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Equilibrium and Kinetics of Interaction of Karaganda Coal Ash with Solutions of Metal Salts

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Abstract—The interaction of solutions of a number of metals with the Karaganda coal ash, resulting in the redistribution of metal ions between the ash and the metal solution, was studied. The character and quantitative characteristics of the process depend on the properties of the metal and its concentration in solution.

Keywords: Ash, metal ions, ion exchange.

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Environmental design is now determined not only by natural processes themselves, but also active human activities. One of the consequences of this activity is the formation of industrial and consumer wastes of various compositions, amounts, and properties. These wastes can be regarded as man-made raw materials and used in various fields of human activity.

One of the most large-tonnage industrial wastes is ash, unburned residue of solid fuels. Ash is widely used in the manufacture of construction materials, in backfilling of spent mine waste, and as a raw material for recovering gallium, scandium, and rare-earth metals [1–5].

In the second half of the twentieth century, the Kazakhstan Joint-Stock Company "Karbid" has discharged into the river Nura a mercury-containing wastewater. This posed a real threat of ecological disaster, which did not take place due to the presence on the river bottom of sediments of Karaganda coal ash, which accumulated the mercury.

The situation described has stimulated a study of sorption and ion-exchange properties of various kinds of coal ashes [6–10]. In these studies, the sorption capacity of ashes for mercury and other metals was determined. Using different metals and varying experimental conditions would made it possible to describe the mechanism of the process, evaluate the influence of various factors on it, and suggest in what cases the ash can be used for metal uptake.

We studied the interaction of the Karaganda coal ash with aqueous the solutions of potassium, cesium, lithium, calcium, barium, copper(II), and lanthanum salts. Using only one kind of the ash and only one relative concentration of the solid and the liquid phases, we focused on the effect of two major factors: the properties of metal ions and their concentrations.

We studied fly ash formed by burning Karaganda coal concentrate at the Alma-Ata thermal power plant-1 in 1995 (hereinafter, KZ-1).

Chemical composition of the ash samples was determined at the Research and Design Institute of Construction Materials (NIISTROMPROEKT, Alma-Ata, Kazakhstan). The data are collected in Table 1.

Previously, the researches with the Department of Physical Chemistry of the Research Institute at the St. Petersburg State University have determined, using a set of standard sieves with apertures from 0.84 to 0.1 mm, the granulometric composition of the ashes. It was found that the bulk of the KZ-1 ash is the form of particles from 0.84 to 0.1 mm in size [8].

Then, the phase and mineralogical compositions of the ashes of various fractions were determined at the Department of Inorganic Chemistry at the St. Petersburg State University (DRON-3 diffractometer, CuK_α radiation). The data obtained are given in Table 2.

As can be seen from the data presented, the ash contains quartz, aluminosilicates, and, in lesser

Table 1. Results of chemical analysis of KZ-1 ash

Ash	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	CO_2	SO_3
KZ-1	0.60	1.56	27.4	55.5	1.56	4.9	1.2	5.87	1.21	0.12

Table 2. Results of X-ray phase analysis of KZ-1 ash. Brief description of fractions

Ash	Fraction no.	Particle size, mm	Fraction content, %	Main components (by XPA data))
KZ-1	1	$0.84 < d$	3	SiO_2 (α-quartz), $Al_2SiO_5^-$, SiO_2 (α-cristobalite), $(Ca_{0.04}Mg_{0.45}Fe_{0.48})$ SiO_3 (pigeonite), amorphous phase.
	2	$0.1 < d < 0.84$	89	SiO_2 (α-quartz), $Al_2SiO_5^-$, amorphous phase, Fe_2O_3 (hematite), Fe_3O_4.
	3	$d < 0.1$	8	SiO_2 (α-quartz), $Al_2SiO_5^-$, amorphous phase.

amounts, iron oxides and silicates, as major components.

For KZ-1, the basicity modulus characterizing a quantitative ratio of the acidic to basic oxides is 0.17 [6, 8].

The dissolution of the coal and lignite ashes, even in aqua regia, is incomplete. At the same time, in contact with distilled water the solutions containing Na^+, K^+, Ca^{2+}, Mg^{2+}, SiO_3^{2-} and other ions were formed [6 , 8].

Ash (0.5000±0.0005-g samples) was brought into contact with 50 ml of 0.1, 0.05, and 0.01 N solutions of metal salts and the kinetics of interaction of the ash with the solution was determined. pH of the suspendsion was measured after 1.3, 1.2, 4.7, 14, and 28 days. Each experiment was performed with six parallel samples. After 7, 14, and 28 days of contact, two ash samples from each series were filtered, dried at room temperature, and weighed.

