

Experimental Studies on Heavy Metal Sorption by Natural Clays Aimed at Drain Water Purification

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Abstract

Sorption properties of bentonite clays of the Kamalino deposit (Krasnoyarsk Territory) have been studied for the purpose of their possible use for purifying the wastewater of sulphide-containing tailing pits from heavy metal ions. By the example of copper (II), an effect of pH value, of sorbate/sorbent ratio and sorbate concentration increase on the redistribution of metal from model solution to the solid phase. Basing on the data concerning the investigation of water extracts from the substance of the Belovo Zinc Plant (Kemerovo Region) and its wastewaters drain the present object is established to be the source of the acidic mine drainage of the most adverse type (insignificant iron content as well as high heavy metals and sulphate sulphur content). It has been demonstrated efficient results concerning wastewater treatment of the Belovo Zinc Plant tailing pits could be obtained with the use of two-stage purification: first, with the application of calcite, and further via the interaction with a clay sorbent.

Key words: copper sorption, naturally occurring clay, acidic mine drainage, tailing pit of pyrometallurgy clinkers

INTRODUCTION

At the present moment the works concerning the sorption ability of clay rocks are mainly devoted to discussing the problem of their possible use as geochemical barriers around the depositories of radioactive waste products (RW) being the most dangerous objects with respect to the environment and human beings [1–3]. At the same time, the pollution of surface and subsoil waters with the wastewaters from the enterprises of ferrous and nonferrous metallurgy also threatens the environment, being though of slow-acting, but a more large-scale character [4–6]. Due to relative ecological compatibility, low cost and availability, the sorption ion-exchange materials based on naturally occurring mineral raw are promising for purifying rock waste piles and ore processing tails those are accumulated in immense amounts (dozens thousand ton) over the territories of mining and concentrating enterprises [7]. Among naturally occurring sorbents, the highest exchange ability is exhibited by bentonite clays:

the cation exchange capacity can amount up to 90–150 mg-eq/100 g [8]. Moreover, there are experimental data concerning the possibility for obtaining modified bentonites with a higher cation exchange capacity [9, 10]. From this point they are second only to humus organic compounds (100–500 mg-eq/100 g).

The present work is devoted to studying the ion-exchange properties of bentonite clays taken from the Kamalino deposit (Krasnoyarsk Territory) with the purpose of their use as sorbents in order to purify wastewater resulted from bulked sulphide-containing tailing pits from heavy metal ions as well as to create a cheap (without additional expenses) geochemical barrier around the mothballed enterprise such as the Belovo Zinc Plant (BZP, Kemerovo Region).

OBJECTS UNDER STUDY AND EXPERIMENTAL TECHNIQUE

A naturally occurring variety of bentonite was used in the experiments. Being in the natural form, it is aggregated to a considerable

TABLE 1

Chemical composition of Kamalino clay samples [11], mass %

| Bore pit No. | SiO ₂ | TiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | FeO | MgO | CaO | MnO | K ₂ O | Na ₂ O | Sum total |
|--------------|------------------|------------------|--------------------------------|--------------------------------|------|------|------|------|------------------|-------------------|-----------|
| 84 | 61.10 | 0.01 | 14.90 | 3.28 | 0.20 | 4.44 | 5.48 | — | 0.62 | 0.23 | 100.48 |
| 98 | 66.0 | 0.53 | 16.90 | 1.99 | 0.04 | 3.60 | 2.03 | 0.08 | 0.63 | 0.11 | 100.21 |
| 143 | 65.45 | 0.17 | 14.76 | 3.43 | 0.31 | 5.12 | 1.50 | — | 0.46 | 0 | 98.76 |

extent, therefore the sample was grinded in a mortar to obtain a visually homogeneous condition, however it was not exposed either to fractional precipitation (decantation from crude fraction), or to the further modifying.

The Kamalino deposit of bentonite clays was discovered in 1960 [11]. Clay occurs in the form of geological unit with the deposit thickness ranging within 10–17 km in the structure of lower-coal sea sediments. The area of the deposit amounts to 10 × 15 km. The resource of naturally occurring bentonite clays of the Kamalino deposit accepted according to SRC, in the B category are equal to 3.6 mln t, amounting to 145.6 mln t in the C₂ category (deposits with the resource more than 20 mln t are considered as large ones). Macroscopically, clays represent rocks light grey, lilac and yellowish in colour. Being in the natural form they are aggregated to a considerable extent, the content of colloid fraction with particle size less than 1.5 μm being equal to 15–20 %. The chemical composition of bentonite clays from the Kamalino deposit taken from different bore pits is presented in Table 1. One can see that a high enough content of CaO and MgO and a lower content of Na₂O and K₂O is inherent in these clays, *i. e.* the clays could be referred to alkaline-earth varieties. The content of iron (III) oxide amounts to 2–4 %. According to data from [11, 12], the Kamalino clays are composed mainly of montmorillonite (60–90 %) with the inclusion of hydromicas (10–30 %), kaolinite (5–10 %) and peach (up to 5 %); more rarely halloysite, beidellite, palygorskite occur; there are quartz and plagioclase present (10–20 %).

