

The sorption of copper ions by gyrolite in alkaline solution

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Sorption of copper ions by synthetic pure gyrolite ($\text{CaO/SiO}_2 = 0.66$; 96 h; 200 °C) in alkaline solutions was examined. When the initial concentration of Cu^{2+} ions is 1 g/dm³, the cation exchange capacity of the gyrolite is 100 mg Cu^{2+} /g after 360 min of sorption at 25 °C. It has been proved that the cation exchange capacity of gyrolite depends on the concentration of copper ions in the $\text{Cu}(\text{NO}_3)_2$ solution, because a five-fold increase of the concentration (from 1.0 to 5.0 g/dm³) reduces the duration of the ion exchange reaction by a factor of three (from 15 min to 5 min). In solutions with higher initial concentrations of Cu^{2+} ions (10.0 and 20.0 g/dm³), the sorption proceeds more intensively and all the copper ions are adsorbed in 1 min. It should be noted that the cation exchange reactions are reversible in alkaline solution, because nearly 90% of the copper ions are adsorbed in a physical process, while the remaining part of the cation exchange process takes place in a chemical reaction. Furthermore, the crystal structure of gyrolite is stable in alkaline solution. The products of sorption were characterized by X-ray diffraction, thermogravimetry–differential scanning calorimetry and Fourier-transform infrared spectroscopy methods.

Key words: *gyrolite; cation exchange; calcium silicate hydrate; X-ray diffraction*

1. Introduction

Greater urbanisation and ever-growing populations have accelerated the problem of collecting and disposing both solid and liquid wastes. The world has to face one of the biggest disasters – pollution. Manmade chemicals, many of them very toxic, can be difficult to recycle and expensive to destroy [1]. Most wastes, hazardous or not, are simply dumped together at the nearest available government-owned land or even thrown into the water. Consequently, it is very important to find a way to minimize the damage. One way to do this is to develop new effective sorption materials [2–7].

The first time calcium silicate hydrates were used for ion exchange almost three decades ago [8–11]. These compounds created a new family of inorganic cation ex-

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changers. The ion exchange capacity of calcium silicate hydrates depends on their chemical composition as well as on the structure of their crystalline lattice. Both, naturally occurring and synthetic, unsubstituted calcium silicate hydrates are noted for their low ion exchange capacity, predetermined by the fact that Ca^{2+} ions in these compounds are inserted between separate layers and connected by a chemical bond with oxygen atoms [12–15]. Extraneous ions may interfere only if this bond is broken up. Importantly, additives increase the capacity of calcium silicate hydrates to extract heavy metal ions from water solutions [9–12, 16–19].

Supposedly, gyrolite can adsorb more chemical elements, because the interlayer sheets, with a thickness of about 2.2 nm (one of the largest in all the calcium silicate hydrates group) in the case of gyrolite, are available for the intercalation of a new guest by controlling the charge of the host [20–22].

Recently, the cation uptake reactions have been studied [23] of the transition metal ions (Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cs^+ , Cd^{2+} , Hg^{2+}) with some synthetic crystalline calcium silicates such as xonotlite, gyrolite and β -wollastonite. The total amounts of ions uptaken by these solids have been found in a descending order: xonotlite – gyrolite – β -wollastonite. Moreover, the quantities of Fe^{2+} , Co^{2+} and Ni^{2+} ions taken up by xonotlite and wollastonite were found to be higher than those of the other cations. On the other hand, gyrolite showed a low selectivity towards different elements.

It should be underlined that the reaction of xonotlite and β -wollastonite with Fe^{2+} , Pb^{2+} , Cd^{2+} and Hg^{2+} leads to the precipitation of goethite [$\text{FeO}(\text{OH})$], hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$], otavite [CdCO_3] and $\text{HgCO} \cdot 2\text{HgO}$ phases. Meanwhile, reaction of Cu^{2+} and Zn^{2+} ions with β -wollastonite or gyrolite leads to the precipitation of gerhardite [$\text{Cu}_2(\text{OH})_3\text{NO}_3$] and zincate [$\text{CaZnO}_2 \cdot x\text{H}_2\text{O}$] phases [23].