The results of kinetic studies showed that the equilibrium interaction is established after seven days. Therefore, the ash samples were brought into a 1-week contact with 0.005, 0.01, 0.05, 0.1, 0.15, and 0.2 N solutions of the salts. Exception was only solutions of lithium chloride, concentration of which was increased by an order of magnitude. After settling, pH of the suspension was measured, the ash sample was filtered

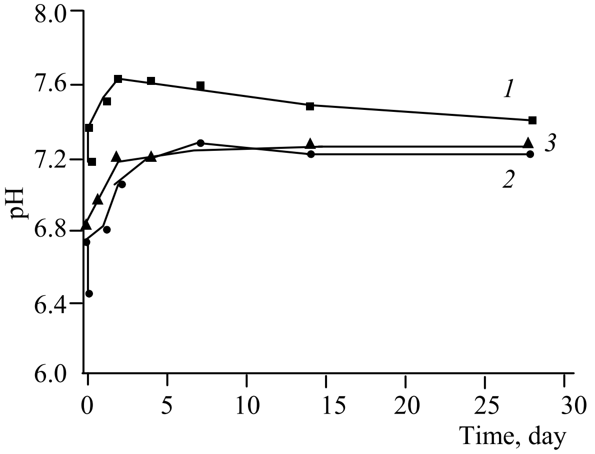

Fig. 1. Variation of pH of the ash suspensions in contact with KCl solutions of varied concentration. Concentration, N: (*1*) 0.01, (*2*) 0.05, and (*3*) 0.1.

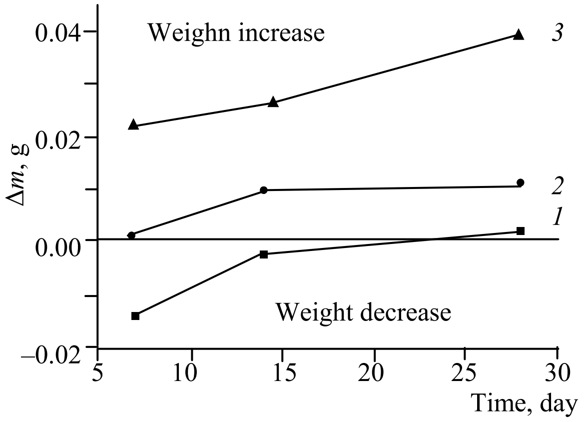

Fig. 2. Change in veight by the ash samples in contact with KCl solutions of varied concentration. Concentration, N: (*1*) 0.01, (*2*) 0.05, and (*3*) 0.1.

through a filter of the known weight, the filter with the ash sample was weighed, and the change in weight by the ash sample was determined. Then, the pH of the filtrate was determined and the equilibrium concentration of the corresponding metal ion was found.

The concentration of potassium, cesium, lithium, calcium, and barium ions was determined by the atomic absorption spectroscopy (AAS-1N spectrophotometer) and that of the lanthanum and copper(II) ions, by the complexometric titration.

EXPERIMENTAL

Alkali metal salts. The study of the kinetics of interaction of ash with the potassium chloride solutions showed that the dependences of suspension pH on the contact time are similar for all the concentrations studied: pH first increases, then decreases, and finally remains constant (Fig. 1). Mass gained by the samples in 0.05 and 0.1 N solutions increases with the concentration of the salt; in a dilute ash solution (0.01 N) the ash mass decreases (Fig. 2). The run of the Δm vs. the time dependencies is similar for all concentrations. The presence of ash in a 0.01 g-equiv. L^{-1} solution increases the equilibrium concentration of the K^+ ions above the initial value, i.e., the ions in the ash pass to the solution. At the same time, increasing the contact time decreases ΔC. For a 0.1 M solution, ΔC is negative, i.e., potassium ions migrate from the solution into the ash, but its modulus value decreases with time (Fig. 3).

It may be suggested that in contact of KZ-1 with the KCl solutions two opposite processes occur. The first process leads to an increase in the concentration of potassium ions in the solution, whereas the second, to its decrease. The first may be dissolution of the potassium-containing ash components (Table 1) or absorption of water molecules from the solution and the second, the ion exchange or non-exchange absorption of KCl. These processes proceed in all the solutions, with the intensity and character of their development determined by the initial concentration of the salt.

The interaction of the ash with KCl, CsCl, and LiCl solutions of varied concentration during a week yielded the same result for all three salt: pH of the suspensions and filtrates vary only slightly with the initial concentration of the salt, pH of the filtrates are always lesser than of the corresponding suspensions (Fig. 4).

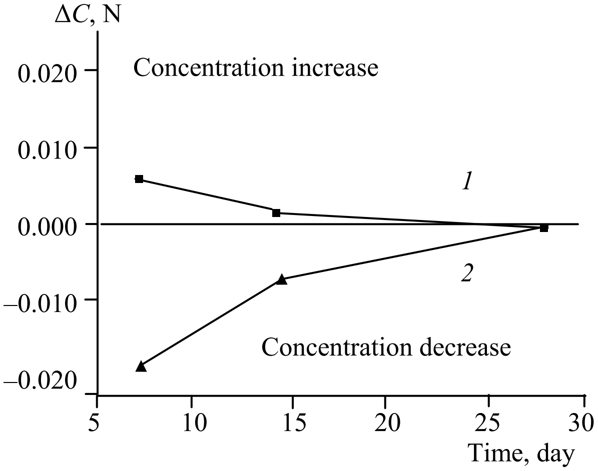

Fig. 3. Change in the concentration of K^+ ions in contact of the ash with KCl solutions of varied concentration. Concentration, N: (*1*) 0.01 and (*2*) 0.10.