The BZP functioned since 1932 till 1990 and produced annually up to 10 thousand ton of Zn and up to 30 thousand ton of H₂SO₄ [13]. Mainly, there was blende concentrate processed produced at the Salair Lead Zinc Concentration Plant. Owing to poor quality of ores, fine mu-

tual germinations of sulphide minerals and the complications of enriching the blende concentrate contained a great number of impurity elements (Cu, Pb, Cd, As, Sb, *etc.*) those were sent to waste piles. For 60 years of operation, as much as about 1 mln t of waste products (clinkers) has accumulated over the territory of BZP. Visually, they represent coarse-grained sand of typical slag with the content of fraction >4 mm equal to 65 %. The clinkers represent mainly sulphide containing waste products with non-uniform chemical composition (Table 2) those are stored in the form of 15 m high bulked waste pile. The waste pile is surrounded with a bypass ditch, from the western side it is adjoined with a bog. The drainage (sedimentation reservoir) is flowing down into a bog and further is entering into the Bachat River. An abundance of secondary minerals on the bank surface indicates the intensity of chemical weathering of clinkers, in this case water in the ditch is dark blue in colour, whereas bottom sediments are white, blue and greenish. Within the first year of field observation (the summer period of 1997) water in the ditch was warm and acidic, whereas copper was

TABLE 2

Chemical composition of BZP clinkers substance [13]

| Component | Content, % | Component | Content, g/t |
|--------------------------------|------------|-----------|--------------|
| SiO ₂ | 15–25 | Cd | 2–400 |
| Al ₂ O ₃ | 3–5 | As | 100–500 |
| CaO | 4–6 | Sb | 500–1000 |
| MgO | 0.3–0.6 | Ag | 150–250 |
| Fe | 3–22 | In | 13 |
| S | 0.5–1.5 | Te | 2 |
| C | 10–25 | Ga | 36 |
| Zn | 0.7–14 | Ge | 8 |
| Cu | 0.3–8.5 | Au | up to 4 |
| Pb | 0.03–0.7 | Se | Traces |

quickly deposited from the solution onto metal pieces. During the ensuing years of field observation, this effect was not observed any more.

As it was mentioned above, for the experiments we used a naturally occurring sample of bentonite clay, light grey in colour (1.3 % K, 1.6 % Ca, and 2 % Fe). The determination of its mineral composition has been performed using an X-ray diffraction analysis (XRD) method at the Laboratory of Cainozoic Geology, Paleoclimatology and Mineralogical Climatic Indicators of the Institute of Geology and Mineralogy, SB RAS (Novosibirsk). Potash feldspar, quartz, montmorillonite (about 30 %), kaolinite, micas have been found out in the sample. An attempt to convert montmorillonite into the Na-form (its interaction with 0.1 M NaNO₃ solution) has resulted in decreasing the sorption properties whereby the modification of montmorillonite in this work was not carried out.

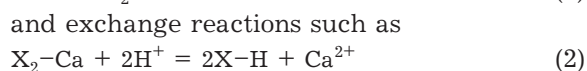
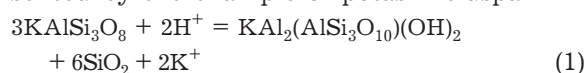
The IR absorption spectra of clay after its interaction with Cu(NO₃)₂ solutions of different concentration were obtained at the Laboratory of Cainozoic Geology, Paleoclimatology and Mineralogical Climatic Indicators of the Institute of Geology and Mineralogy, employing a Bruker Fourier transform mass-spectrometer (Germany) within the range of wave number values of 4000–400 cm⁻¹. A technique of pressing KBr pellets with the substance under investigation was used. At the first stage, we used Cu(II) as a sorbate. The standard was prepared *via* dissolving metal copper in nitric acid; the acidity of the solution (~10⁻⁴ mol/L) was corresponding to acidic value of pH ~ 3. Required pH values (up to neutral acidity range) were reached *via* adding a 0.01 M NaOH solution. A 0.01 M NaNO₃ solution was used as background electrolyte. The experiments were carried out employing conic flasks convenient for placing into a shaker in the beginning of the experiment. The volume of the solution was constant amounting to 100 mL. After several hours of stirring, the flasks were held in a quiescent state up to the end of experiment. Within the next day we measured the medium pH. It should be noted that fast clarification of the solution and the possibility of separating it from the precipitate allowed us to avoid a laborious stage of centrifugation/filtration.

Copper in the solution was determined using a spectrophotometric method (UV-VIS Specord M 40), measuring the optical density (absorbance value) for the complex of Cu(II) with pyridylazonaphthol (PAN) at the wavelength $\lambda = 570$ nm [14]. In the presence of other cations we used an atomic absorption spectroscopy (AAS) method (Perkin Elmer 401). The amount of sorbed cations was estimated from the difference between its concentration in the solution in the beginning (C_{ini}) and in the end of the experiment (C_{eq}). The value of pH was measured with the use of HANNA Instruments R1-02895 device with electronic indication.

This work was also devoted to the investigation of water samples from a bog located near the waste pile, as well as of the extracts from BZP clinkers. The latter were prepared *via* careful stirring a weighed sample portion grinded using a jasper mortar with distilled water and sedimentation. First, the solution above the solid phase looked transparent, but in some days on the bottom of the flask we saw a precipitate in the form of ochre-like flakes. In this case we performed decantation and took aliquots for experiments. A detailed description of the experiments is presented in the following section.