However, in all papers quoted no detailed data can be found on the dependence of the stability of the crystal structures of calcium silicate hydrates on pH of a solution. Moreover, it is very important to identify the influence of pH on the parameters governing the ion exchange reaction.

The objectives of the present work were to explore the cation exchange capacity of gyrolite for Cu^{2+} ions in an alkaline solution, and to evaluate the potential for its application as a new, effective sorption material. The cation exchange reaction mechanism is presented.

2. Experimental

Pure gyrolite was synthesized after 96 h at 200 °C from a stoichiometric composition ($\text{CaO}/\text{SiO}_2 = 0.66$) of calcium oxide (CaO was produced by burning calcium oxide at 950 °C for 0.5 h, specific surface area $S_a = 548 \text{ m}^2/\text{kg}$, evaluated by Blaine's method) and fine-grained $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (ignition losses 21.28%, $S_a = 1155 \text{ m}^2/\text{kg}$) mixture. The dry primary mixture was mixed with water in stainless steel vessels (water/solid ratio of the suspension $W/S = 10.0$). The product was filtered off, dried at

50 ± 5 °C and sieved (the mesh size was 50 μm). Such conditions of the synthesis were chosen according to the previously published data [24, 25].

Ion exchange experiments were carried out at 25 °C in a Grant SUB14 thermostatic adsorber by stirring 1 g of gyrolite in 100 cm^3 of $\text{Cu}(\text{NO}_3)_2$ aqueous solution, containing 1, 5, 10, 20 g/dm^3 of Cu^{2+} ions, for 360 min. Different amounts of NH_4OH aqueous solution ($c = 10\%$) were used to prevent $\text{Cu}(\text{OH})_2$ precipitation and to maintain the alkalinity of the solution. The initial concentration of Cu^{2+} ions and the pH value of the solution are shown in Table 1.

Table 1. Initial concentration of Cu^{2+} ions and pH of solutions

Cu^{2+} ions concentration in the solution [g/dm^3]	pH of solution	The amount of NH_4OH [cm^3]
1	10.38	5.5
5	9.79	8
10	9.69	13
20	9.62	25

The percentage of exchange was determined using a Perkin-Elmer Analyst 4000 spectrometer based on the changes of the concentrations of the cations in the solution and the cations in the gyrolite. The pH value was measured with a Hanna instrument (Hi 9321, microprocessor pH meter).

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

Simultaneous thermal analysis (STA) comprising both differential scanning calorimetry (DSC) and thermogravimetry (TG) was also employed for measuring the thermal stability of gyrolite 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 STA 409 PC Luxx instrument. Ceramic sample handlers and Pt-Rh crucibles were used.

FT-IR spectra were obtained with the aid of a Perkin Elmer FT-IR Spectrum X system. The specimens were prepared by mixing of 1 mg of a given sample with 200 mg of KBr. Spectral analyses were performed in the range of $4000-400\text{ cm}^{-1}$ with the spectral resolution of 1 cm^{-1} . The specific surface area of the raw materials was determined by Blaine's method with an air permeability apparatus (Model 7201, Toni Technik Baustoffprüfsysteme GmbH).

