Technology of producing local liquid parafines for separation of potassium chloride from natural sylvinite

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Abstract. The purpose of this study was to determine the possibility of obtaining liquid paraffins on the basis of by-products available in the local chemical industry, and to compare the product with industrial apolar wound agents in the process of silvinite flotation. The experiments were performed with a secondary liquid product - hexane solution and pyrocondensate. A technological sequence of reagent use to increase the efficiency of the flotation process is proposed. In order to increase the efficiency of the flotation process, the sequence of transfer of reagents to the process and the time of exposure were studied. Experiments have shown that adding 2.5 to 7.5% tetradecane and pentadecane to liquid paraffins derived from hexane used can reduce KCl residue by 2.2%. The technology producing of local liquid paraffins from hexane, a secondary product of Uz-Kor Gas Chemical JV LLC, has been developed.

1 Introduction

The term “flotation” is common in the scientific and technical literature, it is used to purify water from organic substances and solid suspensions, separate mixtures, to accelerate sedimentation in chemical, oil refining, food and other industries.Flotation is one of the main technological processes of enrichment of many minerals due to the separation of fine particles [1-4]. Flocculation processes have long been used successfully in ore beneficiation processes and have probably accumulated the greatest theoretical and practical experience in this area. Selective flocculation is the most promising method of concentration and enrichment of minerals, especially the separation of valuable substances from natural raw materials [5].

The method of flotation enrichment of minerals is one of the most common processes subject to the laws of colloid chemistry. Today, the method is becoming increasingly important because its application helps to enrich non-magnetic and finely dispersed ore with a complex material composition that is not enriched by other classical methods [6].

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Many compounds are used as flotation reagents, but commercial flotation reagents are typically relatively high molecular weight aliphatic amines and liquid paraffins. The main components of flotation reagents used in industry are paraffins containing S11-S22 [7, 8].

The authors [9] of the literature suggest the use of a mixture of oil-like amines and hydrocarbons - kerosene - as a collector. Typically, kerosene contains up to 30% of aromatic hydrocarbons, which negatively affects the selectivity of flotation enrichment of sylvinite ores. In addition, naphthalene hydrocarbons are carcinogenic substances, so it is not important to involve them in the process.

In Silvin flotation, primary aliphatic amines are used as collectors, cationic active reagents, in particular, interacting with the mineral surface of the KCl component and forming a hydrophobic shell on it. This allows the mineral to bind with air bubbles and float into the foam of the concentrate. However, the primary ore contains clay compounds with a developed surface in addition to KCl and NaCl.They are capable of strong dispersion in ore crushing and active adsorption of amine molecules. In terms of the effect of potassium salts on the decomposition process, the fine clay fraction of 0.001 mm is of the greatest interest. The specific surface area of the clay sludge available for cation-active collector-amine is 350-370 m^2 / t. The saline sludge particles are in the form of finely dispersed silvite and halite with a size of 60 μm, which are formed during the extraction, transportation, preparation of ore for flotation and re-grinding directly in the flotation chambers [10].

A method of obtaining liquid paraffin has been proposed: processing the oil fraction in the presence of a solvent with crystalline urea, then separating the formed urea complex from the product paraffinized with paraffin, stepwise washing and disintegration of the complex with liquid separation. As a solvent is used β,β′-dichlorodiethyl ether mixed with methyl ethyl or methyl isobutyl ketone in a 1:1 mass ratio, urea treatment is carried out with the addition of a solvent weighing 180 - 260 kg. washing of the material and complex is carried out with the solvent specified in the first stage and methyl ethyl - or methyl isobutyl ketone in the second stage [11].

During the silvite flotation of paraffin-based petroleum-based emulsions, the possibility of further comparison of their flotation activity with similar indicators of industrial apolar reagents was studied.

The use of paraffin, gas oil, etc. as a collecting reagent is being studied by the authors of the study [12-14]. Depending on the raw materials and processing conditions, they have different compositions and are in the form of a complex mixture of organic substances. The diversity of their composition makes it difficult to study the effects of kerosene and gas oil during flotation. However, it is difficult to determine which components of paraffin and gaseous oil are the most flotation active, and it is difficult to determine what to look for when selecting reagents for these conditions.

It is proposed to use gas oil and crude oil driving products as apolar solvents. A foamless flotation apparatus was used to study the accumulating properties of oil reagents. In the tests, the reagents were first dispersed with the feed in a foamless flotation apparatus. This made it possible to exclude emulsion separation during the flotation process itself. The collection properties of primary products of different composition and the technology of obtaining their fractions were also studied [14-20].

