Obtaining Flotation Reagents Based on Local Raw Materials for Flotation of Silvinite

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ABSTRACT

Currently, the world pays great attention to the enrichment of minerals. The main method of beneficiation of many ores is the flotation method - aimed at increasing the concentration of useful components in minerals mined from the bowels. Surfactants are considered widely used and indispensable substances for various industrial processes, including the flotation production of sylvin from mineral ores. It is worth recognizing the limited range of collective reagents, and their technological characteristics do not always meet the growing requirements of the industry.

Keywords:

Currently, the world pays great attention to the enrichment of minerals. The main method of beneficiation of many ores is the flotation method - aimed at increasing the concentration of useful components in minerals mined from the bowels. Surfactants are considered widely used and indispensable substances for various industrial processes, including the flotation production of sylvin from mineral ores. It is worth recognizing the limited range of collective reagents, and their technological characteristics do not always meet the growing requirements of the industry. Scientific research in the field of creating new collectors is of significant scientific and practical interest for modern theoretical and applied colloid chemistry.

All over the world, in order to obtain effective flotation reagents and create improved flotation technologies, it is necessary to substantiate a number of scientific solutions in this area, in particular: the study of the mechanism of synthesis of surfactants based on local raw materials, the creation of apolar collectors based on local raw materials and industrial waste, the establishment of colloidal -chemical characteristics of ionic and nonionic surfactants and apolar collectors is important from a theoretical and practical point of view.

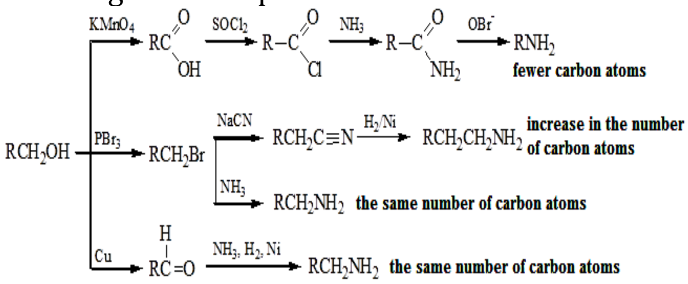
The results of enrichment by means of flotation of mineral copper-zinc [1, 2], copper-lead-zinc [3], copper-molybdenum [4-6], copper-iron [7-9], gold-bearing [10-12], containing precious metals were given[13, 14].

One of the flourishing areas of flotation methods can be seen in wastewater treatment plants of various industries, where fats, oils and suspended solids are removed from wastewater using this method. These units are called dissolved air flotation units [15]. In particular, flotation in this case is used to remove oil from wastewater refineries [16], petrochemical and chemical plants [17, 18], natural gas processing plants and similar industrial facilities [19, 20].

Aliphatic amines are used in many areas of the national economy, as: pharmaceuticals, cosmetology, organic synthesis, construction equipment, in the production of pesticides, corrosion inhibitors, etc.

Classical methods for the preparation of amines are described in many literatures [21–23].

A specific feature of the synthesis of amines by the reduction of nitriles is an increase in the length of the carbon chain, since the resulting primary amine has one more carbon atom than the alkyl halide from which the nitrile was obtained. The Hoffmann cleavage of amides is characterized by the fact that as a result of this reaction, the length of the carbon chain decreases by one atom. This reaction is of interest as an example of an important class of reactions involving a rearrangement step.



Reactions in the gas phase are reversible and proceed with a small thermal effect. In the liquid phase, due to the formation of amine salts, the thermal effect is 84-105 kJ/mol and the reaction is practically irreversible.

$NH_3 + RCl \rightarrow RNH_2{\cdot}HCl$

Aliphatic chlorine derivatives react with ammonia and amines in the absence of catalysts, the rate is described by the second order equation

$R=k[NH_3][RCl]$

Mechanism - nucleophilic substitution:

$$RCl + :NH_3 \rightleftharpoons [\overset{\delta-}{Cl}\cdots R\cdots \overset{\delta+}{NH_3}] \rightleftharpoons R\overset{+}{N}H_3 + \overset{-}{Cl}$$

The reactivity of ammonia and amines varies in the series:

$Alk_2NH \approx AlkNH_2 > NH_3 > ArNH_2$

and chlorine derivatives in the series:

$ArCH_2Cl > AlkCl > ArCl$

N-alkylation is characterized by a series-parallel type of process, since the resulting product is able to interact with the chlorine derivative with the formation of successively primary, secondary and tertiary amines, the latter, upon further processing with chlorine derivatives, gives a quaternary ammonium salt:

$$NH_3 \xrightarrow[-HCl]{+RCl} RNH_2 \xrightarrow[-HCl]{+RCl} R_2NH_2 \xrightarrow[-HCl]{+RCl} R_3N \xrightarrow{+RCl} R_4N^+Cl^-$$

To carry out the process with high selectivity for the primary amine, an approximately 30-fold excess of ammonia with respect to chloroalkane is required; when alkylating aniline, an excess of 10-30% is sufficient.