RESULTS AND DISCUSSION

First of all we have studied the influence of nitrate solutions without sorbate upon changing the pH value of clay suspension immediately after its preparation and in the course of time (Table 3, Exp. 1–4). The following hydrolysis reactions of minerals those could be presented by the example of potash feldspar



promote absorbing a proton and shifting pH value towards neutral region. In the expression for reaction (2) and thereafter X₂-Ca designations a related to an ion-exchange position on the surface of a clay mineral.

From data presented in Table 3 one can see that the pH value of the suspension is the most stable with the pH value of the suspension is

TABLE 3

Experimental results for Cu(II) sorption by bentonite clay

| No. | Solution under investigation | pH _{ini} | pH ₁ | pH ₂ | pH ₄ |
|-----|---|-------------------|-----------------|-----------------|-----------------|
| 1 | 100 mL sol. 0.02 M HNO ₃ + 1 g clay + H ₂ O | 3.04 | 3.38 | 3.78 | 4.24 |
| 2 | 100 mL sol. 0.02 M HNO ₃ + 0.01 M NaNO ₃ + 1 g clay | 2.92 | 3.20 | 3.79 | 4.26 |
| 3 | 100 mL sol. 0.01 M NaNO ₃ + 1 g clay | 7.30 | 7.35 | 7.30 | 7.28 |
| 4 | H ₂ O + 1 g clay | 6.93 | 7.90 | 7.49 | 7.61 |
| | | pH ₁ | Cu, mg/L | pH ₂ | Cu, mg/L |
| | | (Suspension) | (Sorption, %) | | (Sorption, %) |
| 5 | 100 mL sol. Cu(NO ₃) ₂ + 0.01 M NaNO ₃ + 1 g clay | 2.98 | 3.42 (47) | 4.00 | 2.79 (56) |
| 6 | The same + NaOH | 4.07 | 2.28 (64) | 5.27 | 1.91 (70) |
| 7 | The same | 4.60 | 2.16 (66) | 6.30 | 1.20 (81) |
| 8 | « | 5.96 | bdl* | 7.10 | bdl |
| 9 | « | 6.57 | bdl | 7.38 | bdl |
| | | pH ₁ | Sorption, % | pH ₂ | Sorption, % |
| | | (Suspension) | | | |
| 10 | 100 mL sol. Cu(NO ₃) ₂ + 0.01 M NaNO ₃ + 0.1 g clay | 3.71 | 30 | 3.54 | 32 |
| 11 | The same + NaOH | 4.16 | 31 | 4.14 | 36 |
| 12 | The same | 4.89 | 35 | 4.87 | 40 |
| 13 | « | 5.30 | 43 | 5.08 | 44 |
| 14 | « | 5.67 | 45 | 5.33 | 53 |
| 15 | « | 5.76 | 57 | 5.50 | 60 |
| 16 | « | – | – | 6.68 | 89 |
| 17 | « | – | – | 6.93 | 93 |
| | | pH ₁ | Sorption, % | pH ₄ | Sorption, % |
| | | (Suspension) | | | |
| 18 | 100 mL sol. Cu(NO ₃) ₂ + 0.01 M NaNO ₃ | 6.65 | – | 6.66 | – |
| 19 | The same + 0.1 g clay | 6.64 | 53 | 6.54 | 73 |
| 20 | The same | 6.61 | 60 | 6.49 | 71 |
| 21 | The same + 0.2 g clay | 6.75 | 68 | 6.75 | 82 |
| 22 | The same* | – | – | 6.84 | 94 |
| 23 | The same + 0.3 g clay | 6.71 | 71 | 6.81 | 86 |
| 24 | The same | 6.71 | 67 | 6.82 | 86 |
| 25 | The same + 0.4 g clay | 6.72 | 72 | 6.73 | 87 |
| 26 | The same + 0.5 g clay | 6.68 | 80 | 6.83 | 88 |
| 27 | The same | 6.67 | 80 | 6.82 | 89 |
| 28 | The same* | – | – | 6.90 | 97 |
| | | pH ₁ | Sorption, % | pH ₈ | Sorption, % |
| | | (Suspension) | | | |
| 29 | 100 mL sol. 0.01 M NaNO ₃ + 0.5 g clay + 3 mL sol. Cu(NO ₃) ₂ | 6.17 | 71 | 6.06 | 89 |
| 30 | The same + 4 mL | 5.91 | 70 | 5.92 | 85 |
| 31 | The same + 5 mL | 5.83 | 71 | 5.78 | 79 |
| 32 | The same + 6 mL | 5.71 | 62 | 5.76 | 76 |
| 33 | The same + 7 mL | 5.74 | 61 | 5.69 | 73 |
| 34 | The same + 8 mL | 5.62 | 60 | 5.61 | 70 |

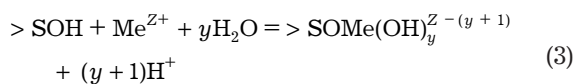
Notes. 1. In Exp. 5–28 Cu(II) content in the solution is equal to ~6 mg/L, in Exp. 29–34 – 2.26 mg/L. 2. pH_{ini}, pH₁, pH₂, pH₄ are pH values measured right after preparing the suspension and in 1, 2, 4 and 8 days, respectively. 3. bdl. – “below the determination threshold level” for the solution employing spectrophotometry technique.