Sources [21 - 23] cited some aproton reagents, such as clarified, tractor and oxidized paraffin, household stove fuel, apolar aromatic reagents AAP-1 and AAP-2, activated flotation reagent AF-2, and thermogazoyl.

Refined paraffin is widely used in the early stages of flotation and to this day in a small number of factories. The predominance of saturated compounds in kerosene has a more selective effect on coal flotation than flavored kerosene, but the flotation rate is slightly lower. The advantages of kerosene clarification are the absence of a specific odor, ease of use, smooth flow of the process, low cost. Kerosene does not have the ability to foam, and

at high consumption it exhibits non-foaming properties. For coal flotation, clarified kerosene is used only in combination with a heteropolar reagent. Its consumption is from 1 to 3 kg / t.

In terms of chemical composition, tractor kerosene is a mixture of saturated, unsaturated and aromatic hydrocarbons. The presence of large amounts (17%) of unsaturated and aromatic hydrocarbons in the molecule compared to refined kerosene, which retains 16-24 carbon atoms, allows increasing the flotation capacity of tractor kerosene. In the flotation of coal in the middle stage of metamorphism, its consumption is 1 - 1.5 kg / t, in the flotation of low metamorphic - 1.5 - 2.5 kg / t.

Oxidized paraffin is a light yellow oily liquid. By oxidation of paraffin containing saturated hydrocarbons at a temperature of 140 - 150 °C in the presence of a catalyst - manganese naphthenate is blown into the air for 2 - 6 hours. Oxidized paraffin contains organic substances containing carboxylic and naphthenic acids, oxoacids, hydroxyl, ether and other groups.As a result, it has some foaming properties and is a more active reagent than clarified paraffin. In practice, it has not found its place due to the need to organize specialized production to obtain it.

Analysis of the literature shows that despite the large number of sources of apolar solvents for flotation enrichment of natural sylvinite ore, in the natural conditions of the republic in summer (July-September) high temperatures (35-45 °C) affect the flotation process and as a enrichment residue. It is important to prevent the transfer of valuable reagents to the waste and, for this purpose, to determine the content of reagents that allow to ensure high technological efficiency of potassium chloride enrichment of sylvinite ore at low and especially high temperatures.

Separation of potassium chloride from silvinite ore by flotation enrichment, production of potassium fertilizers on the basis of OAZ technology "VNII Galurgii" of the Russian Federation is carried out at the expense of crushed raw materials of Tyubegatan deposits up to 1 mm.

Therefore, during our research, we found it necessary to study the optimal technological parameters of flotation enrichment in the presence of synthesized collecting reagents for the ore silvin of the Tubegatan deposit.

The purpose of the study is to obtain the content of apolar solvents that can be used in the flotation enrichment of potassium ore, as well as to scientifically substantiate the effective procedure for the introduction of flattening reagents in the process.

2 Research methods

Chromium-mass spectroscopy was used in the study: Agilent Technology GS 6890 / MS 5973N chromato-mass spectrometer, 30 m × 0.25 mm capillary columns with phenylmethylsiloxane in 5% dimethylsiloxane, gas carrier - hydrogen, injector temperature 280 °C, MS source temperature 230 °C, MS quadrupole temperature – 180 °C, programming thermostat column temperature from 100 to 280 °C, temperature increase limit 10 °C per minute, sample size 1 µl., In addition to physico-mechanical and standard normative methods were used to determine the technological parameters.

Saturated cotton solution of JSC "Dehkanabad Potash Plant" was selected as the object of research. The density of this saturated fabric solution is 1244 kg / m^3, the amount of the main component is 18-35% by mass. and T1, T2, and T3 were selected. The primary ore also contains large specific surface clay additives in the amount of 4 - 15%, the rest of the ore mass consists of sodium chloride (NaCl) and other soluble salts, which adversely affect the flotation enrichment of another sylvin (KCl).

The chemical compositions of three different samples of sylvinite ores, determined based on the requirements of the above standards, are presented in Table 1.

Table 1. Chemical composition of sylvinite ore, wt %.

