ISBN 978-83-66216-62-4

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MONOGRAPH

iScience
Warsaw, Poland - 2022

KARAGANDA TECHNICAL UNIVERSITY

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Barite flotation in salt solutions: Monograph / N.K. Omarova, R.T. Sherembaeva, A.A. Zhorabek; iScience Sp. z o. o. – Warsaw, 2022 – 97 p.

ISBN 978-83-66216-62-4

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DESIGNATIONS AND ABBREVIATIONS

GOST - state standard;
AUIMRM - All-Union Institute of Mineral Raw Materials;
flotareagent – flotation reagent;
Gintsvetmet - State Institute of Non-Ferrous Metallurgy;
SB RAS - Siberian Branch of the Russian Academy of Sciences;
DGP "VNIITSVETMET" - subsidiary of the state Enterprise Research Institute of Non-Ferrous Metallurgy;
FO - fusel oil;
VDMP - probably - deterministic planning method;
tech process – technological process;
с-т – concentrate;
t. – tails;
ex– - the original product;
с-т «n» п – re – clearing concentrate;
хв. «n» п – re – clearing «n» tails;
βPb – lead content;
εPb – lead extraction;
εBaSO4 – extraction of barite;
β BaSO4 – barite content;
FAFOTO - fatty acid fraction of tall oil;
DSSAM – disodium salts of sulfoyantaric acid monoesters.

INTRODUCTION

Processing of ores of heavy non-ferrous metals at processing plants is mainly carried out by flotation, which is associated with the use of a large amount of water.

Mining and processing enterprises are a source of environmental pollution, primarily due to the impact on the hydrosphere and atmosphere of accumulated overburden and processed rocks in dumps and tailings dumps. The negative impact on the environment is caused by pollution of natural waters and soil by oxidation products of heavy metal minerals: copper, lead, zinc and iron. Therefore, the technologies currently used for mining, processing and processing of ores involve the maximum use of recycled water supply, which significantly reduces the discharge of untreated wastewater and environmental pollution.

Such effluents include heavy metal ion-saturated effluents formed as a result of atmospheric oxidation of dumps and stored tailings, as well as effluents of other consumers of water resources.

Domestic and foreign experience confirms the possibility of effective use of recycled water at processing plants of non-ferrous metallurgy. At the same time, it should be taken into account that the cost of recycled water is 2-4 times less than fresh [1].

The water consumption per 1 ton of processed ore during flotation enrichment is 4-6.5 m^3. With the full use of recycled water supply, the consumption of fresh water during flotation is reduced by 1-1.5 m^3/t.

The conservation of water resources, as well as the prevention of environmental pollution, is a major socio-economic problem. One of the solutions to this problem is the development of measures to reduce the consumption of fresh water in technological processes per unit of production and reduce the discharge of wastewater into reservoirs.

In recent years, certain work has been done at non-ferrous metallurgy enterprises to solve the problem of preventing pollution of reservoirs with industrial waters. Before discharge into reservoirs, industrial wastewater is clarified and purified with or without reagents in special containers or tail storages.

Capital expenditures for the construction of wastewater treatment facilities for medium-capacity factories alone amount to 30-40 million tenge [2].

The operating costs for wastewater treatment are also high and amount to 35-50 million tenge per year: at the same time, the main item of expenditure is the cost of reagents for treatment.

The introduction of recycled water supply has a positive effect on sanitary and hygienic factors, which often cannot be directly determined, but are crucial.

Further development of enrichment schemes with circulating water supply should be based on the scientific foundations of flotation in saline waters. In a certain sense, it can be considered that the implementation of circulating water supply brings the conditions for conducting the flotation process closer to the so-called "salt flotation", the mechanisms of phenomena in which have not yet been fully disclosed [4].

In this work, the features of barite flotation were studied under the conditions of using recycled water characterized by a high degree of salt accumulation and in relation to the flotation of this mineral from the tail product after the separation of sulfides on the example of ores of the Karagailinskoye lead-barite deposit.

CHAPTER 1. CHARACTERISTICS OF THE PROPERTIES OF BARITE AND BARITE ORES, TECHNOLOGY OF ENRICHMENT OF BARITE-CONTAINING RAW MATERIALS

1.1 Properties and application of barite

The mineral barite is similar in appearance to celestine and calcite. Among anhydrous sulfates, barite ranks second in prevalence.