3. Results and discussion

Synthetic gyrolite was characterized by XRD, STA, and FT-IR spectroscopy to evaluate its purity (Fig. 1). XRD analysis showed that in the $\text{CaO-SiO}_2 \cdot n\text{H}_2\text{O-H}_2\text{O}$

system pure gyrolite within 96 h at 200 °C was formed. The most characteristic peak of gyrolite (d spacing 2.2390 nm), not characteristic of other calcium silicate hydrates, was identified. Moreover, in the X-ray diffraction patterns, the peaks were determined by d spacings equal to 0.1262, 0.8371, 0.4197, 0.3732, 0.3511, 0.2803, 0.2141 nm, which are also typical of gyrolite (Fig. 1a). The results of XRD were confirmed by other analyses. On the DSC curve, a broad endothermic peak at 145 °C reflects the loss of physisorbed and interlayer water from the crystal structure of gyrolite (Fig. 1b). The other exothermic peak at 853 °C is associated with recrystallization of this compound into wollastonite. The shape of the absorption bands of the FT-IR spectrum, its multiplicity and width also are characteristic of gyrolite (Fig. 1c).

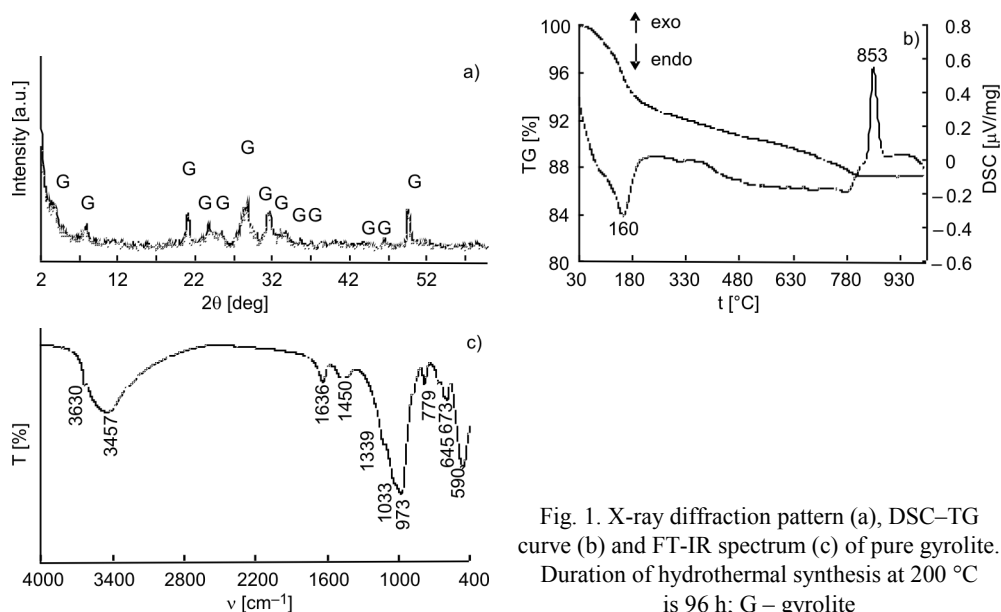


Fig. 1. X-ray diffraction pattern (a), DSC–TG curve (b) and FT-IR spectrum (c) of pure gyrolite. Duration of hydrothermal synthesis at 200 °C is 96 h; G – gyrolite

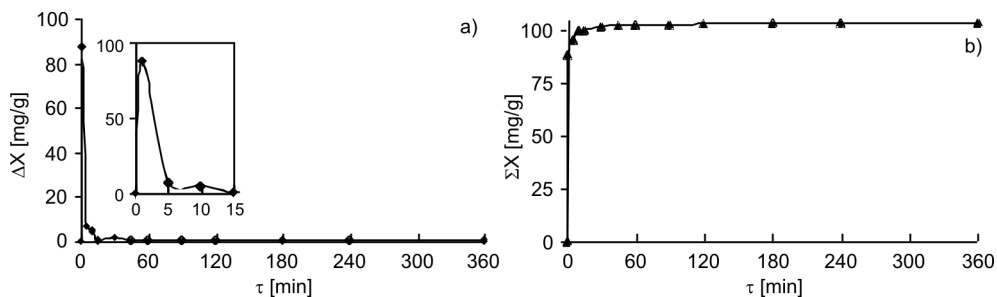


Fig. 2. Differential (a) and integral (b) kinetic curves of Cu^{2+} ions adsorption from $\text{Cu}(\text{NO}_3)_2$ solution at the initial concentration of Cu^{2+} ions of 1.0 g/dm³, at 25 °C