Ore	KCl	NaCl	$MgCl_2$	$CaCl_2$	н.о.	H_2O
T-1	13,5	65,39	2,10	2,31	15,0	1,7
T-2	25,8	64,90	1,40	2,1	5,0	0,8
T-3	35,1	55,37	0,23	0,4	7,2	1,7

As can be seen from the data in Table 1, samples even from the same deposit vary greatly in the content of the main components and their main constituents are halite, sylvin and n.d. The insoluble residue isolated from ore samples is represented by silicate (illite, chlorite, quartz, potassium feldspar) and non-silicate (anhydrite, dolomite, magnesite and hematite) minerals. The content of silicate minerals in n.d. changed from 20 to 100%.

It is known that Uz-Kor Gas Chemical JV produces polyethylene and polypropylene polymers in hexane solvent with the participation of Cycler-Natt catalyst. In this industry, along with polymer products, liquid secondary raw materials are formed, which are the products of oligomerization of the primary monomers. At present, the composition of the oligomer has been studied in detail by chromatographic method, and it has been shown that the composition contains mainly hydrocarbon fractions of normal structure C_{12} - C_{20} [24].

Liquid paraffins of normal structure C_{14} - C_{18} boiling at 135 °C were separated by the method of fractional separation of the used secondary liquid hexane raw material under laboratory conditions in a vacuum drive (650 mm.sim.ust.) Equipped with a deflegmator, thermometer, Libix refrigerator. The density of the obtained hydrocarbons at 20 °C is 745 kg /m^3.

3 The results obtained and their analysis

To achieve the goal, the agents were first tested on model samples. R1-R3 solutions were prepared for testing of local liquid paraffins (LLP) obtained on the basis of secondary hexane of the gas-chemical complex of Uz-KorGasChemical JV LLC as an apolar solvent. As an object of comparison, the "foreign analogue" (FA), currently purchased from abroad and used by JSC "Dehkanabad Potash Plant" in the enrichment of sylvinite ores, was used (Table 2).

Table 2. Results of flotation of liquid paraffins in 22 ± 1 °C temperature model samples.

indicator		Model samples					
		P1		P2		P3	
		FA	LLP	FA	LLP	FA	LLP
Productivity, %:							
	Concentrate	42,3	39,1	31,5	31,2	17,5	19,4
	residue	57,7	60,9	68,5	68,8	82,5	80,6
KCl mass fraction, %:							
	Concentrate	89,2	90,1	89,4	88,9	87,4	87,9
	residue	21,26	24,25	7,55	8,12	5,70	3,84
Allocated KCl,%:							
	Concentrate	75,46	70,46	84,5	83,21	76,56	85,26
	residue	24,54	29,54	15,5	16,79	23,44	15,74

The data from the table show that the "foreign analog" solution has a high efficiency in solutions with a relatively large number of main components. If these two apolar collectors are compared in terms of concentrate yield and KCl content, the “foreign analogue” and

local liquid paraffin show that at the same consumption, the concentrate yield in the first apolar solvent is 3.2% higher. However, under the influence of local liquid paraffin, the content of KCl in the flotation product is 0.9% higher, which indicates that local liquid paraffin is more effective. These results are of practical importance and are the basis for the high selectivity activity of local liquid paraffin. Hence, the mass ratios of the initial salts in the model samples have a large effect on the efficiency and selectivity of the apolar solvent.

In the first model sample, as the temperature of the initial solution increases, the total amount of salts in the saturated saline solution increases mainly due to the increase in the amount of potassium chloride. However, an increase in temperature leads to an increase in the surface activity of the additives in the composition as well as the activity of the collecting reagents. Therefore, the temperature dependence of the efficiency of apolar collectors was also studied. Fig. 1 and Fig. 2 show the results of these studies.

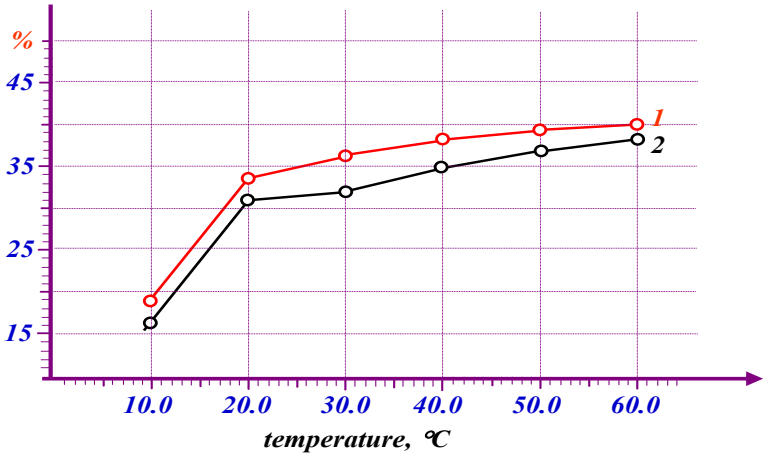

Fig. 1. Yield of flotation concentrate of P3 model sample with collector consumption 10 g / t:1) FA; 2) LLP.