Crystals in the form of a prism, tetrahedron, plate. Fine or coarse powder. Radiant and needle-like fibers. Formations in the form of feathers and plaque. It's all about the same substance — barite. Despite its long history and wide distribution, the properties of barite, according to some scientists, have not been fully studied. This allows us to hope for new discoveries related to the substance that is formed due to the interaction of barium salts with water and iron ores.

Barite is heavy, but fragile. In this respect, it is very similar to graphite: according to the Mohs scale, its hardness is less than 4 points, as is the material for the production of pencils. The mineral can be easily crushed, which is good for mining plants: barite processing is a fast and easy process. It is characteristic that when a stone is split, it always breaks up into even parts — this was noticed in ancient times and began to attribute mystical properties to the gem. In the Middle Ages, barite was widely used in occult affairs, served as a talisman for many famous people, in particular, the sixteenth US President Abraham Lincoln.

In most cases, the mineral barite is colorless or has a pale cream color. But often there are bright crystals of all shades of the rainbow. For example, there is a deposit of blue barite in Brazil. Deposits of pink stone were found in Asia. Mother-of-pearl deposits are often found, in particular, in Kazakhstan— one of the leaders of the world's mineral extraction. The color of the crystals is influenced by impurities: the composition of the mineral may include quartz, galena, calcium, lead, strontium. The color has no effect on the physico-chemical characteristics of barite and its application.

It is known that the floatability of minerals is largely determined by its crystal chemical characteristics. The ability of the mineral surface to interact with water and reagents depends on the surface energy of the mineral, the value of which in some cases is in a symbiotic relationship with the energy of the crystal lattice. The energy of the crystal lattice is one of the indicative characteristics of the surface properties and for barite according to Fersman is 525 kcal / mol, according to Kapustinsky 559 kcal / mol.

The surface properties of minerals depend both on the geometry of the arrangement of ions in the lattice and on the genesis of the mineral.

Barite crystallizes in rhombic syngony, the barium cation is surrounded by twelve oxygen ions belonging to seven different SO_4 groups.

The destruction of crystals in most cases is carried out along certain crystallographic planes.

The most probable planes of destruction are shown in Figure 1.

When the bonds in barite are broken, the cations appear to be in "hollows", while the rows of anions seem to protrude above the cations. The cations are somewhat buried in comparison with the anions, and therefore, first of all, in the aqueous phase, during grinding, the anions must come into contact with water. There are two rows of external barium ions in barite, which are "immersed" below the surface by 1 A and 3 A, respectively.

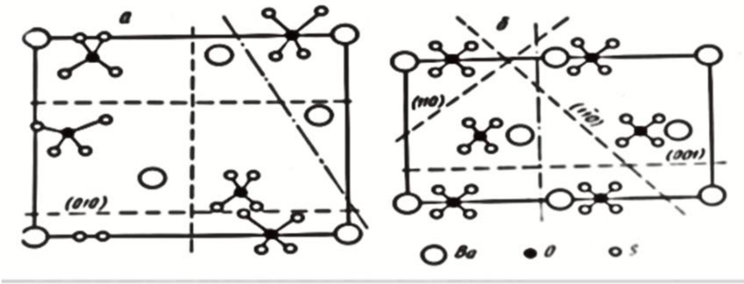


Figure 1 – The most probable planes of destruction of barite crystals a and b - projections on different planes

The main consumer of ground barite and barite concentrates is drilling equipment. One of the main properties of barite - high density - finds use in almost all spheres of life. Due to this quality, the mineral is used for weighing drilling fluids. It is used mainly for deep drilling for oil and gas. Approximately 60-90% of all extracted barite is used for this purpose.

The use of barite in industry is based on the following technological properties: a) high specific gravity; b) white color; c) chemical inertia; d) ability to absorb X-rays.

Consumers of barite concentrates are also:

1. Paint and varnish industry - production of white, non-ferrous and silicate-protective, as well as printing inks (consumption of barite from 10 to 80% of the weight of the commercial product). In the powdered state, barite dissolves in sulfuric acid, and forms a precipitate when interacting with water. This allows the mineral to be used for the manufacture of paints, whitewash, enamels. Among other unusual properties of barite, it should be noted the ability to fluoresce and luminesce;

2. Rubber industry - production of hard rubber grades (tires, hoses), as well as rubber products for working with X-rays;
3. Paper industry - production of special grades of paper;
4. Production of various plastics;
5. Production of explosives;
6. Production of X-ray absorbers;
7. Glassmaking - barite is added to the glass mass to homogenize it and give the glass a special shine;
8. Production of artificial marble, sealing wax, soap, etc.;
9. In ceramics, for the production of white-knitting products;
10. Production of hydraulic barium cement, stable in seawater.