* Independent examining in another series of experiments.

shifted towards the region of slight alkalizing (up to pH ~ 7.5).

Table 3 also demonstrates data concerning the sorption level of copper (II) from the solution onto 1 g of clay depending on the pH value of the solution and on the duration of experiment (Exp. 5–9). As a whole, with the increase in pH the amount of absorbed cations increases from 50 to 80 %. One can see that in 2 days of the experiment the copper sorption level has increased, however this fact cannot be interpreted as an immediate influence of the sorption process duration (as it is known, this requires several hours). The reduction of copper content could be caused by changing the pH value of the suspension due to the interaction between the solution and the sorbent (see Table 3). At $\text{pH}_{\text{ini}} > 6$ the amount of copper in the solution has appeared to be lower than the level of reliable determination with the use of the method chosen, therefore for a detailed consideration of the process within the range of neutral pH we used a higher solution/sorbent ratio.

Figure 1, *a* demonstrates the influence of solution pH upon the process of Cu(II) sorption. The character of the curve, *i. e.* an abrupt dependence of passing copper into the solid phase on the value of pH at constant ionic strength 0.01 could indicate a significant role of adsorption, *i. e.* the formation of charged surface complexes [15, 16] according to the reaction



where $> \text{SOH}$ is related to the position on the surface of any mineral participating in the formation of a surface complex and dissociation process according to equation (3a). For the given series of the experiments the characteristic point corresponds to $\text{pH}_{50} \sim 5.2$. The distribution coefficient was calculated according to the formula $K_d = (C_{\text{ini}} - C_{\text{eq}})V / (C_{\text{eq}} \cdot m)$ (4) where V is the volume of the solution, L; m is the mass of the sorbent. For acidic solutions at pH 5.08 and 5.33 the value of K_d amounts to 0.7 and 1.0 L/g, respectively (see Table 3, Exp. 13, 14). Basing on the distribution coefficient we calculated the metal sorption level:

$$\text{Me}_{\text{sorb}} = K_d / (K_d + V/m) \times 100 \% \quad (5)$$

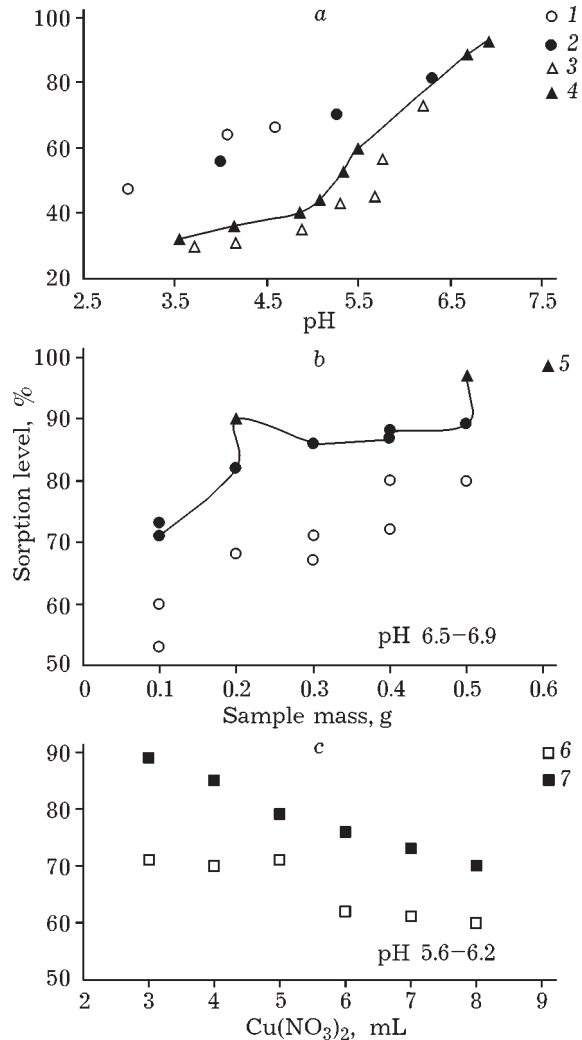


Fig. 1. Cu (II) sorption level depending on the solution pH (*a*), sorbate/sorbent ratio (*b*) and initial $\text{Cu}(\text{NO}_3)_2$ concentration (*c*) in 0.01 M NaNO_3 electrolyte solution at the temperature of 25 °C: 1, 2 – weighed clay portion 1 g/100 mL of solution; 3, 4 – 0.1 g clay/100 mL of solution; 5 – data of independent examining the influence of the S/L ratio upon the process of copper sorption from solutions containing 0.2 and 0.5 g of clay; 6, 7 – for the solutions initially containing 2.26 mg/L Cu (II), with adding 0.5 g clay/100 mL of solution; 1, 3, 6 – the fraction of absorbed copper in a day; 2, 4, 7 – repeated determining in several days.