The results of ion exchange experiments showed that the cation exchange capacity of gyrolite depends on the concentration of copper ions in the $\text{Cu}(\text{NO}_3)_2$ solution. It

was noticed that the cation exchange reaction proceeds rapidly in the first minute of the adsorption process. The amount of adsorbed Cu^{2+} ions in the crystal lattice of gyrolite is equal to 88 mg Cu^{2+} /g at the initial concentration of Cu^{2+} ions of 1 g/dm³ (Fig. 2a). Upon prolonging the duration of the sorption process, the concentration of Cu^{2+} ions in the solution slightly decreases, and after 15 min all the Cu^{2+} ions are incorporated into the crystal structure of gyrolite (100 mg Cu^{2+} /g) (Fig. 2b).

It should be noted that the cation exchange capacity of gyrolite increases greatly in the 5.0 Cu^{2+} g/dm³ solution. The amount of adsorbed copper ions in the crystal lattice of gyrolite is equal to 450 mg Cu^{2+} /g after 1 min (Fig. 3a). In this case, all the Cu^{2+} ions in the solution were incorporated in the adsorbent structure after 5 min of sorption (Fig. 3b).

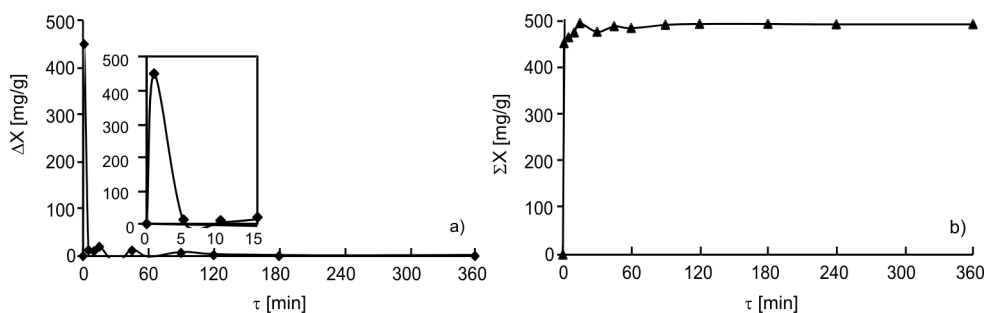


Fig. 3. Differential (a) and integral (b) kinetic curves of adsorption Cu^{2+} ions from $\text{Cu}(\text{NO}_3)_2$ solution at the initial concentration of Cu^{2+} ions of 5.0 g/dm³ at 25 °C

Thus, the five-fold increase in the Cu^{2+} ion concentration (from 1.0 to 5.0 g/dm³) shortens the duration of the ion exchange reaction by a factor of 3 (from 15 min to 5 min). As expected, in the solutions having higher initial concentrations (10.0 and 20.0 g/dm³), the sorption proceeds more rapidly and all copper ions are adsorbed in 1 min.

Several authors [8–11, 18] reported that the partial exchange $\text{Ca}^{2+} \leftrightarrow \text{M}^{2+}$ proceeds at the same time in both directions, i.e. the cation exchange reaction of these ions is reversible. Meanwhile, our results have shown that the partial exchange $\text{Ca}^{2+} \leftrightarrow \text{Cu}^{2+}$ is not in equilibrium, though the character of the desorption kinetic curves is close to that of the adsorption curves (Figs. 4–7). Most of the Ca^{2+} ions are released from the crystal lattice of gyrolite in the first minutes of sorption, and their concentration remains more or less the same, even when the process is prolonged. However, all Cu^{2+} ions were incorporated in the crystal lattice of gyrolite after 1–15 min (depending on the initial concentration of the solution), meanwhile the desorption of Ca^{2+} ions began only after 15 min, when the initial concentration of the solution was 1.0, 5.0 g Cu^{2+} /dm³ (Figs. 4, 5).