The medicinal properties of the mineral have long been known and are widely used in various fields of medicine. Thus, the unique ability to delay X-radiation is used in the arrangement of X-ray rooms. The exceptional transparency of minerals is used for the production of lenses, magnifying glasses, microscopes, and other laboratory and diagnostic equipment not only in the field of medicine.

Barite is also used as a filler and weighting agent for special concretes, a filler mixed with latex and hot asphalt in road construction, as a flux for melting yellow copper.

Table 1 - Technical requirements for barite concentrate

№ п/п	Name of indicators	Unit of measurement	Grades			
			top	1	2	3
1	Specific gravity, not less than	г/см^3	4,25	4,20	4,00	3,80
2	The content of barium sulfate in terms of dry matter, not less than	%	95	90	Not standardized	
3	Moisture content, not more than: in dry in wet	%	5,0 14,0	5,0 14,0	5,0 14,0	5,0 14,0
4	The content of water-soluble salts, no more, including Ca	% %	0,30 0,025	0,35 0,05	0,40 0,06	0,45 0,07
5	Fineness of grinding-remains on the sieve up to -0.074 mm, no more	%	10,0	10,0	10,0	10,0
6	Fraction content minus 10 microns, no more	%	10,0	15,5	25,0	30,0

It is necessary to maintain a stable import flow of barite from permanent partners in the Republic of Kazakhstan in the economic conditions of the Customs Union countries, and also consider the possibility of forming new import flows of barite raw materials from China, India and Laos.

In the first half of the XX century, both mining and barite processing plants were located directly in Germany, England, Italy, France and the USA, import-export supplies did not exceed 20% of consumption. The use of barite was mainly for the production of paint filler (over 50% of consumption) and barium chemicals. If in 1950 the world production and consumption of barite was 1.3 million tons, then in 1960 it grew to 2.8 million tons, and by 2020 – 8.2 million tons.

It should be noted that Kazakhstan is the largest baritone-bearing region in the world. More than 30% of the world's reserves of barite ores are contained in its bowels, with 80% of them falling on barite - sulfide ores, 20% on deposits of the barite type proper.

The main reserves of barite are concentrated in Central Kazakhstan and some of them, about 24%, are in Southern Kazakhstan. In the period up to the mid-90s, barite concentrates were obtained mainly by processing barite-polymetallic ores by flotation.

Currently, the main area of application of barite concentrates is their use as weights of drilling fluids in drilling oil and gas wells

Currently, purely monobarite sources have been discovered and are being involved in processing. The emerging growth in the production of oil and gas products of the Republic of Kazakhstan will increase the volume of drilling, and in this regard, the consumption of barite concentrates will also increase.

1.2 Characteristics of barite ores

The methods of enrichment of barite-containing ores depend on the type of ore and its structural features.

According to M.A. Eigeles, there are the following main technological types of barite ores [6]:

1. Quartz-barite ores. Coarse-grained differences of this type are enriched by washing with subsequent ore picking of the washed ore. Medium-grained ones are enriched by jigging, and fine-grained differences of this type are enriched by flotation or concentration on tables.
2. Calcite-barite ores. Ore grading or gravity methods enrich ores of coarse and medium-grained structure. Fine-grained ores are enriched by flotation.
3. Fluorite-barite ores. Selective flotation is the most effective method of ore enrichment of this type, with the help of which conditioned barite and fluorite concentrates can be obtained.

4. Sulfide-barite ores.
5. Barite ores containing iron oxides. Ores of this type are enriched most difficult. Coarse-grained ores with a low iron content are enriched by ore picking with subsequent washing. From fine-grained ores, the largest amounts of iron minerals can be removed by concentration on tables or by decripitation. Acid washing removes limonite and other ochre minerals from barite, and magnetic separation removes magnetic iron ores.

Rich calcite- barite and quartz-barite ores are enriched only by washing and sorting by hand.

