

ION EXCHANGE METHODS IN LEAD AND ZINC TECHNOLOGY

Utilization of liquid extraction for the further processing of the alkaline solution produced alleviates the problem of valuable components extraction. It is known, that phenol bearing reagents as the extractants of metals from alkaline solutions can be successfully used [1, 2]. The selective properties of these reagents are defined by the chelate mechanism of their interaction with the elements under the special conditions of the process.

We have established that for the extraction of ions of non-ferrous metals amino- and hydroxyl-containing oligomers are rather promising. For extraction reworking of obtained lead-zinc-containing alkaline and ammoniac solutions we selected the obtained by way of polycondensation of paratertbutylphenol with formaldehyde in presence of ammoniac catalyzer. For extractant preparation phenol-amino-formaldehyde oligomer (the molecular mass 460 g/mol) was dissolved in purified kerosene with addition of octanol for stabilization of extractant solution.

Studying the process of lead and zinc extraction from ammonium and alkali solutions it was established that increase of the extraction duration in the interval from 0 till 20 minutes metal distribution coefficient grows up to 3,3-4,5 and remains practically unchanged during next 10 minutes.

In determining the influence extractant concentration on the extraction factors it was found out that metal extraction and distribution grow in the interval of the oligomer concentrations 0,1 - 0,5 mol/dm³ (fig.1).

Relation of the water and organic phases volumes has significant role not only in the process of mass transfer but also for obtaining extractants with high metal content in them. While carrying out the experiments it was found out that the optimal is the phase ratio $V_R:V_W = 1:6$.

Dependence of lead and zinc extraction on the mole relation of soda and ammonium hydroxides has the maximum in the field $CNaOH:CNH_4OH = (3:2)-(2:3)$ (fig.2), and the character of the dependence is preserved under the summarized concentration of soda and ammonium hydroxides 4 and 6 mol/dm³. The presence of the maximal values is explained by the fact that with ammonium concentration growth in the initial solution alongside with hydroxoforms extracted ammoniac metal complexes are formed.

Maximal extraction of lead and zinc is observed in ratio of $CNaOH:CNH_4OH = (3:2)-(2:3)$ and the summarized concentration of soda and ammonium hydroxides < 6 mol/dm³. High values of the coefficients of metal distribution during their extraction by selected agent all over investigated pH interval and in more concentrated solutions of soda hydroxide allow to make a conclusion that all hydroxoforms of metals beginning with $M(OH)^-$ are extracted. The extraction is showed to be limited by diffusion factors.

Separation of metals is carried out at the stage of re-extraction on two levels: firstly, zinc is extracted by 0,5 M solution of saline acid (99,8 %), then lead is re-extracted by the solution of acetic acid of the same concentration (88,5 %).

It was found out that extraction of hydrox forms and ammonia metal complexes is implemented according to the chelate mechanism. On the base of physical and chemical methods of analysis the composition of extracted lead and zinc complexes was defined $([M(OH)_n(NH_3)_m(H_2O)_{2-n-m}R_2]^{n-})$.

Phenolformaldehyde resins are widely used in different branches of industry [3]. However, they are practically inapplicable as sorbents. With the purpose of imparting to them of sorption or oxidation-reduction properties phenol is often substituted for di- or three-oxybenzenes [4]. An introduction in their composition of functional groups, such as amino-, sulfo-, carboxy- and others improves sorption properties of ion-exchangers and imparts to them selectivity.

Previously, we have established that for the extraction of ions of lead and zinc amino-and hydroxyl-containing oligomers are rather promising. For the creation of sorbents of a such-like type we have studied condensation of dioxybenzenes (resorcinol, pyrocatechol and hydroquinone) with hexamethylene-diamine (GMDA) and formaldehydes (CH₂O). In the absence of catalysts, the yield of the final product is low (20-25 %), and the properties of the obtained materials do not meet the requirements, established for ionites: low characteristics of mechanical strength, chemical stability and ion-exchange capacity. In this connection there have been tested catalysts of the acidic and basic types, as well as hydrogen peroxide.

The studies have shown that ammonium hydroxide participates in the reaction of polycondensation not only as a catalyst, but also for the creation of additional active functional groups $=NH$ and $-NH_2$. To the latter supposition there testify an increase in the intensity of absorption bands at 1380 and 1650 cm^{-1} in IR-spectra of the obtained materials, corresponding to above-mentioned functional groups.

