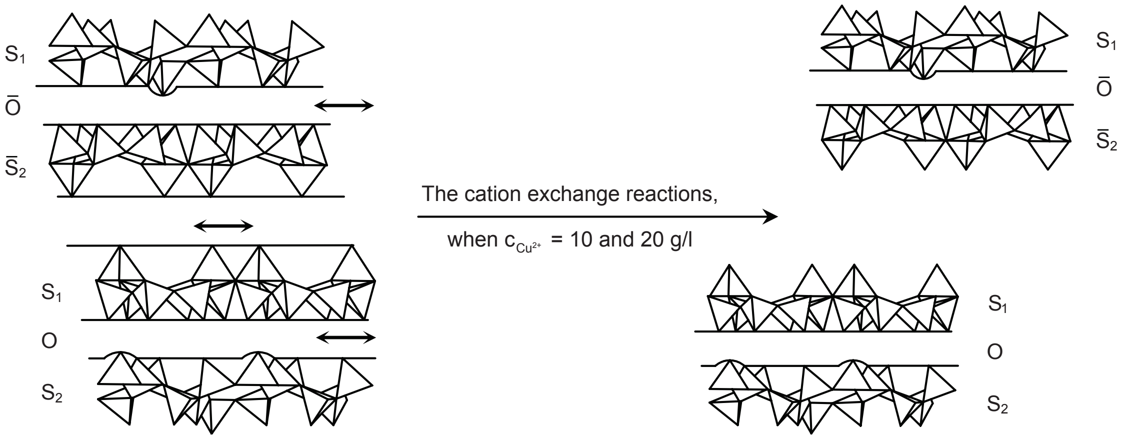
Generally, the uptake of Cu^{2+} ions by the solids was higher than Ca^{2+} ions released, with increasing reaction time or metal ion concentration. The non-stoichiometry arises from limited partial destruction of gyrolite silicate chains (Figure 7). This is due to the concentration (nature) of the M^{2+}-solutions. At the beginning, the cation exchange reactions proceed very intensively between Ca^{2+} ions and Cu^{2+} ions, which concentration are 10.0 and 20.0 g/l in the initial solution (Table 1). However, by prolonging the duration of sorption, the interlayer sheet of gyrolite structure was destroyed and all Cu^{2+} ions were released again in to solution (Figure 7). The exchange reaction mechanism (Ca^{2+} ↔ Cu^{2+}) in gyrolite may take place from edge and planar surface sites as well as from interlayer Ca^{2+} sites (Figure 7).



a)

b)

Figure 6. Diferential (a) and integral (b) kinetic curves of Ca^{2+} ions desorption from crystal lattice of gyrolite. The initial concentrations of Cu^{2+} ions in the solution, g/l: 1 - 1.0; 2 - 5.0; 3 - 10.0; 4 - 20.0.



a) b)

Figure 7. Schematic drawing of the crystal structure of pure gyrolite (a, by S. Merlino [22]) and during the cation exchange reactions (b).

It should be noted that the cation exchange reactions are not reversible process. In order to confirme this fact, after sorption process (25°C, 360 min, in the solution the amount of Cu^{2+} ions is 1 g/l) the Cu-substituted gyrolite was dryed up and immersed in distilled water. It was proved that Cu^{2+} ions did not appear in the solution after 360 minutes at 25°C.

Thus, our research allows to state that the cation exchange reactions are specific to chemisorption process. The adsorption process using gyrolite as adsorbent is different than sorption into zeolites or some clay minerals, where processes are reversible.

CONCLUSION

1. Synthetic pure gyrolite prepared under hydrothermal conditions (CaO/SiO_2 = 0.66; 96 h; 200°C) can be used as cation exchanger for the separation of heavy metal cations. The cation exchange reactions of ($Ca^{2+} \leftrightarrow Cu^{2+}$) depend on reaction time and concentration of solution: the cation exchange capacity (Σx) of gyrolite is equal to Σx = 54.32 mg Cu^{2+}/g when $c_{Cu^{2+}}$ = 1.0 g/l and the sorption time is 360 min at 25°C; when $c_{Cu^{2+}}$ = 5.0 g/l, it's cation exchange capacity increases till Σx = 144.81 mg Cu^{2+}/g.
2. It was determined that the cation exchange reactions are not reversible and specific to chemisorption process.
3. The crystals structure of gyrolite is quite stable in the solution when initial amount of Cu^{2+} ions is 1 g/l and its stability decreases in the solutions with lower *pH* values. Partial replacement ($Ca^{2+} \leftrightarrow Cu^{2+}$) led to amorphization of the gyrolite crystals (lattice) and stimulate the formation of new compounds: gerhardite, gyrolite gel and C–S–H(I).