Complex ores, both fluorite and sulfide, are practically enriched only by flotation.The thermal enrichment method was first developed at AUIMRM. The method is based on the ability of some coarse-grained monomineral barite ores to crack when heated. Barite turns into a fine powder when heated, and the minerals of the impurity do not crack and their grains do not decrease in size.

Barite ores, characterized by a complex composition and containing precious metals - gold and silver, are enriched with combined technological schemes combining hydrometallurgical and processing processing, ensuring the production of barite concentrates with high extraction of precious metals into an independent product [7].

Barite is a mineral that is barium sulfate ($BaSO_4$). In some varieties, barium is partially replaced by strontium (baritocelestin, celestobarite), lead (hokutolite, anglesitobarite), calcium (calcitobarite). Barite crystals are tabular or prismatic; the color is white, gray, pink, yellow, brown depending on impurities (iron and manganese oxides, sulfides of non-ferrous metals and iron, clay and organic matter). The whiteness of high-grade barite reaches 98%. Occasionally there are transparent crystals of optical barite. Barite is usually developed in the form of aggregates – granular, lamellar, radiant- and columnar-fibrous.

Viterite is a mineral consisting of barium carbonate ($VaSO_3$), its crystals are short-prismatic, tabular, dipyramidal; the color ranges from white to yellow. Viterite forms granular, columnar, kidney-shaped, fibrous and leafy aggregates. The physical properties of barite and viterite are similar, the chemical properties are sharply different. The density of these minerals ranges from 4.3-4.6 g /cm^3, hardness 2.5-3.5 (barite is somewhat inferior to viterite in hardness). Both minerals have a glassy luster, turning into a resinous one.

Barite is characterized by high chemical resistance, practically insoluble in water, weak acids and organic compounds. Viterite is unstable in acids and dissolves quite quickly even in water.

1.3 List of minerals found in ores of barite deposits

There are more than 60 names of minerals found in the ores of barite deposits. Non–metallic minerals include quartz, dolomite, calcite and fluorite, ore minerals include iron (pyrite, magnetite, hematite, siderite, limonite), lead (galena, cerussite, anglesite), zinc (sphalerite, smithsonite), copper (chalcopyrite, chalcosine, bornite, cuprite, covellin), silver (argentite, stroymeierite, native silver), and native gold.

Barite is used in three main directions: for the production of clay solutions weighting in oil and gas drilling (more than 75%), as inert and weakly active fillers (16-18%) and raw materials in the production of barium compounds (6-8%). As an inert heavy filler, it is used in special rubber, in the production of plastics, some types of paper, in asbestos products, cement and various building materials, as well as in paints, varnishes and enamels (mainly for the manufacture of lithopone).

The ability of barite to absorb radioactive radiation (including X-rays) allows the use of materials containing it in X-ray technology.

Transparent colorless barite crystals are used as optical raw materials. Barite and viterite are the only raw materials for the production of barium compounds used in the chemical industry, pyrotechnics, metalworking, mechanical engineering and other areas of the national economy.

Currently, the structure of barite consumption is changing, which is due to the introduction of barium-containing ceramics in the electric power industry, which has superconductivity at high temperatures, as well as the growth of nuclear energy and the reduction of nuclear weapons, since barite is the cheapest component of protective installations and structures.

Viterite can be used as a raw material for the production of barium compounds, primarily (after purification) of technical barium carbonate. Due to its light solubility, viterite is unsuitable as a weighting agent.

Barite and viterite occur together in nature, and viterite has, as a rule, a subordinate meaning. It is usually present in barite ores in the form of minor impurities, but sometimes its content reaches 30-45% (the Settlingston, Morrison and Longaleut deposits in the UK, Arpaklenskoye and Ely-su in Turkmenistan).

The CIS deposits, in the ores of which the viterite content was significant, have been worked out. Barite, which has a high chemical resistance, is well preserved in the weathering zone (viterite decomposes quickly under these conditions), but during subsequent movement along the slope due to its low hardness, it quickly collapses and dissipates.

This makes it possible to form deposits of barite (barite loose, barite sands), as well as eluvial and sometimes slope (deluvial) placers in the zone of weathering of barite-containing ores and rocks (Medvedevskoye deposit in Russia). Placers of more distant demolition are not formed.