UE "Dekhkanabad Potash Plant" accounts for the bulk of the demand for amines. Amines are used in the production of potassium chloride in the flotation process. The annual demand for amines is more than 250 tons, each ton of production is purchased from abroad for 3000 US dollars. The demand for amines is growing even more. Amines are not produced in the Republic, despite the fact that there are raw materials necessary for the synthesis of amines - high fatty acids, fusel oil, food industry waste, urea and sodium chloride.

The aim of the study is the synthesis and study of new highly efficient amine collectors for the flotation enrichment of sylvinite ores.

The object of the study is industrial waste from oil and fat production - soap stock and the gas chemical complex of JV Uz-Kor Gas Chemical LLC - liquid paraffin, sylvinite ores of the Tyubegatan deposit. In this work, sylvinite ore from the Tyubegatan deposit, taken from different regions of this deposit, was also used as an object [24].

The subject of the research is methods for the synthesis of aliphatic amines based on soap stock, methods for obtaining apolar collectors, determination of the composition and colloid-chemical properties of flotation reagent systems in order to improve the technologies for enriching sylvinium ores.

Research methods. The dissertation used the main physico-chemical (X-ray phase, electron microscopic, IR, UV spectrophotometric, chromatographic, thermogravimetric) and colloid-chemical (conductometric, stalagmometric) methods for analyzing the objects under study. The calculations of the obtained experimental data were carried out using special computer programs MS Word, Matlab and MS Excel. Extensive research has been carried out to replace traditional blowing agents such as T-80, T-66, etc., used in the flotation of various mineral ores, with foaming agents based on waste and locally produced raw materials.

Methodology. In a 1 liter round-bottom flask equipped with a thermometer that reaches almost to the bottom of the flask, 60 g of urea and 130 g of a mixture of fatty acids (obtained from soap stock) are placed. A condenser is attached to the flask and the mixture is heated with an electric mantle heater. When the temperature reaches 140°C, urea goes into solution and a rather rapid evolution of gas occurs, which lasts for several minutes. Within 4 hours. The temperature is maintained at 170-180°C and then allowed to cool.

As soon as the temperature drops to 110-120°C, 400 ml of 5% sodium carbonate solution are carefully added through the refrigerator and the mixture is shaken vigorously. The mixture is cooled in an ice bath and the reaction product is filtered off on a Buchner funnel. The dried preparation is slightly colored.

The crude preparation is boiled for several minutes with 200 ml of 95% ethanol and a small amount of decolorizing charcoal. The mixture is filtered without suction and 800 ml of water are added to the filtrate. The resulting thick mass is cooled in a bath of ice and salt and the drug is filtered on a Buechner funnel. The resulting reaction product is almost colorless; it is air dried. The yield is 44-48 g (up to 84% theoretical).

By evaporating the filtrate under reduced pressure and re-precipitating the residue from a mixture of 20 ml of 95% ethanol and 80 ml of water, an additional 3-4 g (5-6%) of the substance is obtained.

The synthesis of amines is carried out in three stages. In the first step, the acid amide is obtained by exposing a mixture of fatty acids to urea. In the second step, the acid amide forms a primary amine based on the Hoffmann rearrangement reaction. At the third stage, the primary amine reacts with alcohol to form a secondary amine.

A solution obtained by dissolving 25.0±0.5 g of fatty acids in methyl alcohol in an amount of 90 g was mixed with a solution of 4.6 g of sodium in 145 ml of methyl alcohol. After good stirring, 16 g (0.1mol) of bromine are added. The resulting solution is heated on a water bath for 10 minutes. Then acetic acid is added until a weakly acidic medium is formed, and methyl alcohol is distilled off. The remaining part is washed with water until the complete disappearance of sodium bromide and dissolved in naphtha. To eliminate fatty acid amide residues, the naphtha solution is filtered. The naphtha is removed and the residue is recrystallized in residual ethanol twice. The net yield of fatty acid methyl ester (melting point 61-63 °C) is 24-27 g (84-94%).