Data presented in Fig. 1 and Table 3 indicate that there is a positive (simbasic) dependence of Cu(II) sorption level on the mass of weighed sample portion, *i. e.* on the solution/sorbent ratio, within the range of 100/0.1–100/0.5 at pH 6.5–6.8 (Exp. 18–28). The present range of pH values is chosen in order to estimate the standard cation exchange capacity (CEC_{st}) which is usually calculated at pH 6.5. The data of recurrent determining copper in the solution in 4 days indicate an increase in the metal

sorption level (see Fig. 1, b). The results concerning the sorption of copper in the independent series of long-term experiments with the use of clay weighed portion 0.2 and 0.5 g in mass are presented therein, too. One can see that the difference between them amounts to less than 10 %, and taking into account that the value of pH therein is 0.1 units higher (within each series, alkalization with NaOH is independently carried out) this value could be considered a good convergence. For every weighed sample portion, we calculated the sorption capacity of clay sorbent with respect to copper (II). At a low metal/sorbent ratio, this value amounts to 0.1 g-eq/100 g, whereas at a high metal/sorbent ratio it is equal to 0.03 g-eq/100 g. Hence, in spite of increasing the copper sorption level with the increase in the weighed sample portion, the occupancy density of sorption centres on the surfaces of the solid phase in the case of a high metal/sorbent ratio is much lower (*i. e.* the relative amount is observed to decrease).

Figure 1, c and Table 3 also demonstrate data concerning the sorption level for copper cation depending on its content in the solution. The solution/sorbent ratio in these experiments (see Table 3, Exp. 29–34) amounted to 100/0.5, the volume of copper aliquot (~2 mg/L) was within the range of 3–8 mL. The duration of the experiment has been increased up to 8 days with the purpose of studying the possibility of beginning the desorption process (at such high sorbate/sorbent ratio values) that is an extremely undesirable process proceeding with long-term storage of utilized waste products in real time. It was revealed that at the volume of copper aliquot amounting to 3 and 8 mL the sorption level for copper in 8 days has amounted to 89 and 70 %, respectively. The calculated K_d values are equal to 1.63 and 0.46, respectively. The data obtained indicate that at a high content of sorbate the action efficiency of absorption centres is diminished. At the same time an insignificant decrease in the value of pH should be noted in connection with increasing the aliquot of $\text{Cu}(\text{NO}_3)_2$, which makes the corrections to the process of cations redistribution in the solid phase. Judging from the results of dynamic experiments (sampling in 2, 4, 8 days), desorption phenomena were not revealed, *i. e.* in the course of time an increasing amount of copper passes into the solid phase.

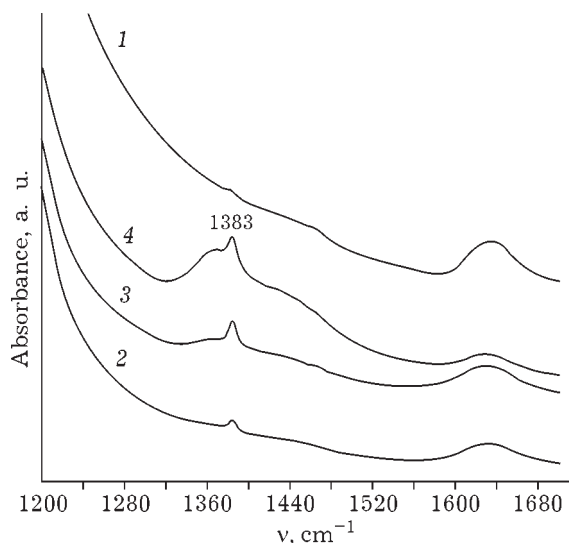


Fig. 2. IR spectra of initial clay sorbent (1) and after its interaction with $\text{Cu}(\text{NO}_3)_2$ solutions with different concentration (2–4) (see Table 3, Exp. 29, 31, 34).

Figure 2 demonstrates IR absorption spectra within wave number range of 1680–1200 cm^{-1} for clay after the interaction with $\text{Cu}(\text{NO}_3)_2$ solution of different concentration. This range has appeared the most informative for studying the sorption phenomena: in particular, as compared to the initial sample (curve 1), the spectra of clay after contacting with $\text{Cu}(\text{NO}_3)_2$ (curves 2–4) demonstrate an additional absorption band ranging within 1360–1383 cm^{-1} , inherent in asymmetric valence vibrations of nitrate ion. To all appearance, this fact indicates the formation of copper nitrate since similar bands are inherent some heavy metal nitrates [17]. Moreover, the intensity of the absorption band at 1640 cm^{-1} , responsible for deformation vibrations of adsorbed water molecules within interlayer space of laminated silicates is observed to decrease [18]. This fact indicates that copper cations are incorporated into the interlayer space to displace a part of water molecules located therein. The reduction of absorption intensity for a wide band at 3400 cm^{-1} (which is not presented) corresponding to valence vibrations of the same water molecules represents an additional confirmation. In more details, the present question will be elucidated in the following paper.

The sorption of heavy metals from real solutions has been investigated in the series of experiments with an extract from BZP clinkers as well as with samples taken from the drain-

age and sedimentation bog. First, we prepared the extract from clinkers with a water/rock ratio equal to 20/L. Within the muddy brownish solution (pH 2.35), the total content of copper amounted to 146 mg/L. It should be noted that in this case, prior to determining the optical density (absorbance), an aliquot should be diluted which, in turn, results in decreasing the reliability of the results. Then the solution (undiluted) was exposed to sedimentation without decantation during a week. In the course of this time a friable sediment of iron hydroxides (red in colour) has been formed at the bottom of the flask, whereas the acidity of the solution appeared to correspond to pH 2.78. The residual content of copper in the solution has amounted to 46 mg/L, *i. e.* as much as 68 % of copper have passed to the solid phase under precipitation.