Furthermore, calcium ions are released into the solution only when all the copper ions are incorporated into the crystal lattice of gyrolite. It is presumed that the Cu^{2+} ions are intercalated in the interlayer sheets at the beginning of the sorption process, when the *d* spacing of this compound (2.2000 nm) is important. Calcium ions are re-

leased from the crystal lattice of gyrolite into the solution when the charge of the host is changed in order to maintain its neutrality.

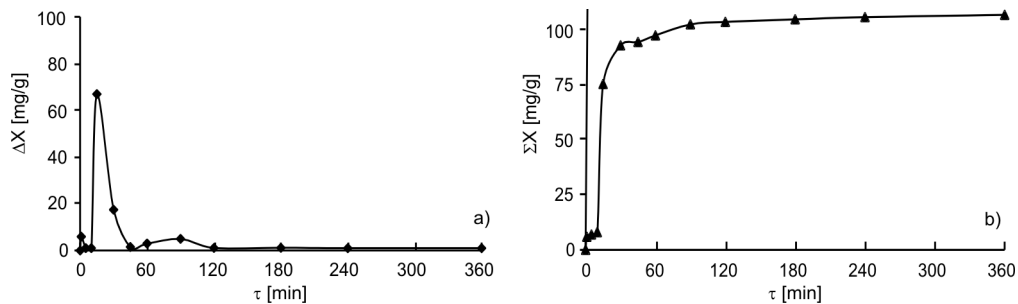


Fig. 4. Differential (a) and integral (b) kinetic curves of Ca^{2+} ions concentration in $\text{Cu}(\text{NO}_3)_2$ solution at the initial concentration of Cu^{2+} ions of 1.0 g/dm^3

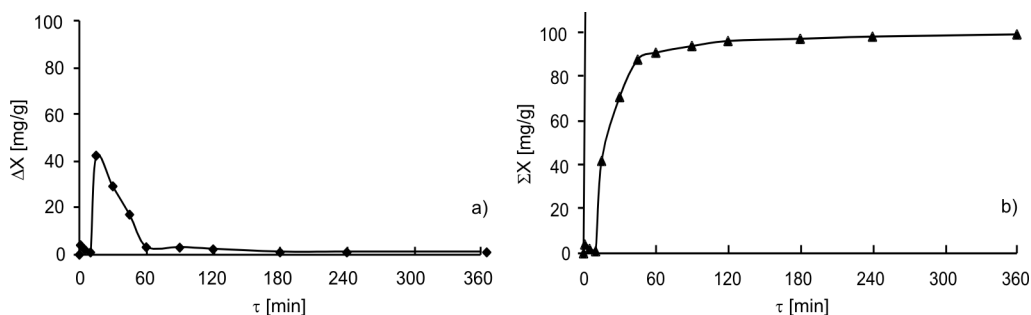


Fig. 5. Differential (a) and integral (b) kinetic curves of Ca^{2+} ions concentration in $\text{Cu}(\text{NO}_3)_2$ solution at the initial concentration of Cu^{2+} ions of 5.0 g/dm^3