20 ml of water 70 g of the product and 30 g of calcium oxide are mixed well. The mixture is distilled off and the distillate is extracted with naphtha. The solution of naphtha is first dried in the presence of potassium chloride, and then with metallic sodium, then the solvent is removed and the resulting substance is distilled off twice in the presence of metallic sodium. The yield of pure amine (liquefaction temperature 36±1°, boiling point 238-301°C) is quantitative.

The results obtained and their discussion. The flotation activity of amines is indirectly characterized by the amount of adsorption of their molecules on mineral crystals and the turbidity of its aqueous solution, which depends on the solubility, as well as the critical micelle concentration (CMC). Prepared 3 model solutions with different concentrations, in which the mass ratios of NaCl and KCl are: 1:1 (P1); 1:0.5 (P2) and 1:0.25 (P3), while the total salt content in the solution did not exceed 50%. To prepare solutions, salts dried to constant weight at a temperature of 120°C were quantitatively transferred into volumetric flasks with a capacity of 1000 cm3, dissolved in distilled water, bringing the solution to the mark.

Laboratory experiments were carried out on an FML 240 flotation machine. SA consumption for all flotation processes, regardless of the content of the main component, was 10 mg per kg of salt mixture. The research results are given in table1.

Table 1
Results of flotation of model solutions at 22±1°C using the synthesized amine

Indicator	Model solutions		
	P1	P2	P3
Exit, %: Concentrate tail	41,2 58,8	30,5 69,5	19,6 80,4
Mass fraction of KCl, %: Concentrate tail	97,2 17,0	91,3 7,8	90,8 4,3
Extraction of KCl, %: Concentrate tail	80 20	83,6 16,4	89 11

As the data in Table 1 shows, a decrease in the concentration of potassium chloride in the composition of the mixture leads to an increase in the yield of its extraction from this mixture. Probably, the lower recovery factor P1 is due to the lack of amine quantities for the adsorption of its molecule on the entire surface of the floated material. Under the influence of amine P3 is more fully floated, which shows the sufficiency of the amount of the collector. Therefore, for the flotation of sylvinite ores with a mass content of the main component of more than 20%, the required amount of this amine is more than 10 g per ton of ore (this amount is calculated using the CMC value). It is well known that the floatability of potassium chloride from sylvinite ore will be affected by the temperature of the solution as a key factor. An increase in temperature will affect the solubility of potassium chloride more than that of sodium chloride. Therefore, an increase in temperature favors an increase in the yield of the flotation processes. In Figure 1 illustrated curves characterizing the effect of temperature on the extraction of potassium chloride from the mixture. As the curve shows, as a result of an increase in the temperature of the solution from 20 to 30 °C, an increase in the extraction of KCl from P3 by 20% is observed. The decrease in this indicator with a further increase in temperature is associated with the structural features of the surfactant and an increase in the proportion of desorption of its particles from the interface.

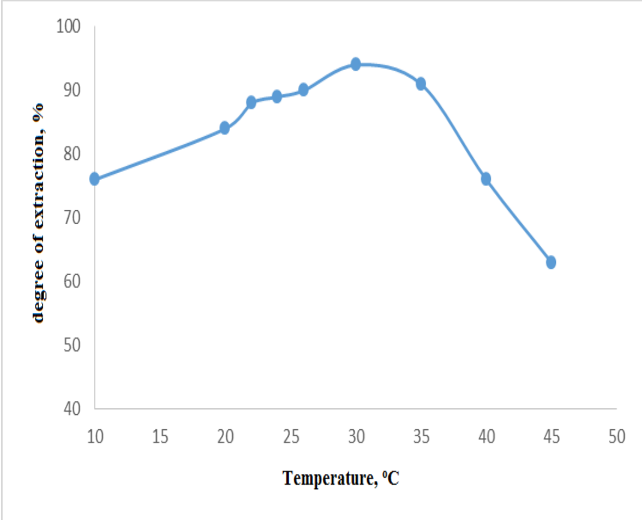


Fig.1. Effect of temperature on the degree of extraction of KCl from P3.

As the research results showed, the optimal temperature for extracting KCl from model solutions using the developed amine varies in the temperature range of 22<35 °C.