This fact could be interpreted as a process of naturally occurring autopurification of waste water drains for due to the sorption of metals onto iron hydroxides we have described earlier for different technogenous man-caused objects [13, 19]. The experiments concerning the sorption onto clay in acidic solutions did not give any positive results, whereas the alkalization with NaOH solution results in appearing some feculence, hydroxide sediment and, likely, bentonite colloids, therefore further we prepared

an extract a greater water/rock ratio to determine the content of other metal cations employing AAS method. Before carrying out the measurements, the extract was exposed to sedimentation within several days.

Data concerning the composition of initial solutions (extracts from BZP clinkers) and after the solution interaction with a clay sorbent are presented in Table 4. One can see that at the ratio between water and BZP clinkers equal to 100, too acidic solutions (pH < 3) are formed again, wherein the content of Fe, and Cu amounts up to several tens of milligrams per liter. With the increase in the water/rock ratio up to 500 the acidity of the solution decreases insignificantly. The results of the experiments with a multiple decrease of weighed clinker portions, subjected to interaction with water, allow us to estimate the scale of acid potential for the substances under storing. With adding of 0.1 and 1 g of clay sorbent to 100 mL of the solution with the ratio water/BZP clinker ratio equal to 500/1, the content of copper decreases by 8 and 50 %, respectively, the content of zinc decreases by 6 and 28 %, respectively (see Table 4, Exp. 3, 4). Quite good results obtained concerning the sedimentation of metals (50 % Cu and 28 % Zn) as well as water purification down to MPC level for these

TABLE 4

Composition for initial solutions (extract from BZP clinkers) and for solution after the interaction with a clay sorbent comparing to the data of field testing

| No. | Solution under investigation | pH | Content, mg/L | | | |
|-----|---|---------|---------------|-----------|---------|-----------|
| | | | Cu | Zn | Ca | Fe |
| 1 | Water/clinker = 100/1 | 2.82 | 115 | 37 | 18.8 | 35.7 |
| 2 | The same, 500/1 | 3.22 | 24 | 1.8 | 4.1 | 33.0 |
| 3 | The same with 0.1 g clay | 3.35 | 22 | 1.7 | 9.8 | 30.0 |
| 4 | The same with 1 g clay | 3.86 | 12 | 1.3 | 20.9 | 17.6 |
| 5 | Drainage, 1999 | 3.4–3.8 | 790–300 | 1600–600 | 550–510 | 9–11 |
| 6 | The same, 2005. | 5.3–6.2 | 89–310 | 120–210 | 220–270 | 0.18–0.38 |
| 7 | The same, 2008 | 3.3 | 3000 | 1700 | 280 | 15 |
| 8 | Sedimentation bog, 2005 ($n = 6$)* | 4.7–5.1 | 440–490 | 350–390 | 480–520 | 0.17–0.63 |
| 9 | The same, 2008 ($n = 4$) | 3.4–4.0 | 912–2500 | 1355–1600 | 390–600 | 4.3–8.8 |
| 10 | Bog, sample for experiment | 4.03 | 1260 | 1232 | 366 | bdl. |
| 11 | Precipitate from 100 mL | – | 74 | 48 | 41.6 | 18.3 |
| 12 | The same after interaction with CaCO ₃ (s) | 4.9 | 950 | 1030 | 360 | bdl. |
| 13 | The same after interaction with clay (1 g/100 mL) | 5.0 | 920 | 1010 | 350 | bdl. |

Notes. n is the number of samples; bdl. – below the determination threshold level or no signal.

3rd hazard class elements (1 mg/L) are of purification of no practical interest due to a significant sorbent consumption. At the same time one can see, that water hardness increases due to calcium carryover from clay belonging to alkali-earth varieties. The solution (see Table 4, Exp. 4) contains 17.6 g/L of iron whose intense hydrolysis begins only at $\text{pH} > 3$. The comparative analysis of the composition of experimental extracts under discussion (Exp. 14) and of the solutions from draining ditch around clinkers, taken for different years *in situ* (Exp. 5–7) demonstrates that the content of Cu, Zn and Ca in the drainage is several hundred times higher. This fact means that the process of iron leaching accompanied by sedimentation of its hydroxides with the removal of a part of heavy metals into the sediment takes place, however the amount of Fe(III) is not sufficient (see Table 2). There is a distinct relationship observed between the solution pH and the content of Fe, Cu, Zn, Ca (see Table 4, Exp. 5–7). The oscillations of drainage composition could be caused, first, by hydrodynamical regime in the warm season of year.