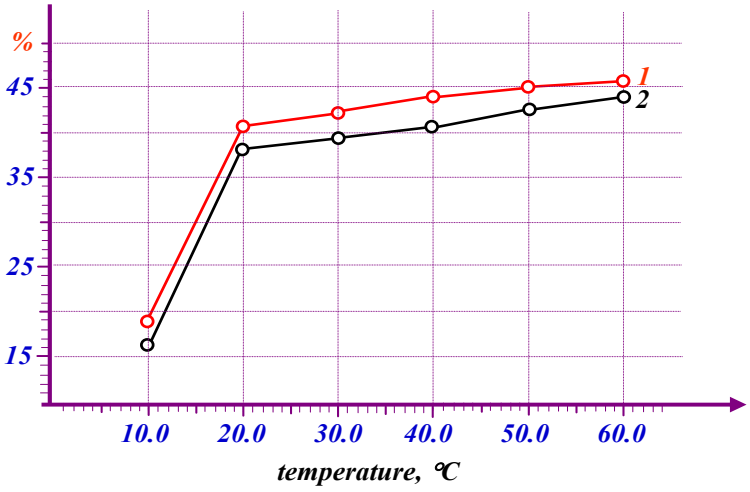

Fig. 2. Yield of flotation concentrate of P3 model sample with collector consumption 15 g / t:1) FA; 2) LLP.

At all temperature limits, the yield of concentrate is higher than the imported foreign

analogue: an increase in temperature from 10 to 40 °C increases the yield of concentrate by 23%, an increase in aproton consumption of 5 g / t in the P1 model observed a 5% increase even at low flotation temperatures. No sharp changes in concentrate yield were observed with increasing temperature at 45°C.

When local liquid paraffins are used as apolar solvents at low temperatures, it is possible to see that the concentrate yield conforms to the norms at high temperatures, even though the concentrate yield is low. Tables 3 and Table 4 below compare the flotation rates of a mixture containing different amounts of potassium chloride and insoluble chemicals of apolar accumulations.

Table 3. Results of correlation of insoluble waste amounts with FA content in flotation enrichment of model samples.

Amount of insoluble waste,%	3	6	12	3	6	12	3	6	12
Indicators	Model samples								
	P1			P2			P3		
Foreign analog									
Productivity, %:									
Concentrate	40,1	39,3	36,2	30,1	28,7	26,9	17,1	16,2	15,1
resedue	59,9	60,7	63,8	68,5	71,3	73,1	82,9	83,8	84,9
KCl mass fraction, %:									
Concentrate	87,3	86,8	83,1	89,4	87,2	83,2	87,4	82,1	79,5
residue	22,4	14,1	21,8	7,9	8,9	9,5	5,4	6,5	6,6
Allocated KCl, %:									
Concentrate	72,18	72,6	68,4	84,5	79,9	76,3	77,0	70,7	68,2
residue	27,82	27,4	31,6	15,5	20,1	23,7	23,0	29,3	31,8
Local liquid paraffins									
Productivity, %:									
Concentrate	39,5	39,1	35,1	29,2	27,6	25,8	17,3	16,6	15,2
resedue	60,5	60,8	64,9	70,8	72,4	74,2	82,7	83,4	84,8
KCl mass fraction, %:									
Concentrate	86,4	84,8	81,2	89,3	86,8	84,1	88,6	83,2	80,8
residue	23,7	22,6	23,9	8,83	10,2	10,3	4,9	6,0	6,3
Allocated KCl,%:									
Concentrate	70,36	70,54	64,8	80,5	76,5	74,0	79,0	73,5	70,0
residue	29,64	29,46	35,2	19,5	23,5	26,0	21,0	26,5	30,0

As a result of scientific research, a technology for producing liquid paraffins on the basis of hexane, a secondary product of the industry, has been developed.

Table 4. Technical, functional and qualitative characteristics of local liquid paraffins.