The presence of hydrogen peroxide significantly improves sorption properties of resins due to the participation of peroxidic groups in the complex formation. Incidentally, in this case the process duration reduces considerably even at insignificant amounts of hydrogen peroxide.

Nitric and phosphoric acids as reagents that catalyze the process and regulate pH of the medium also contribute additional functional groups in the sorbent structure. Necessity of their introduction in the reaction mixture has been confirmed by the improvement of sorption properties and chemical stability of the final products. The studies have shown that $pH \sim 3$ is an optimal value, at lower pH an active dissolving of the formed compounds takes place, proceeding faster in the presence of phosphoric acid.

An order of reagents addition and pH of the media plays a significant role upon the synthesis of aminophenolic sorbents. In the case CH_2O is added before GMDA the yield of the final product constitutes 50-53 % in relation to the summary mass of the indicated substances, in case of the reversed order – is the yield of polymers increases up to 64-72 %. The yield of resins is growing with an increase of CH_2O quantity; however, ion-exchange properties of the obtained polymer products deteriorate. This may be connected with an increase in the linking degree of macromolecules, and therefore, unavailability of the functional groups.

A study of temperature effect upon the process has shown that at $60\text{ }^\circ\text{C}$ and lower the obtained resins are chemically and mechanically unstable, and above $100\text{ }^\circ\text{C}$ their yield decreases. Obviously, at low temperatures no sufficient cross-linking of the polymer links occurs, above $100\text{ }^\circ\text{C}$ a partial decomposition of the obtained compounds takes place with a simultaneous growth of cross-linking due to intermolecular reactions and isolation of the water, included to macromolecular structure.

The latter supposition has been confirmed by the results of thermogravimetric studies: the temperature of the beginning of decomposition lies in the area of $105-120\text{ }^\circ\text{C}$ and should be related to water removing. At the temperatures of $270-300\text{ }^\circ\text{C}$ the samples are destructed by 50 %, their complete decomposition is observed at $350-400\text{ }^\circ\text{C}$.

According to the data of elemental analysis the quantitative content is as follows: 57,2-59,9 % C; 7,6-8,4 % H; 11,9-12,1 % N; 19,6-23,3 % O depending on terms of synthesis.

On the basis of the data of IR-spectroscopy and elemental analysis one may conclude, that both three- and tetra-substituted aromatic nuclear, interconnected by methylene bridges and amino groups as well as OH-groups are present in the polymer structure.

A sorption ability of aminophenolic polymers in relation to ions of some non-ferrous metals has been estimated in dependence on the structure of ionites. Sorption conditions (duration of the contact of a sorbent with a metal-containing solution, concentration and pH of the initial solutions, the nature of metal) [5].

It has been established that upon the extraction of ions of lead and zinc resorcinol-based sorbents are most preferable. Pyrocatechol-based resins possess a greater affinity to zinc ions. It was clearly shown that zinc and lead are extracted by the sorbents in the narrow pH range of the medium, which testifies to a high selectivity of the obtained ionites.

Maximum extraction of metal ions (80-97 %) synthesized ionites falls on the pH region of 8-12, (fig. 3).

On the basis of literature and experimental data we offered extraction method of alkaline and ammoniac-alkaline lead-zinc-containing solutions with the use of chelat-forming agent. It is known, that phenol bearing reagents as the extragents of metals from alkaline solutions can be successfully used. Extraction occurs by chelate mechanism.

We found out that for successful metal separation re-extraction should be carried out in two stages.

By the condensation of two-atom dioxybenzenes (pyrocatechol, resorcinol and hydroquinone) with formaldehyde and hexamethylene-diamine in the presence of initiating additions of the acidic and basic type, as well as hydrogen peroxide, there have been synthesized phenol bearing ionites, which practically extract ions of lead and zinc.