After contact with the ash, the sample mass certainly increases with increasing initial concentration of the salt; for KCl and CsCl Δm goes from negative to positive values and for lithium chloride, whose concentration was increased, it is always positive (Fig. 5). The data obtained are in good agreement with the results of the kinetic studies (Fig. 2). Noteworthy, in the order Li–K–Cs the $\Delta m = f(C)$ dependence shifts to the left, i.e., at equal initial concentrations of the salt the sample weight after contact is the larger, the heavier is the cation.

The dependences of equilibrium concentration of the potassium, cesium, and lithium ions on the initial concentration of corresponding metals are entirely different and unclear (Fig. 6). In the case of potassium, the concentration increase observed in several experiments may be explained by dissolution of its compounds present in the ash composition, whereas in the case of cesium and lithium, present in trace amounts, from 0.6 to 17.1 g per ton, this explanation is wrong [1, 2].

Calcium and barium salts. The interaction of ash with the solutions of calcium and barium chloride leads to the change in the kinetic dependences: initial jump of the suspension pH is much faster, variations upon prolonged sedimentation are significantly smaller, and the variation itself is directed upwards (Fig. 7). The sample mass is proportional to the concentration of the solution, time of contact, and the atomic weight of the metal salt (Fig. 8). The concentrations of the solutions always varied only slightly (within the determination error).

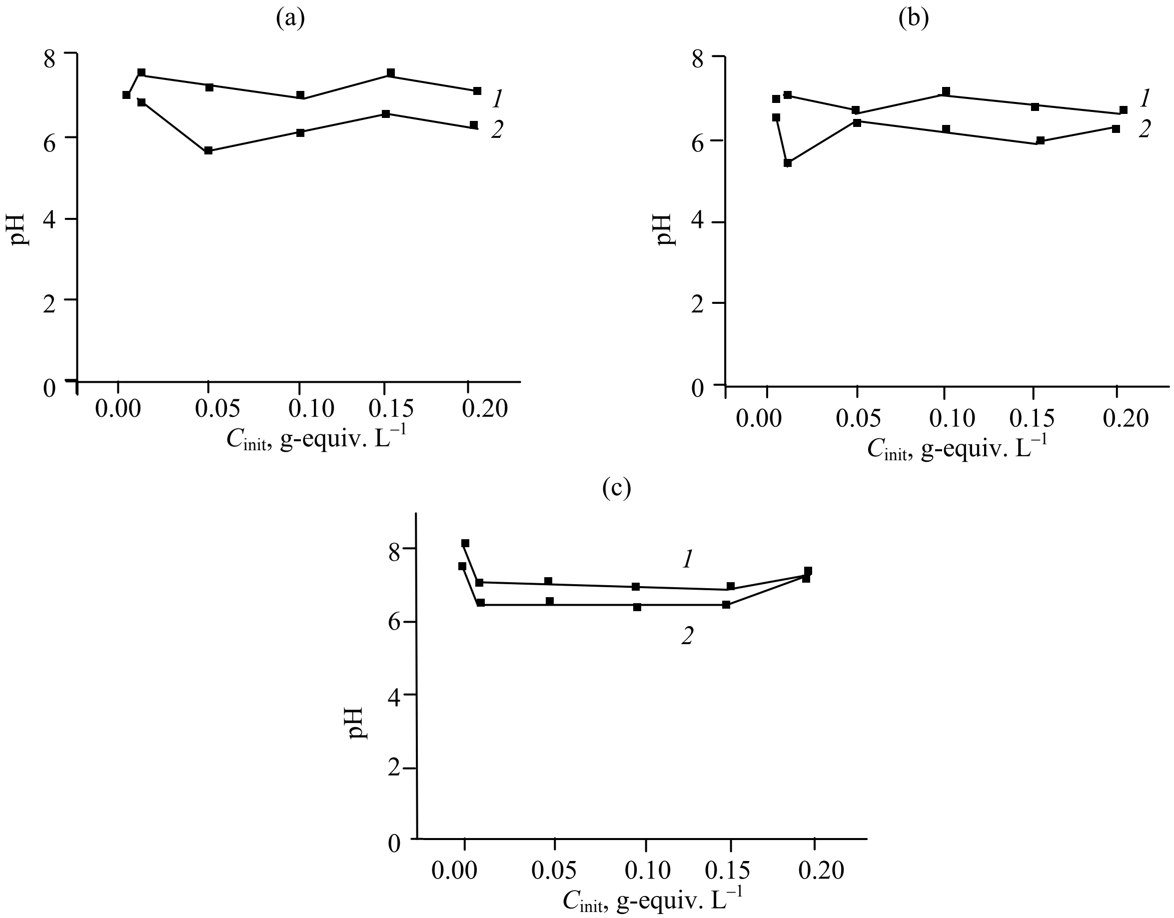

Fig. 4. pH of (*1*) suspensions and (*2*) filtrates vs. the initial concentration of the solution. Solution: (a) KCl, (b) CsCl, and (c) LiCl.