Barite deposits are divided by genesis into hydrothermal, carbonatite, sedimentary and residual. Viterite is present only in hydrothermal deposits. Among hydrothermal deposits, vein and metasomatic deposits are distinguished; sometimes veins and metasomatic deposits of barite occur together within the same ore field or even a deposit.

Vein deposits are represented by veins or, less often, lenticular bodies that perform cracks. The veins have mainly a steep drop, an unstoppable power and a complex morphology. They often branch, forming apophyses, break up into two or more parallel veins. Within the veins, there is usually an alternation of inflations, in which the power reaches 5-10 m or more, and pinches, where barite is completely replaced by quartz, calcite or replaced by areas filled with clay.

Deposits of this type are characterized by the presence of single extended veins (hundreds of meters long in strike and fall, sometimes 1-2 km long) or a series (10-20) of short veins (tens of meters in fall and strike) arranged in a chain or backstage.

Barite breccias are often found, represented by clastic material cemented with barite. The composition of the ores of vein deposits varies widely. There are ores both with a low barite content (several percent) and almost monomineral.

Quartz and calcite are usually present in ores, the amount of which varies very widely (often they almost completely fill individual sections of barite veins), often fluorite (its content is sometimes higher than barite), sulfides of zinc, lead, iron, copper and other metals.

In a number of deposits in individual veins or sections of veins, metal sulfides constitute the main value of ores, and barite is an associated component. Viterite is contained in significant quantities only in the ores of vein deposits. Vein-type deposits in a number of countries (Russia, Kazakhstan, Italy, Greece, Great Britain) are the main source of barite production.

Of particular value are vein deposits with a high content of barite (sometimes with almost monomineral barite ores), which can be used in most industries without enrichment.

The most typical vein deposits are Beganskoye (Ukraine), Jalairskoye, Badamskoye, Tukzhskoye (Kazakhstan), Chordskoye, Apshrinskoye and the fields of the Kutaisi group (Georgia).

Metasomatic deposits contain lenticular or formation-like bodies of barite ores, often lying in accordance with the host rocks. The works of many metasomatic deposits contain sulfides of lead, zinc, copper, iron and other metals.

Often metal sulfides are the main value of these ores, barite is only a passing component.

The metasomatic deposits include Zhayremskoye, Bestube, Kentobe, Zhumanai (Kazakhstan), Quartzite Sopka (Altai Krai).

Barite sometimes contains organic substances that turn it black. However, the sedimentary origin of some deposits is controversial. Deposits of this type include a number of deposits in the states of Arkansas and Nevada (about 40% of all US barite reserves), in the CIS - the Chiganak field (Kazakhstan).

Residual deposits of barite are eluvial and, less often, slope placers composed of clays, sands and loams containing fragments of barite. Due to the easy enrichment, these ores, despite the low content of barite (15-30%), are of industrial importance.

In the USA, almost 40% of all barite reserves are contained in residual deposits (in the states of Missouri, Tennessee and Georgia).

No independent deposits of this type have been identified in the CIS, separate placers are known at the Medvedevskoye (Russia) and Jalairskoye (Kazakhstan) deposits. Carbonatite deposits, whose ores are characterized by a significant content of barite, are unknown in the CIS.

In the ores of some carbonatite deposits in the USA, the barite content is 10-30%, reaching 50%. When rare-earth elements are extracted from these ores, a barite concentrate is obtained along the way.

Barite ores by their mineral composition are divided into essentially barite (including barite-viterite), quartz-barite (including viterite), calcite-barite, fluorite-barite, sulfide-barite, iron-barite, iron-fluorite, as well as clay- and sand-barite. Essentially, barite ores mainly consist of barite, together with which viterite is present in some deposits.

Other minerals (quartz, calcite, iron oxides, metal sulfides, etc.) are contained in insignificant amounts. These ores are developed mainly in hydrothermal deposits, sometimes forming independent bodies, but more often they gradually turn into quartz-, calcite-, fluorite- and sulfide-barite ores.

Ores of this type predominate in the hydrothermal deposits of the Kutaisi group (Georgia), Kentobe, Zhumanai and the sedimentary Chiganak deposit (Kazakhstan). They are also found in the weathering crust of the Ushkatyn III and Zhayrem deposits (where they gradually turn into sandy- and clay-barite ores). In quartz-barite ores, along with barite, there is a significant amount (30-45%) of unevenly distributed quartz, in calcite-barite – calcite (up to 70%). Other minerals (iron oxides, metal sulfides, etc.) are contained in small quantities. These ores (along with substantially barite ores) are developed in the hydrothermal deposits of Georgia (Chordskoye) and Kazakhstan (Kentobe and Jalairskoye).