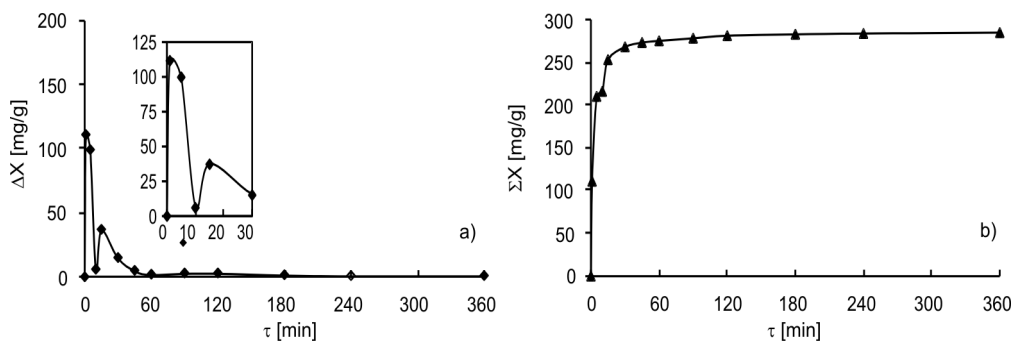


Fig. 6. Differential (a) and integral (b) kinetic curves of Ca^{2+} ions concentration in $\text{Cu}(\text{NO}_3)_2$ solution at the initial concentration of Cu^{2+} ions of 10.0 g/dm^3

Notably, an increase in the concentration of the copper ions in the solution accelerated the desorption of calcium ions. The concentration of released Ca^{2+} ions in the solution was greater than $100 \text{ mg Ca}^{2+}/\text{g}$ after 1 min, when $c_{\text{Cu}^{2+}}$ was equal to

10.0 g/dm^3 (Fig. 6a). The desorption process of calcium ions terminated after 60 min ($275 \text{ mg Ca}^{2+}/\text{g}$) because the concentration of ions was almost the same when the duration of sorption was prolonged, and after 6 h their concentration was equal to $284 \text{ mg Ca}^{2+}/\text{g}$.

Unexpected results were obtained with $20 \text{ g Cu}^{2+}/\text{dm}^3$ because the concentration of desorbed Ca^{2+} ions in the solution was $20 \text{ mg Ca}^{2+}/\text{g}$ (Fig. 7). The main reason might be the alkalinity of the solution. In this case, the pH was over 10 during the ion exchange experiment.

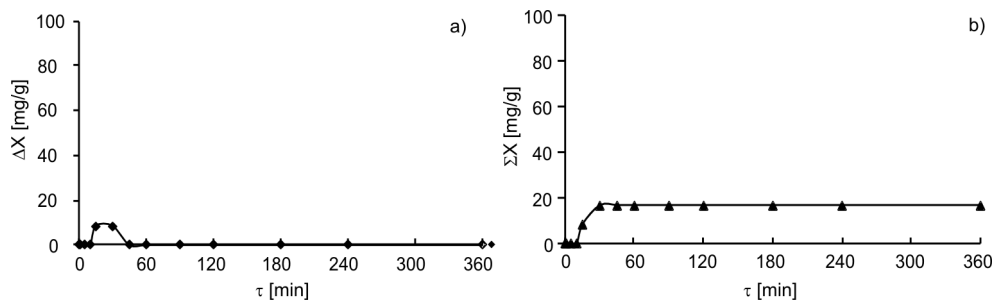


Fig. 7. Differential (a) and integral (b) kinetic curves of Ca^{2+} ions concentration in $\text{Cu}(\text{NO}_3)_2$ solution at the initial concentration of Cu^{2+} ions of 20.0 g/dm^3

The amounts of Cu^{2+} ions adsorbed from the solutions of various concentrations are listed in Table 2.

Table 2. The amount of adsorbed Cu^{2+} ions

$c_{\text{Cu}^{2+}}$ in the solution [g/dm^3]	The amount of adsorbed Cu^{2+} ions [mg/g], at 25°C after 6 h of the sorption		
	Calculated from the data of differential and integral kinetic curves [mg/g]	Determined in the adsorbent [mg/g]	Average [mg/g]
1	100	100	100
5	500	490	495
10	1000	1000	1000
20	2000	1998	1999

As far as we know, this is the first time that cation exchange reactions have been seen to be reversible in alkaline solution. It has been proven that Cu^{2+} ions are released from the crystal lattice of gyrolite into solution during desorption. Nearly 90% of the copper ions were physisorbed, while the remaining ions took part in the chemical reaction. Thus, the sorption process in gyrolite is similar to the same process in clay minerals or zeolites. The amount of Cu^{2+} desorbed in the solution is given in Table 3.