After a week of contact, suspension and filtrate pH was virtually independent of initial concentration, with pH of the suspension significantly higher (Fig. 9). The mass loss recorded in dilute $CaCl_2$ solutions in several experiments is at variance with the data on the kinetic study. However, in most cases the mass was increased and this increase was proportional to the concentration of the solution and the atomic weight of the cation salt (Fig. 10). The concentration of the Ca^{2+} ions in the solution slightly increased in comparison with the initial value at low concentrations and decreased at high concentrations (Fig. 11). As for K^+ ions, the above result can be accounted for by the occurrence of the opposite processes: absorption of calcium ions by the ash and dissolution of its calcium-containing components. The concentration of barium decreased or remained constant.

Lanthanum and copper salts. As in most cases described above, pH increases or, on the contrary, gradually decreases after the ash is kept in contact with the solutions of lanthanum and copper chlorides, respectively (Fig. 12). In both cases, the relative stabilization of pH values occurs earlier than in the case of the salts of alkali and alkaline-earth metals. The mass of the samples increases (Fig. 13). The concentration of the lanthanum ions in 0.01 and 0.05 N solutions remains constant (upwards fluctuations are within the determination error). After the ash is kept in a 0.1 N solution, the equilibrium concentration becomes lesser than initial value, with ΔS proportional to the interaction time (Fig. 14).

After seven days of interaction, pH of the suspensions and filtrates is lower than in the previous cases. Probably, this is due to the properties of the solutions (Fig. 15). The sample mass increases proportionally to the concentration of the solution, with difference in Δm for the ashes kept in contact with the lanthanum and copper chloride solutions

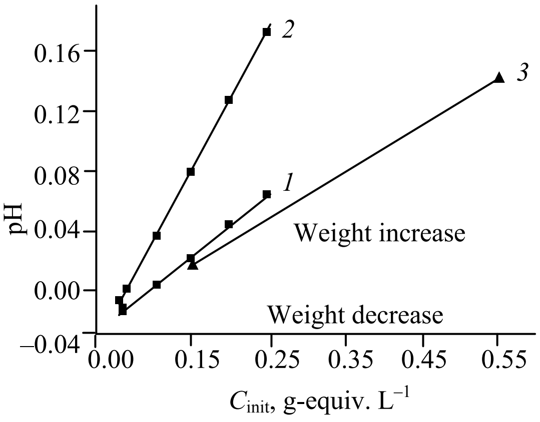

Fig. 5. Change in the sample mass vs. the concentration of the solution. Solution: (*1*) KCl, (*2*) CsCl, and (*3*) LiCl.

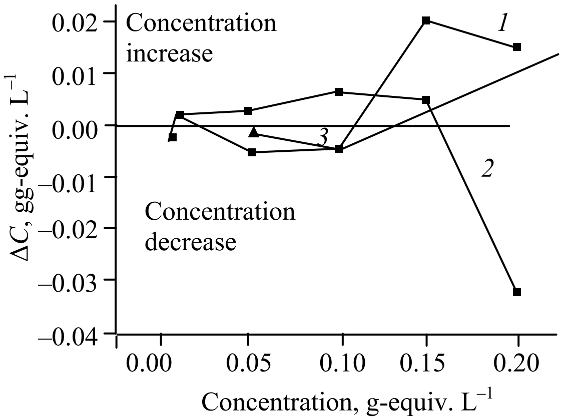

Fig. 6. Dependence of equilibrium concentration of the K^+ ions on the initial concentration of the solution. Solution: (*1*) KCl, (*2*) CsCl, and (*3*) LiCl.

lesser than reasonable values (Fig. 16). The concentration of the lanthanum ions in the filtrates is constant (within the determination error), whereas that of copper sharply decreases, with this decrease proportional to initial concentration (Fig. 17).

RESULTS AND DISCUSSION

The results obtained confirm the previous theses about the complexity and ambiguity of acid-base and sorption properties of ash in solutions [9]. The interaction proceeds rather slowly and at least 7 days are required for establishing the relative equilibrium. In this case, several processes may occur, such as dissolution, precipitation of sparingly soluble compounds, ion exchange, and non-exchange absorption.

The components of the ash dissolve to various extents and with different rates, with alkaline components apparently most soluble. By the formal parameter, the basicity modulus, the Karaganda coal ash refers to the so-called “acidic” type. At the same time, in contact with water and electrolyte solutions, marked alkalization of the solution [6], accompanied by passage of Na^+, K^+, Ca^{2+}, and Mg^{2+} ions, occurs.

pH 7.45 also characterizes the ash as a solid base [9]. The dissolution of the ashes in the solutions intensifies with decreasing pH. In the above experiments it had to be the most intense in the case of $LaCl_3$ and $CuCl_2$ solutions. Probably, for this reason, the mass of the samples in these solutions increases to lesser extent than would be expected (Fig. 16).