A long industrial practice has shown a decrease in the extraction of the main component in the concentrate due to the negative effect of insoluble impurities on the floatability of sylvite. This negative impact is greatly increased with an increase in the total content of silicate minerals in insoluble sediment (i.s). The presence of traces of clay minerals leads to an overconsumption of collector reagents, in our case, amine, because minerals like clay structures are excellent surfactant sorbents. This situation leads to a deterioration in the quality of the concentrate and an increase in the negative effect of water-insoluble impurities on the entire process of Cl flotation. Therefore, this section also presents the results of studies to establish the influence of i.s. and its composition at different temperatures on the degree of extraction of KCl.

The sorption activity of all impurity components increases with increasing temperature, thereby worsening the floatability of sylvite. So i.s., consisting only of clay and only of non-clay minerals in the amount of 1% in the composition of the P3 mixture causes a decrease in the degree of extraction of KS1 by 64 and 17%, respectively. These data were obtained at a mother liquor temperature of 20±1°C. An increase in temperature to 35 °C leads to an extreme decrease in the extraction of the required component. In figure2 the results of studies of the influence of the amount and composition of n.d. on the floatability of KS1 from model solutions. Increasing the temperature from 20 to 40 °C will have a strong effect in the case of content in n.d. clay minerals and a lesser degree of non-clay impurities. In this and other cases, the presence of an i.d. will negatively affect the degree of enrichment of mineral ores.

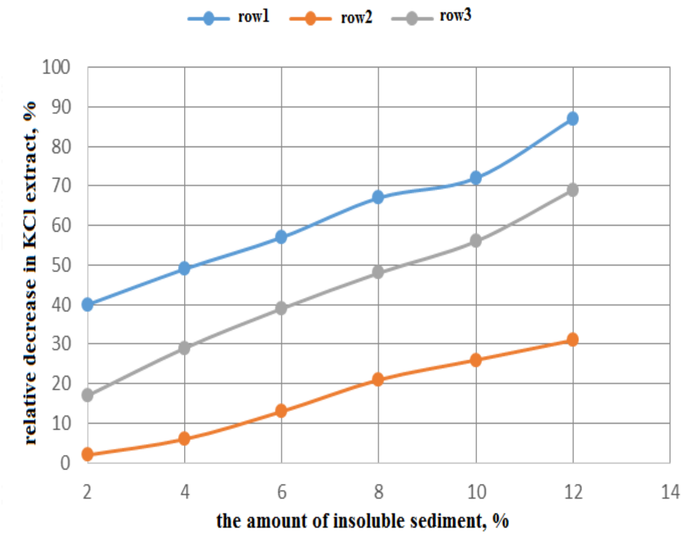


Fig.2. Influence of quantities i.s. in the composition of the model solution P3 on a relative decrease in the degree of extraction of KCl (20±1 °C):
1) clay impurities; 2) non-clay impurities;
3) clay impurities : non-clay impurities in 1:1.

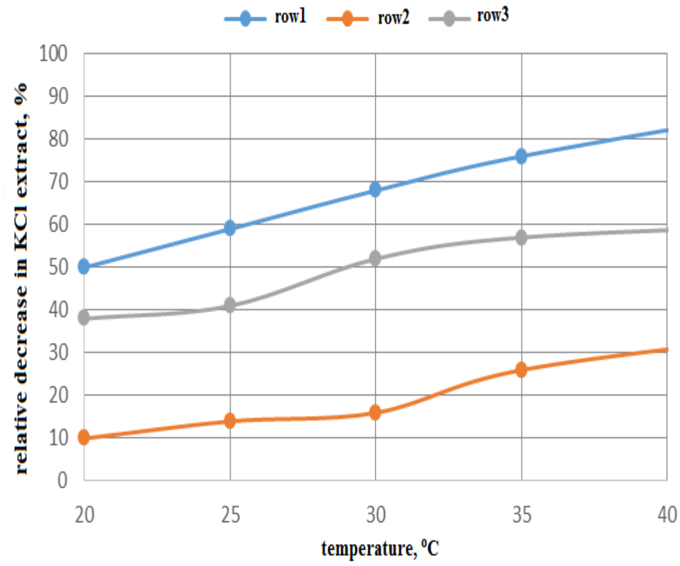


Figure 3. Influence of solution temperature and composition of i. in an amount of 5% by weight of salts for a relative decrease in the degree of extraction of KCl:
1) clay impurities; 2) non-clay impurities;
3) clay impurities : non-clay impurities in 1:1.