Table 3. The amount of Cu^{2+} desorbed in solution

$c_{\text{Cu}^{2+}}$ in the solution [g/dm ³]	The amount of adsorbed Cu^{2+} ions from Table 2	The amount of desorbed Cu^{2+} ions [mg/g] at 25 °C after 60 min of desorption		
		[mg/g]	[%]	Average [%]
1	100	91	91	90
5	495	445.5	90	
10	1000	900	90	
20	1999	1779.1	89	

In order to identify the stability of gyrolite, the products of sorption were characterized by numerous methods of instrumental analysis. The X-ray powder diffraction analysis showed that the structure of gyrolite did not change during the sorption. In the X-ray diffraction pattern, the most characteristic peak (d spacing 2.2000 nm) of gyrolite was identified. This principal reflection did not change over the duration of the cation exchange reaction (Fig. 8).

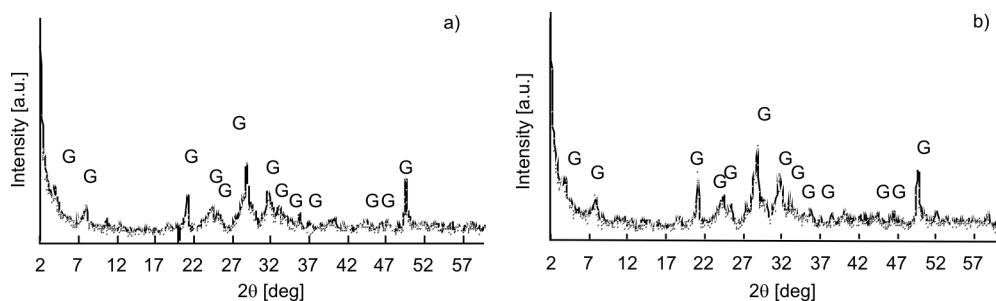


Fig. 8. X-ray diffraction patterns of gyrolite after adsorption (25 °C, 360 min) at the concentration of Cu^{2+} ions: a) 1.0 g/dm³, b) 5.0 g/dm³

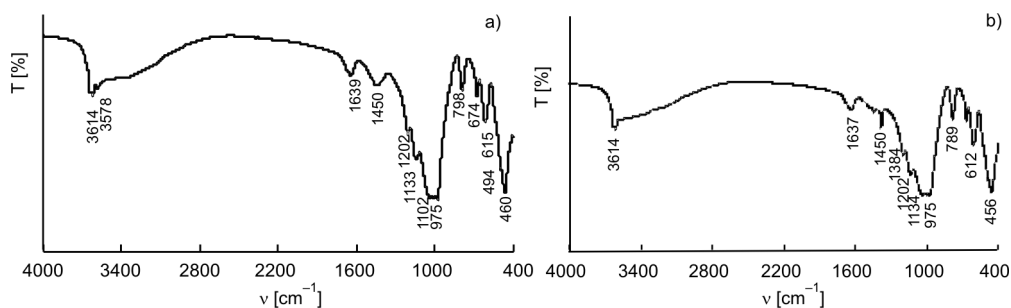


Fig. 9. FT-IR spectra of gyrolite after adsorption (25 °C, 360 min) at the concentration of Cu^{2+} ions: a) 1.0 g/dm³, b) 5.0 g/dm³

The results of XRD were confirmed by FT-IR spectroscopy. The presence of a very weak, sharp band at about 3630 cm⁻¹ confirms the presence of OH⁻ groups

bound in the structure, while the presence of a broad band, located at 3457 cm^{-1} , and of a weak one, at 1636 cm^{-1} , may be due to the physically adsorbed water. Also, FT-IR spectroscopy data show that after the sorption process the intensities of absorption bands characteristic of gyrolite at about 1450 , 1339 and 1033 cm^{-1} are the highest (Fig. 9).