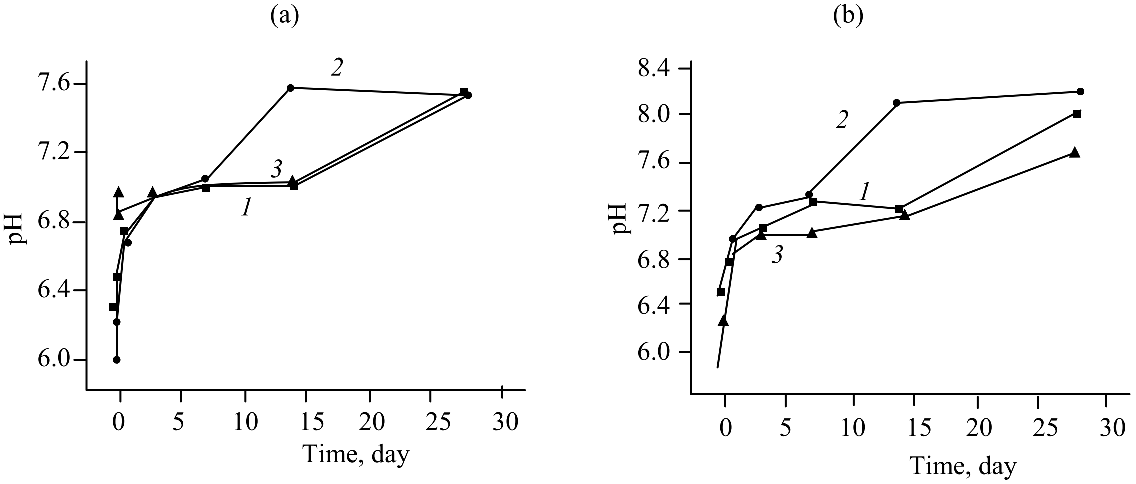

Fig. 7. Change in pH of the ash suspensions in contact with (a) $CaCl_2$ and (b) $BaCl_2$ solutions of varied concentration. Concentration, N: (*1*) 0.01, (*2*) 0.05, and (*3*) 0.10.

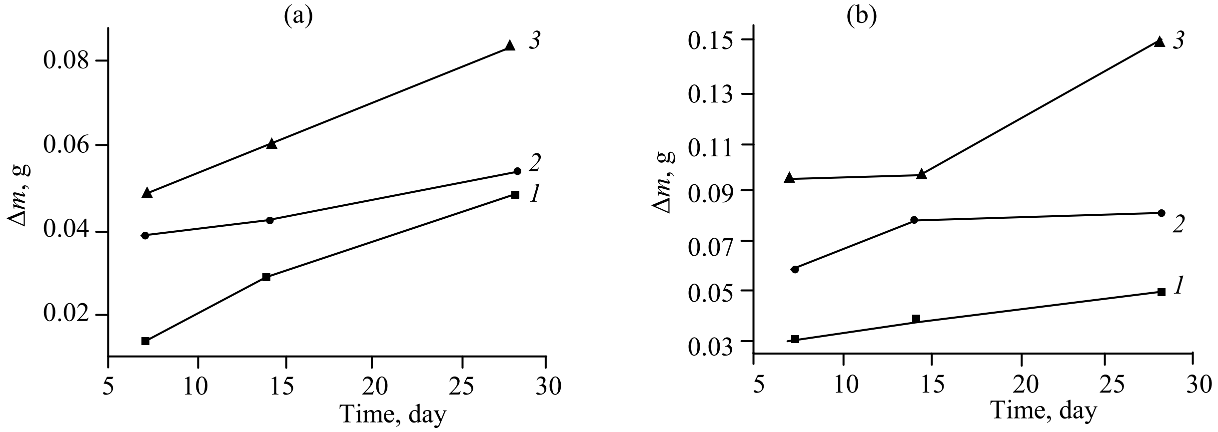

Fig. 8. Change in mass by the ash samples in contact with (a) $CaCl_2$ and (b) $BaCl_2$ solutions of varied concentration. Concentration, N: (*1*) 0.01, (*2*) 0.05, and (*3*) 0.10.

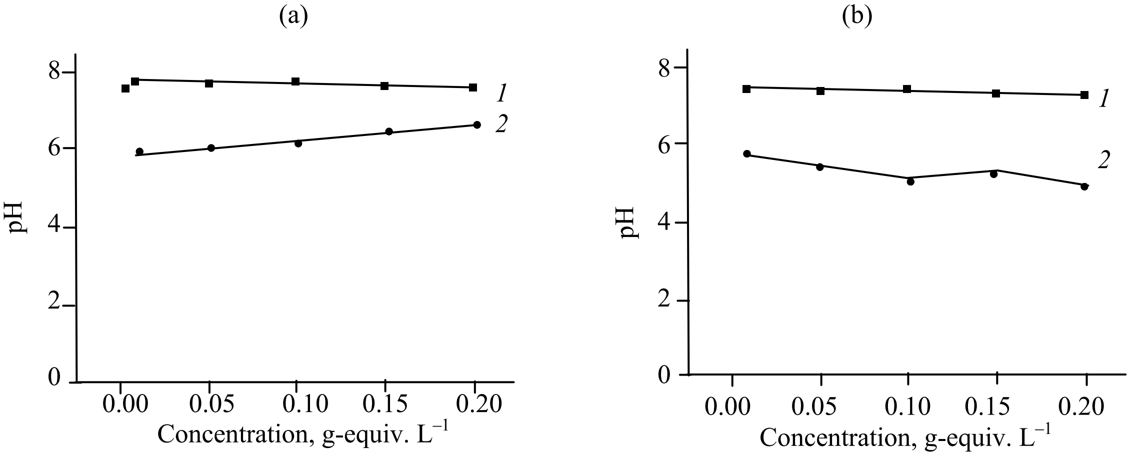

Fig. 9. Change in pH of (*1*) suspensions and (*2*) filtrates on the initial concentration of the solution. Solution: (a) $CaCl_2$ and (b) $BaCl_2$.