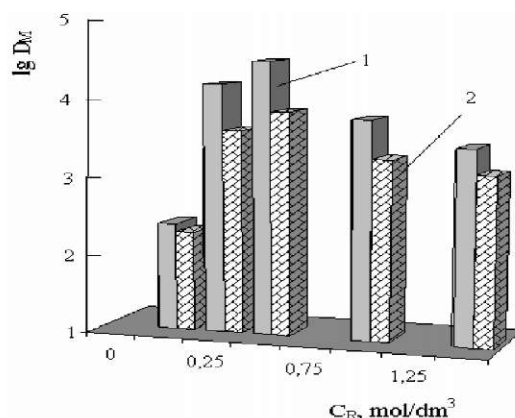


Fig.1 – Influence of the extractant concentration on the value of zinc (1) and lead (2) distribution coefficients

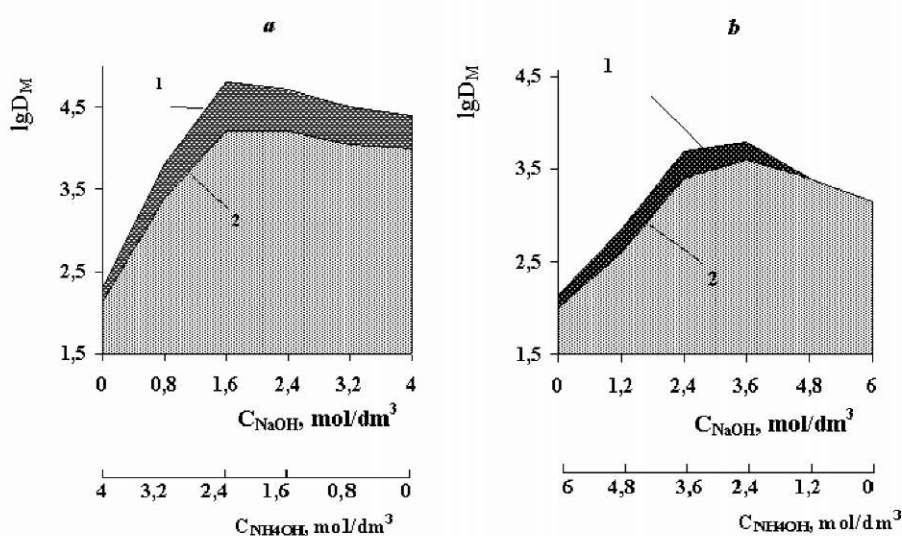


Fig. 2 – Influence of the mole relation of soda and ammonium hydroxides on the value of zinc (1) and lead (2) distribution coefficients
a – the summarized concentration of soda and ammonium hydroxides 4 mol/dm³;
b – the summarized concentration of soda and ammonium hydroxides 6 mol/dm³

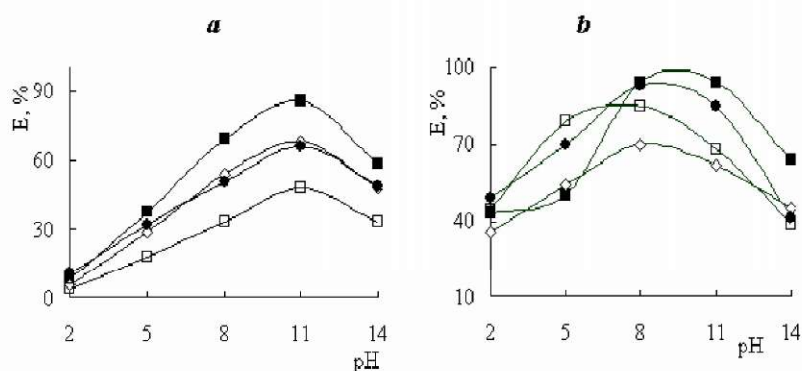


Fig. 3 - The effect of pH of the initial solutions upon sorption of lead (a) and zinc (b) by phenol bearing ionites on the basis of: • - resorcinol (HNO₃ catalyst); • - hydroquinone (HNO₃ catalyst); • - pyrocatechol (H₃PO₄ catalyst); • - pyrocatechol (HNO₃ catalyst)

LITERATURE

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Резюме

Статьяда күрделі құрамды сулы ерітінділерден хелаттүзуші фенол құрамды реагенттермен қорғасын мен мышты экстракциялау және сорбциялау нәтижелері келтірілген. Сілтілі реагентті ерітінділерден ион астыру әдістерін қолданумен ауыр түсті металдарды селективті бөліп алудың нақты мүмкіндігі көрсетілген.

В статье представлены результаты экстракции и сорбции свинца и цинка хелатообразующими олодсодержащими реагентами из водных растворов сложного состава. Показана реальная возможность активного извлечения тяжелых цветных металлов из растворов щелочных реагентов с использованием обменных методов.

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