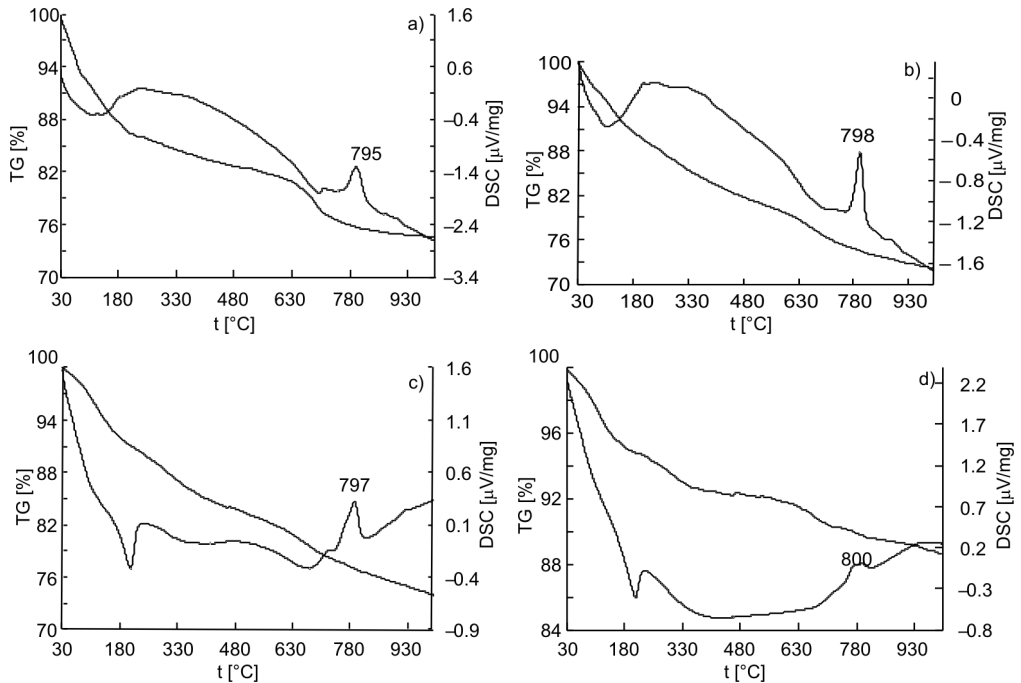


Fig. 10. DSC–TG curves of gyrolite after adsorption (25 °C, 360 min); concentration of Cu^{2+} ions, g/dm^3 : a) 1.0, b) 5.0, c) 10.0, d) 20.0

After the sorption process, the same thermal effects as in pure gyrolite (water dehydration and recrystallization to wollastonite) were identified. However, the temperature of the exothermal effect (853 °C) decreases by about 50 °C after the cation exchange reaction, as was identified in the DSC curve at the temperature range of $795\text{--}800\text{ °C}$ (Fig. 10).

4. Conclusions

The cation exchange capacity of gyrolite depends on the initial concentration of copper ions in the $\text{Cu}(\text{NO}_3)_2$ solution, because a five-fold increase in the concentration (from 1.0 to 5.0 g/dm^3) shortens the duration of the ion exchange reaction by a factor of three (from 15 min to 5 min). In the solutions having higher initial concentrations

(10.0, 20.0 g/dm³), the sorption proceeds more intensively and all copper ions are adsorbed in 1 min.

The cation exchange reactions are reversible in alkaline solutions, because nearly 90% of the copper ions are physically adsorbed, while the remaining ions take part in the chemical reaction.

During the sorption process, the crystal structure of synthetic pure gyrolite is stable in alkaline solution, when pH is at most 9.5. Meanwhile, the temperature of an exothermic effect, typical of recrystallization into wollastonite, decreases by about 50 °C after the cation exchange reaction.

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