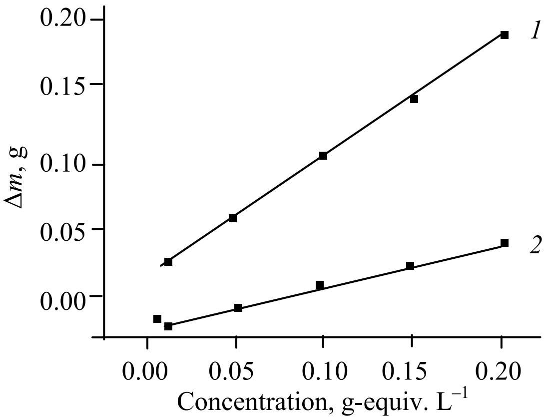

Fig. 10. Mass change vs. the concentration. Solution: (*1*) $CaCl_2$ and (*2*) $BaCl_2$.

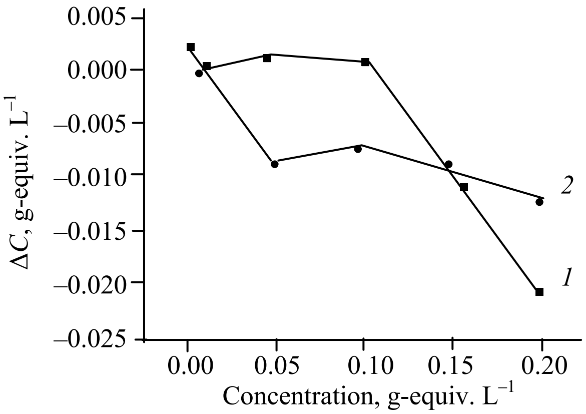

Fig. 11. Change in the concentration of the metal ions for (*1*) $CaCl_2$ and (*2*) $BaCl_2$ solutions.

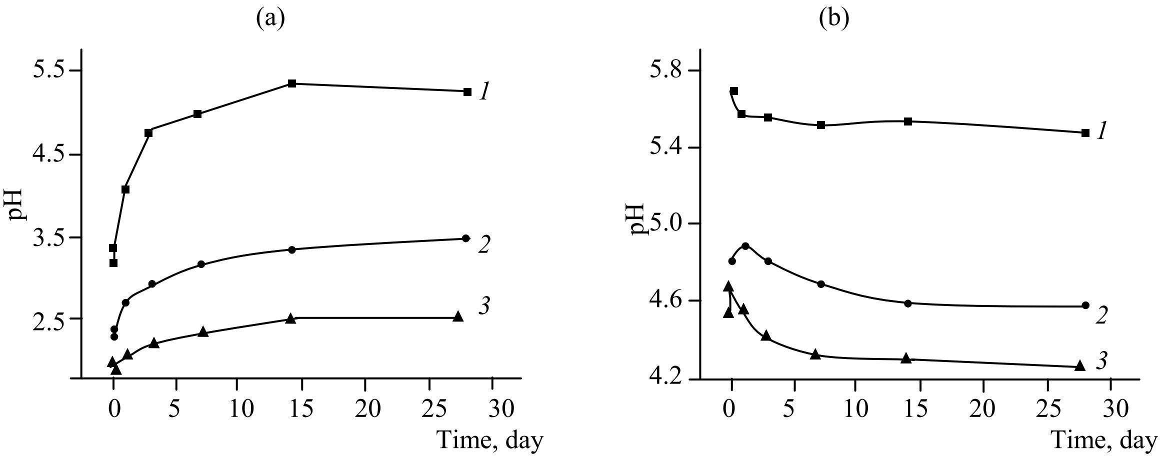

Fig. 12. Change in pH of the ash suspensions in contact with (a) $LaCl_3$ and (b) $CuCl_2$ solutions of varied concentration. Concentration, N: (*1*) 0.01, (*2*) 0.05, and (*3*) 0.10.