The data of experiments with the samples taken from a sedimentation bog indicate that there is no additional purification occurring. Alongside with gypsum, azurite and malachite the mineralogical composition of bottom sediments includes highly-soluble mixed metal (hydro) sulphates, amorphous silica, alumina and even $\text{Na}_2\text{Ca}(\text{SO}_4)_2$. Just these compounds determine the content of metals in the solution. We have undertaken an attempt to perform detoxification of acidic contaminated waters with a high Me(II)/Fe(III) ratio under laboratory conditions *via* the interaction with the clay chosen. When storing under laboratory conditions, the sample of water from the sedimentation bog (see Table 4, Exp. 10) again exhibited the formation of reddish sediment with high iron content, whereas its content in the solution is lower than the determination threshold level for AAS. The presence of calcium in the sediment, to all appearance, could be connected with gypsum. With interacting between these solutions and weighed clay portion (10 g of clay per 1 L of the solution) the content of metals in the solution has not decreased, and the value of pH has increased by 0.5 units (results are not

presented). Basing on this fact, the authors proposed that in order to purify solutions, it is much more efficient to carry out their interaction first of all with limestone (a potential source is presented by host rocks of the Salair ore field) and then with clay. We have performed the interaction between a sample taken from a sedimentation bog and calcite (pure mineralogical variety) (see Table 4, Exp. 12). Though the calcite has been taken in excess, the solution pH remained constant within several days ($\text{pH} \leq 5$). Visually, blue phases precipitated covering grinded calcite grains; the process being inhibited. In several days, the solution was added with clay (see Table 4, Exp. 13), but this

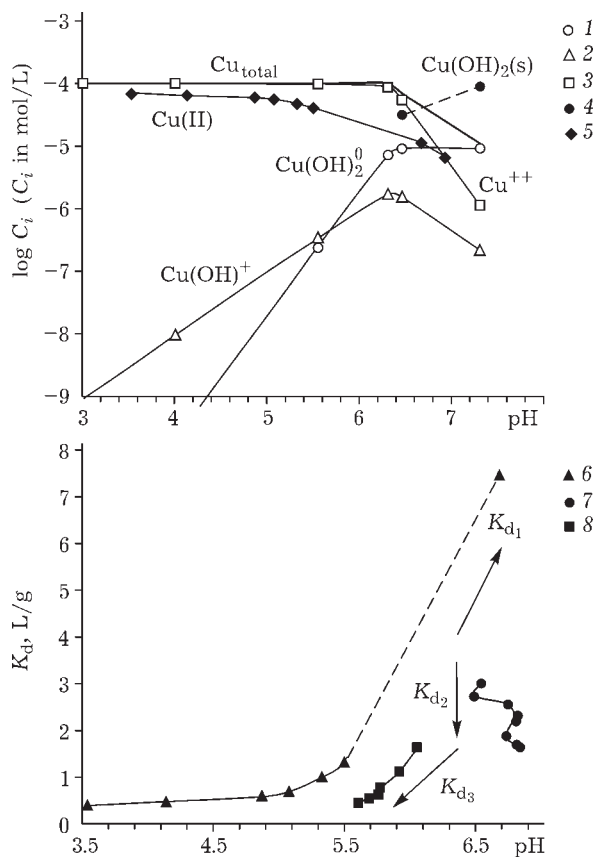


Fig. 3. Copper species ($\text{Cu}_{\text{total}} \sim 10^{-4}$ mol/L) in nitrate solutions (0.01 M NaNO_3) (1–3) and the variation of copper distribution coefficient (K_d) between solid phase and the solution (6) depending on pH: 4 – the amount of solid phase in the system without a sorbent; 5 – the total content of copper in the solution after the interaction with clay during 2 days ($\text{S/L} = 0.1 : 100$); 7, 8 – changing K_d with increasing S/L (7) and increasing the initial concentration of sorbate (8).

resulted in the fact that only 27 % of copper and 18 % of zinc has passed into the solid phase, and this happened mainly due to the formation of secondary minerals at the first stage rather than due to the sorption.

The ability of bentonite clays for absorbing the ions of different type is known for a long time being investigated rather completely. However, in solving a partial problem one consider that it is appropriate to study in an empirical manner the ability of clays depending on the solution pH value, on the sorbate/sorbent ratio, on the content of metals to determine sorbent/sorbate distribution coefficients.

Figure 3, *a* demonstrates the species of copper (II) existing in nitrate solutions, depending on pH value preset *via* adding NaOH alkali solution. The calculations were carried out with the use of HCh software package including UNITHERM database [20]. The formation of simple and stable oxide CuO was inhibited via eliminating it out of thermodynamic database (black and grey earthy precipitates inherent in CuO formation were not observed really in the experiments), whereas, the possibility that hydroxide Cu(OH)₂(s) to occur, greenish in color was however supposed. From the calculated data presented in Figure 3, *a* one can see that copper (Cu_{total} ~ 10⁻⁴ mol/L) exists in solutions in the form of Cu²⁺ species up to pH 6.8, whereas with the increase in pH values Cu(OH)₂ hydroxo complex begins prevail. Decreasing the content of copper at pH 6.5 and 7.3 could be connected with the formation of solid phase such as Cu(OH)₂(s). It should be noted, that the formation of copper hydroxide results in removing the metal from solution, however, at pH 6.5, for example, its equilibrium content is higher than 4.5 mg/L, whereas the MPC for this element amounts to 1 mg/L. Figure 3, *a* also presents the data concerning the content of copper in the experimental solution after the interaction with clay during 2 days (see Table 3, Exp. 10–17). It is seen that within the range of pH values where the formation of solid phase Cu(OH)₂ could begin, there is not enough copper in order to form an intrinsic phase, since a part of copper is deposited onto the surface of the sorbent. Hence, the presence of the sorbent radically changes the mechanism of microelements redistribution between the solution

and the solid phase. This fact implies that the criterion which is appealed for the selection of the sorption region such as “the sorption takes place within the range of element concentration lower than that resulting in the formation of intrinsic phases”, being based on the calculation of saturation indices for solutions before the interaction with a sorbent, appears to be not always true.