Quartz and calcite-barite ores often alternate with sulfide-barite ores, sometimes they turn into pure quartz, calcite, quartz-calcite veins or form independent bodies. Quartz-barite (siliceous-barite) ores of the Chiganak deposit are a thin interlayer of substantially-barite ores and interlayers of siliceous rocks (jasper). Fluorite-barite ores are composed mainly of barite and fluorite, quartz and calcite are also usually present, often sulfides of lead, zinc, copper and other metals. Ores of this type are relatively rare.

Almost monomineral differences are often found. The actual barite deposits are the main source of high-quality barite used as weights and fillers in varnishes and paints, as well as for the production of barium compounds. According to ore reserves (in million tons), the actual barite deposits are divided into very large (more than 5), large (0.5–5), medium (0.1–0.5) and small (less than 0.1). Complex deposits include barite-polymetallic, fluorite-barite and complex iron-fluorite-rare earth-barite deposits, during the processing of ores of which barite can simultaneously be extracted into its own concentrate.

The main importance among them are barite-polymetallic deposits. Within these deposits, represented by sulfide-barite ores, there are often independent bodies or parts of these bodies composed essentially of barite ores (Quartzite hill). Large reserves of residual (sandy- and clay-barite) ores are often concentrated in the weathering zone.

The content of barite in sulfide-barite ores is usually 5-20%, sometimes 40-70%, in independent bodies of substantially barite ores often exceeds 70%, sometimes reaching 90%.

The mineral association is represented, in addition to barite, by sulfides of lead, zinc, iron, copper, in some cases noble metals (Au, Ag) are present in an amount sufficient for associated extraction, and the non-metallic complex is composed of quartz, calcite, dolomite, chlorite, modified feldspar, sometimes fluorite. Barite concentrates obtained from these ores are mainly used as weights of drilling fluids.

Complex iron-fluorite-rare earth-barite deposits, although they have large reserves of barite, but do not play a significant role in its production.

According to the reserves of barite (in million tons), complex deposits are divided into very large (more than 20), large (from 10 to 20), medium (from 1 to 10) and small (less than 1). 10. An additional source of barite production may be the tailings of processing plants that previously processed ores of barite-polymetallic deposits without extracting barite (for example, in the Salair ore management). The possibility of economically profitable extraction of barite from drilling fluids after drilling wells is not excluded, which is already practiced in the USA.

1.4 Study of technological properties of ores

Technological properties of barite (siderite) ores, as a rule, are studied in laboratory and semi-industrial conditions on mineralogical, small technological, laboratory, enlarged laboratory and semi-industrial samples.

With the existing experience of industrial processing of easily enriched ores, it is allowed to use an analogy confirmed by the results of laboratory studies. For difficult-to-enrich or new types of ores that have no experience in processing, technological studies of ores and, if necessary, products of their enrichment should be carried out according to special programs agreed with interested organizations.

Sampling for technological studies at different stages of geological exploration should be carried out in accordance with the standard "Solid Minerals and rocks. Technological testing in the process of geological exploration". In the process of technological research, it is advisable to study the possibility of pre-enrichment and (or) separation into grades of extracted ore in heavy suspensions, using large-batch sorting of ore mass in transport containers, and for ores with a high yield of lump fraction (-200+20 mm) – the possibility of their radiometric separation.

With positive results of pre-enrichment studies, it is necessary to clarify the industrial (technological) types of ores that require selective extraction, or confirm the possibility of gross extraction of ore mass. Further tests of ore processing methods by traditional methods of deep enrichment (gravity and flotation) are carried out in accordance with the standards (Flotation methods of enrichment) and (Gravity methods of enrichment).

To identify technological types and grades of ores, geological and technological mapping is carried out, in which the sampling network is selected.

All natural ore varieties identified at the deposit should be characterized by mineralogical and small technological samples selected according to a certain network.

According to the results of their tests, geological and technological typing of the ores of the deposit is carried out with the allocation of industrial (technological) types and grades of ores, the spatial variability of the material composition, physico-mechanical and technological properties of ores within the selected industrial (technological) types is studied and geotechnological maps, plans and sections are compiled.