The possibilities of neutralizing or mitigating the negative effects of i.s. with a change in the amounts of the introduced collector were explored. As a result, it was found that the amount of insoluble impurities contributes to the determination of the costs of collecting reagents. Extraction dependency i.s. in the froth product of flotation from the consumption of the flocculant is shown in Fig.4. It has been established that an increase in the collector flow rate increases the yield of sylvite into the concentrate, however, this change in the collector flow rate, in contrast to the nature of the effect on the flotation of the main component, leads to an increase in the sludge flotation i.s. up to a certain limit, after which an increase in the flow rate of the collector does not cause sharp changes in the recovery of i.s. into concentrate.

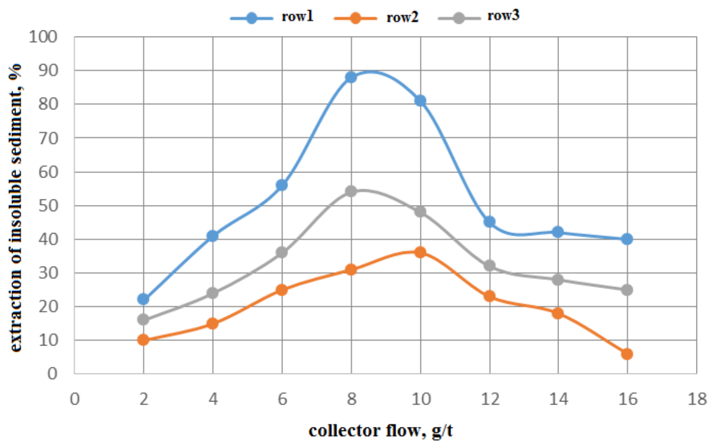


Fig.4. Influence of the collector consumption on the recovery of i.s. into concentrate (content i.s. 5% by weight of the mixture, solution temperature 22±1 °C: 1) clay impurities; 2) non-clay impurities; 3) clay impurities: non-clay impurities in 1:1.

As the curves of the diagram show, the dependence of the extraction of the insoluble residue into the concentrate on the consumption of the collector has an extreme character. Especially, which is confirmed under the conditions of the presence of clay minerals in the composition of i.s. Increasing the cost of the collector to 16 g/t does not give the desired enrichment results, because. The possible degree of extraction of clay impurities into the concentrate is at least 40%. The extremum at the degree of extraction coincides with 8 g/t collector consumption. The range of the extremum of the degree of extraction of non-clay substances corresponds to the relatively high consumption of the collector (10 g/t). However, the degree of extraction of non-clay impurities in the concentrate is about 38% of the total content of i.s. An increase in temperature causes a noticeable shift in the extremum of the extraction of clay substances to higher collector flow rates, and for non-clay substances, on the contrary, in the opposite direction of values in the horizontal axis.

Thus, the results show that the increase in i.s. in the flotation feed negatively affects the yield and purity of the concentrate. By adjusting the amount of collector introduced, it is impossible to prevent the negative effects of impurities. Therefore, to ensure the maximum extraction of sylvite from the ore, it is necessary to completely remove insoluble impurities before the flotation processes of the main component, either mechanically or chemically.

Conclusion

The conducted studies established the variability of the mineral composition of the sylvinite ore of the Tyubegetan deposit and their water-insoluble impurities. The content of basic sylvin varies within 13.0-38%, and water-insoluble impurities from 6 to 19%. The implementation of a set of studies on the development and application of new types of surfactants - amines obtained on the basis of soap stock fatty acids, for the flotation of sylvinite ores based on individual substances and secondary raw materials, made it possible to scientifically substantiate the possibility of rational and purposeful use of these raw materials to create effective import-substituting flotation reagents for enrichment sylvin.

The optimal conditions for carrying out the process of isolating fatty acids from the soap stock and synthesizing a mixture of aliphatic amines on their basis were determined: first, fatty acids are converted into amides at 140°C for 4 hours under the influence of ammonia. The resulting amide was converted to nitriles in the presence of an Al2O3 catalyst at a temperature of 270–295°C. To obtain amine mixtures with a purity of 98%, it is necessary to carry out the hydrogenation of nitriles in the presence of a nickel catalyst at a temperature of 170–180°C, at hydrogen pressure and total pressure of 40 and 56 atm, and process duration of 2–2.5 hours.

The effect of the main physicochemical parameters and structural features of the hydrocarbon radical of flotation reagents on their flotation activity and selectivity in sylvite flotation was studied. It has been established that the floatability of sylvite increases with the combined use of amine and liquid paraffin, which is also associated with a high content of the C20-24 fraction in the amine and cyclic compounds in the liquid paraffin.

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