The sorption-exchange capacity of the Kamalino clay sample chosen has appeared to be somewhat lower than that inherent in classical bentonite, especially in cases when the weighed portion of clay amounted to more than 0.1 g/100 mL of the solution. It is connected with the fact that the Kamalino clays contain minerals those are not present in classical bentonite clays, as well as they contain a less amount of montmorillonite. In the case of mixed sorbents, it is not reasonable to carry out any model recalculations. Figure 3, *b* demonstrates data concerning the distribution coefficient K_d for different series of experiments. The arrows indicate the direction of increasing the value of K_d depending on pH increase (K_{d_1}), weighed sample portion increase (K_{d_2}) and the concentration of cations sorbed (K_{d_3}). The maximal values of K_d were obtained at pH > 6, at the concentration of copper approximately equal 10⁻⁴ mol/L, and at the ratio S/L = 0.1/100 (see Fig. 3, curve 6). The portion of this line at pH 5.5–6.7 is plotted by dotted line since a gentler slope area is quite probable to be observed in this region, but experimental points are absent therein. As it is known, the source of acidic mine drain is presented by sulphide-containing objects, and not so much the absolute content of sulphides is important, as the ratio between the amounts of acid-producing and acid-absorbing minerals [21]. Water extracts of the BZP clinker substance are characterized by a considerable medium acidity, however iron leaching, its oxidation and precipitation as Fe(III) hydroxides in the course of time represents an “internal” reserve for decreasing the toxic loading of the environment. According to the medium pH value and the content of copper, the extract from BZP clinkers with the ratio S/L = 1/500 (see Table 4, Exp. 2) has appeared to be close to the sample prepared in 0.01M NaNO₃ electrolyte solution (see Table 4, Exp. 5). Despite of a complicated composition of the ex-

tracts of BZP clinkers, the data for both solutions concerning the amount of copper deposited onto 1 g the clay sorbent was also comparable (about 50 %). However, practical use of the results obtained with the development of purification methods for drain wastewaters of the Belovo clinkers appears to be impossible. Real water/rock interactions (about 1 mln t) for some decades have resulted in the formation of solutions wherein the concentration of heavy metals and calcium is hundreds times higher than the data we have obtained *in vitro*. Hence, adding them with a sorbent in reasonable S/L ratio would not give rise to positive results. These highly mineralized solutions use to migrate into a sedimentation bog into and subsoil waters, which is indicated by geophysical data obtained via vertical electric sounding.

Some encouraging results have been obtained after two-stage wastewater treatment, *i. e.* after adding calcite and clay. However they also require for additional examination and substantiation. In particular, already in the course of the experiment we observed the formation of secondary phases, whereas as the *in situ* process proceeding the layer of solid products on the surface of calcite would increase to hinder the access of solution. This fact can result in decreasing the permeability of the layer of secondary minerals and, hence, in decreasing of diffusion rate through this layer till a complete process ceasing. The calculations performed with the use of HCh software package have demonstrated that adding calcite to drainage water and increasing the pH value of the solution up to pH 6 could result in the formation of the phases such as brochantite/langite, *i. e.* aqueous Cu(II) sulphates.

CONCLUSION

1. By the example of Cu(II), an interaction has been studied between heavy metal cations and naturally occurring bentonite clays. A slight sorption dependence on pH value in acidic solutions and abrupt one with alkalization has been quantitatively established, which, to all appearance, could be caused by different contributions of ion exchange and adsorption (the formation of charged surface complexes).

2. A necessity has been demonstrated for optimizing the choice of sorbent amount (the S/L ratio). Notwithstanding the fact that the increase in a clay weighed portion results in an increase in the fraction of copper passed into the solid phase, the occupancy level for sorption centres on the surface of the solid phase could decrease (*i. e.* the relative amount decreases). The increase in the metal concentration influences in a similar manner. These laws are described for the first time at the quantitative level.

3. An average coefficient is recommended for Me(II) distribution between the Kamalino clay and low-concentration neutral electrolyte solution being equal to 2 L/g. Since many authors use logarithmic units, the parameter we have recommended is $\log K_d = 3.3$.

4. The technogenous object chosen belongs to the most adverse ones which exhibit not only high acid producing potential, but also a low content of iron in the solid matter of clinkers. The first factor is indicated by a high acidity of water extracts even with a multiple reduction of the S/L ratio (1 : 500) in the experiments. The second factor determines the *in situ* formation polyionic solutions with high concentration of metals those are at equilibrium with secondary minerals (intrinsic phases).

5. Preliminary data indicate that there is a possibility for complex detoxification of drain water around similar objects via preliminary neutralization and further additional purification employing clay sorbents.

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