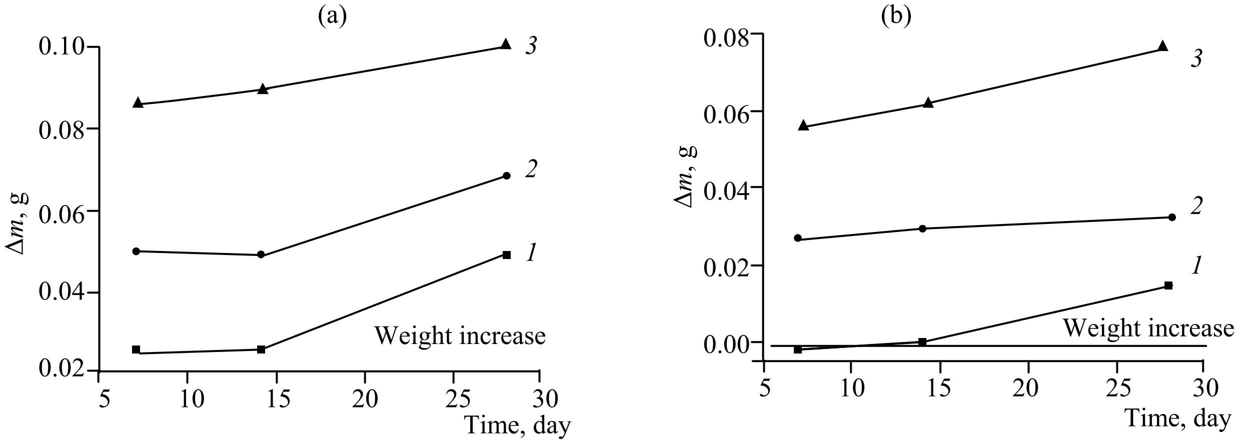

Fig. 13. Change in mass by the ash samples in contact with (a) $LaCl_3$ and (b) $CuCl_2$ solutions of varied concentration. Concentration, N: (*1*) 0.01, (*2*) 0.05, and (*3*) 0.10.

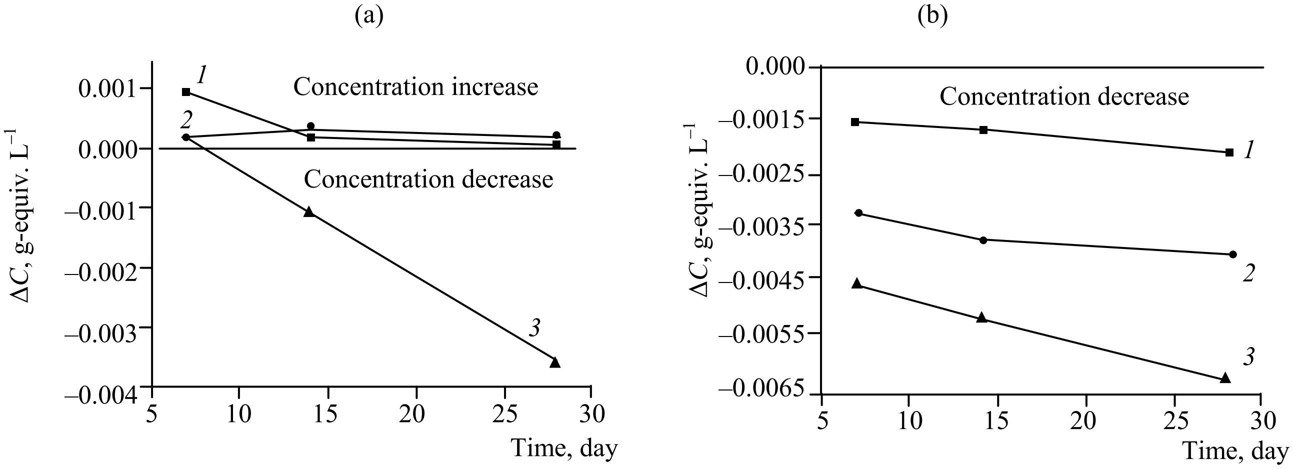

Fig. 14. Change in the concentration of the metal ions in contact of the ash with (a) $LaCl_3$ and (b) $CuCl_2$ solutions of varied concentration. Concentration, N: (*1*) 0.01, (*2*) 0.05, and (*3*) 0.10.

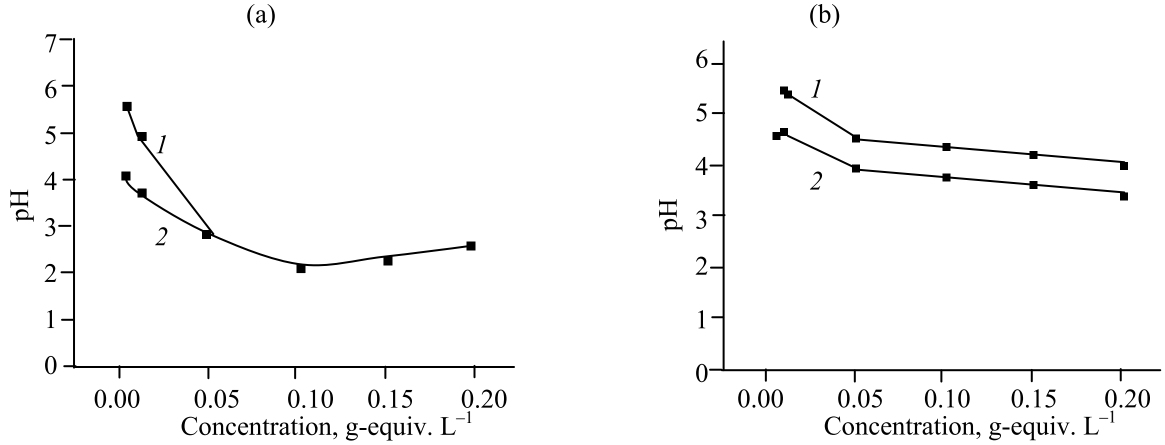

Fig. 15. pH of (*1*) suspensions and (*2*) filtrates vs. the initial concentration of (a) $LaCl_3$ and (b) $CuCl_2$ solutions.