References

1. Labhestwar N., Shrivastava O.P.: Ind.J.Chem.Soc. *27*, 999 (1989).
2. Shrivastava O.P., Komareni S.: Cem.Concr.Res. *24*, 573 (1994).
3. Shrivastava O.P., Shrivastava R.: Ind.J.Chem.Soc. *78*, 392 (2001).
4. Shrivastava O.P., Shrivastava R.: Cem.Concr.Res. *31*, 1251 (2001).
5. El-Korashy S.A.: J. of Ion Exchange. *15*, 2 (2004).
6. El-Korashy S. A., Al-Wakeel E. I., El-Hemaly S. A., Rizk M. A.: Egypt.J.Chem. *45*, 723 (2002).
7. Komarneni S., Roy R., Roy D. M.: Cem.Concr.Res. *12*, 773 (1982).
8. Komarneni S., Roy D. M.: Nature. *221*, 647 (1983).
9. Komarneni S., Roy D. M.: J.Mater.Sci., *20*, 2923 (1985).
10. Komarneni S., Tsuji M.: J.Am.Ceram.Soc. *72*, 1668 (1989).
11. Tsuji M., Komarneni S.: J.Mater.Sci. *4*, 698 (1989).
12. El-Korashy S. A.: Monatsheft Für Chemie. *128*, 599 (1997).
13. El-Korashy S. A., Al-Wakeel E. I.: Egypt.J.Chem. *42*, 237 (1999).
14. Al-Wakeel E. I., El-Korashy S. A., El-Hemaly S. A., Rizk M. A.: J.Mater.Sci. *36*, 2405 (2001).
15. El-Korashy S. A.: Monatshefte Für Chemie. *133*, 333 (2002).
16. Meyer J. W., Jaunarajs K. L.: Am.Mineral. *46*, 913 (1961).
17. Shaw S., Henderson C. M. B., Clark S. M.: Am.Mineral. *87*, 533 (2002).
18. Števula L., Petrovič J.: Cem.Concr.Res. *13*, 684 (1983).
19. Baltakys K., Siauciunas R.: J.Mater.Sci. *41*, 4799 (2006).
20. Miyake M., Iwaya M., Suzuki T.: J.Am.Ceram.Soc. *73*, 3524 (1990).
21. Winters M. A., Richter J. D., Sagar S. L., Lee A. L., Lander R. J.: Biotechnol. Prog. *19*, 440 (2003).
22. Merlino S.: Mineral.Mag. 52, 377 (1988).
23. Garbev K.: *Ph. D. Thesis*, Forschungszentrum Karlsuhe GmbH, Karlsruhe 2004 (In German).
24. Baltakys K.: *Ph. D. Thesis*, Kaunas University of technology 2006 (In Lithuanian).

SORPČNÍ VLASTNOSTI GYROLITU PRO MĚDNATÉ IONTY

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Byly studovány sorpční vlastnosti syntetického gyrolitu (CaO/SiO_2 = 0.66; 96 h; 200°C) pro mědnaté ionty. Stabilita a kationtová výměnná kapacita gyrolitu závisí na koncentraci mědnatých iontů v roztoku $Cu(NO_3)_2$. Krystalická struktura gyrolitu je zcela stabilní pouze pro počáteční koncentraci Cu^{2+} 1 g/l a jeho výměnná kapacita je rovna 54.32 mg Cu^{2+}/g po 360 minutách sorpce při 25°C. V roztocích s vyšší koncentrací $c_{Cu^{2+}}$ = 5.0; 10.0; 20.0 g/l probíhá výměnná reakce intenzivně na počátku adsorpčního procesu. Množství adsorbovaných Cu^{2+} iontů v krystalické mřížce gyrolitu je po 15 minutách 94 mg Cu^{2+}/g pro $c_{Cu^{2+}}$ = 5.0 g/l, 580 mg Cu^{2+}/g pro $c_{Cu^{2+}}$ = 10.0 g/l a 1480 mg Cu^{2+}/g pro $c_{Cu^{2+}}$ = 20.0 g/l. Částečná výměna $Ca^{2+} \leftrightarrow Cu^{2+}$ vede k amorfizaci krystalické struktury gyrolitu a stimuluje tvorbu nových sloučenin: gerharditu, gelu gyrolitu a C–S–H(I). Sorpční produkty byly charakterizovány RTG difrakční, termální analýzou a infračervenou spektrometrií s Fourierouvou transformací.