Name of indicators	**Indicators**
1. Fractional composition:	
Initial boiling point	less than 150°C
Final boiling point	not much 310°C
2. Mass fraction of n-Alkanes	less than 99.8%
Including:	
C11 and lower n-alkane mass fraction	not more than 0.1%
C18 and higher n-alkane mass fraction	not more than 0.1%
3. Mass fraction of aromatic hydrocarbons	less than 0.005%
4. Mass fraction of water-soluble acids and bases	no
5. Density at 20°C, limit	720 - 760 kg / m^3
6. External condition	Clear ransom-free liquid, without additives, including water

The technology of local liquid paraffin production is based on the purification of used hexane from the volatile part of the secondary product of Uz-Kor Gas Chemical JV LLC,

followed by separation of the main product (fraction C11-18) by driving and the process of driving at atmospheric pressure takes:

1. Loading the raw material.
2. Azeotropic removal of the main (head) fraction.
3. The main product is liquid paraffin, consisting of C11-18 fraction.
4. Filter the cube residue.

Driving process conditions:
Temperature - 150 - 280 °C
Pressure - atmosphere
The method is periodic (Fig. 3).

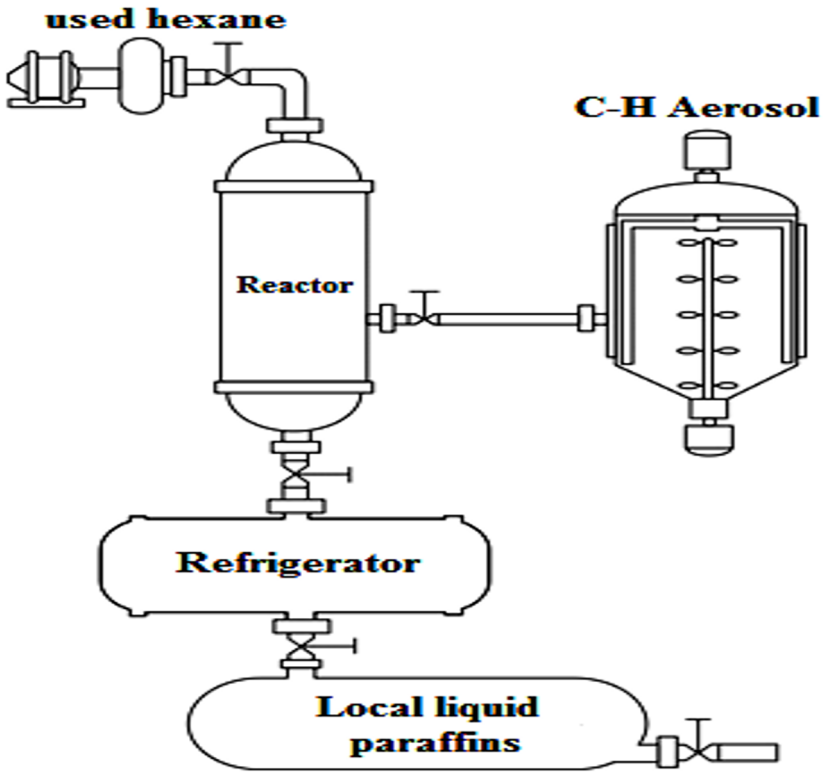

Fig. 3. Principled technological scheme of domestic liquid paraffin production.

1 m^3 of raw material is loaded into a 1.6 m^3 reactor by means of a liquid pump and steam is sent to heat the mixture. The density of the raw material at 20 °C before crushing is 712 kg / m^3. As the temperature rises to 65 °C, the product begins to melt. The thermometer readings in place quickly rise to 105 °C and then the process slows down.

Each control of the temperature in the reactor is carried out by the laboratory of the enterprise with samples of density and viscosity. Density is determined by hydrometric method, mass by organoleptic method. When the temperature rises to 115 °C according to the thermometer, the density of the sample taken from the reactor should be 746 kg / m^3 and the smell and compatibility should be consistent with the foreign analogue. After that, the driving process is stopped. After cooling, the product is filtered and packed in 1000-liter polyethylene containers.440 liters of liquid paraffins are obtained from 1 m3 of used

hexane. The obtained liquid paraffins are sent to the reagents department for use in the flotation separation of potassium chloride.

4 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 mass content of clay minerals in them is 35-60 %, which causes changes in the technological parameters of sylvite flotation processes. 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 and cyclic compounds in the composition of liquid paraffin

The technology of producing local liquid paraffins from hexane, a secondary product of Uz-Kor Gas Chemical JV LLC, has been developed.

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