The precipitation of sparingly soluble compounds was certainly observed in absorption of mercury(II) ions, which are present on the ash surface in the form of HgO [7]. At this stage of the study, it may be suggested that copper(II) compounds precipitate. Though pH of the solution was lower than in the beginning of the copper hydroxide precipitation (Fig. 15), we cannot exclude that the surface of particles of the solid phase had a more alkaline pH than the liquid phase.

In favor of the above suggestion is unusual run of the solution pH vs. the interaction time curve for copper chloride solution (Fig. 12). At the same time, for alkali, alkaline-earth metals, and lanthanum the formation of sparingly soluble compounds is improbable (pH, at which the hydroxide begins to form, is ~8 [11]).

Absorption of these metal ions can be accounted for by the ion exchange mechanism. In a number of cases, this suggestion is confirmed by a decrease in the M^{z+} concentration, gain in mass by the ash samples, and run of the pH curve. The above phenomena are observed for calcium, barium, lanthanum, and, with assumption made for the formation of hydrolyzed compounds, copper salts. On the contrary, the interaction with the solutions of alkali metal salts mostly caused an unusual increase in the M^{z+} concentration. However, the above findings should be considered in view of the complex composition of equilibrium solutions.

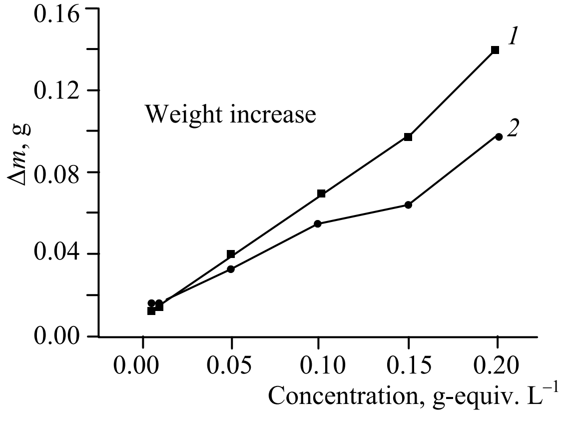

Fig. 16. Change in the sample mass vs. the concentration of (*1*) $LaCl_3$ and (*2*) $CuCl_2$ solutions.

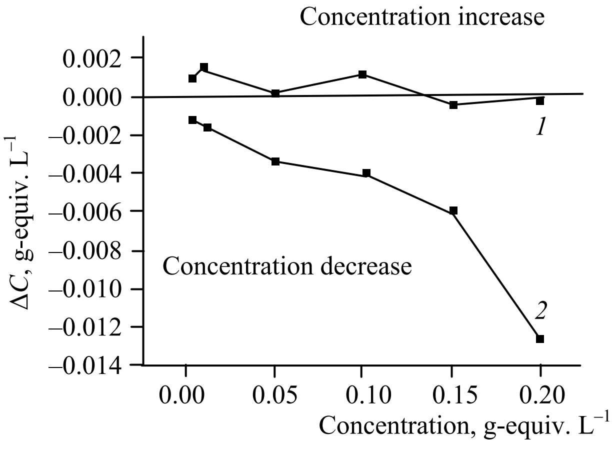

Fig. 17. Change in the concentration of the metal ions for (*1*) $LaCl_3$ and (*2*) $CuCl_2$ solutions.

Finally, we can not exclude the possibility of non-exchange absorption of the solution components, which can be different for the solvent and the solutes. However, this suggestion does not explain the nature of the pH, Δm, and ΔS dependences on the concentration and properties of the ions.

In all probability, upon contact of the ashes (including KZ-1 grade) with electrolyte solutions, several parallel processes occur. These are dissolution of the solid phase, ion exchange, and the precipitation of sparingly soluble compounds. Two or more processes in the same or opposite direction can also occur. For example, in contact of the ash with the solutions of easily hydrolysable metals the ion exchange and the precipitation processes may occur simultaneously, leading to the same process, i.e., extraction of metal ions from the solution. On the contrary, the dissolution of the ash components and absorption (both exchange and non-exchange) of the ions comprising the solid phase (i.e., K^+) yields opposite result.

CONCLUSIONS

All studies (both current and previous) make us possible to describe the course of the interactions between the ash and the electrolyte solutions, made reasonable suggestions about the character of the processes occurring therewith, and forecast with a certain degree of confidence the behavior of thermal station ash under certain conditions. For example, the interaction of Karaganda coal ash with aqueous solutions of salts of div- and trivalent metals, including heavy metals (to which belong mercury, copper, lead, cadmium, etc.), will cause more or less effective transition of these metals into solid phase and dissolution of a part of the ash. However, in this case, the released ions are less dangerous than the heavy metal ions. Thus, the given ash can be used as inexpensive sorbent of toxicants.

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