The technological properties of all selected industrial (technological) types of ores should be studied on laboratory and enlarged laboratory samples to the extent necessary to select the optimal technological scheme for their processing and determine the main technological indicators of enrichment and the quality of the products obtained.

At the same time, it is important to determine the optimal degree of ore grinding, which will ensure maximum exposure of valuable minerals with minimal clogging and dumping them into tailings. The results of laboratory tests, if necessary, are checked by semi-industrial tests.

The latter serve to verify technological schemes, clarify technological and economic indicators of processing and confirm that the concentrates obtained as a result of testing meet the requirements of the relevant technical specifications and state standards.

Samples for semi-industrial tests should characterize individual industrial types of ores or mixtures of industrial grades in ratios corresponding to the volume of their joint extraction and processing at the factory.

Semi-industrial technological tests are carried out in accordance with the program developed by the organization performing technological research, together with the subsoil user and agreed with the project organization. Sampling is carried out according to a special project.

With the intended use of barite concentrate as a weighting agent for drilling fluids, it is mandatory to conduct research on the possibility of gravitational enrichment of ores.

Enlarged laboratory and semi-industrial technological samples should be representative, i.e. meet the chemical composition, textural and structural features, contrast in the content of valuable components, physical and other properties of the average composition of barite (viterite) ores of this industrial (technological) type.

Interlayers of substandard ores, as well as host rocks and various inclusions that cannot be isolated during mining should be included in the composition of technological samples.

To assess the technological properties of ores of deep horizons of deposits that are difficult to access for the selection of representative laboratory and especially semi-industrial samples, it is necessary to use the revealed patterns in the change in the quality of barite (viterite) ores of the upper studied horizons and the results of geological and technological mapping.

When studying the enrichment of barite (viterite) ores, the degree of their oxidation, mineral composition, structural and textural features, as well as physical and chemical properties of minerals are studied, the presence of associated components and harmful impurities is established using techniques and methods of technological mineralogy.

The fractionability and pulverizability are evaluated, sieve, dispersion and gravity analyses of different ore classes are carried out.

The technological scheme of enrichment is selected, the number of stages and the stadium size of grinding are set.

The methods of enrichment and refinement of concentrates and industrial products containing associated components are determined.

The material composition and technological properties of barite (viterite) ores should be studied in detail, ensuring the receipt of initial data sufficient to conduct an objective feasibility study of the effectiveness of the proposed technological solutions when considering exploration conditions and designing a technological scheme for their processing with complex extraction of the components contained in them of industrial importance.

In addition, it is necessary to justify the feasibility and effectiveness of testing the process of large-batch radiometric sorting of ores in transport tanks during the operation of the deposit. Industrial (technological) types and grades of ores should be characterized according to the corresponding indicators provided by the conditions, the main technological parameters of enrichment and chemical processing (yield of concentrates, their characteristics, extraction of valuable components in separate operations, through extraction, etc.) are determined.

The reliability of the data obtained as a result of semi-industrial tests is evaluated on the basis of technological and commodity balance.

The difference in the mass of the industrial component between these balances should not exceed 10%. Processing indicators are compared with those obtained at modern processing plants for processing barite ores.

For associated components, it is necessary to find out the forms of finding and the balance of their distribution in the products of enrichment and conversion of concentrates, as well as to establish the conditions, possibility and economic feasibility of their extraction.

The possibility of using recycled water and waste obtained with the recommended technological scheme for processing mineral raw materials should be studied, the characteristics of products sent to the tailings storage (volume, size and residual concentration of reagents) and recommendations for cleaning industrial effluents are given.

Barite and siderite ores, as a rule, require enrichment. Rich substantially-barite ores are usually enriched by washing and manual sorting, and in some cases are used without prior enrichment.

Sand-clay-barite ores of eluvial placers are most easily enriched: barite can be obtained after washing and sorting.

The enrichment schemes are stadial depending on the textural and structural features of ores. The main method of enrichment for the extraction of barite from fine-grained and complex ores is flotation.

Barite refers to easily flotation minerals with the use of carboxylic acids, alkyl sulfates, as well as cationic reagents as collectors.

When processing sulfide-barite ores – the main source of barite production - barite concentrate is obtained from the tailings of sulfide flotation.

The scheme of enrichment with a tinted ore grinding of 65-90% - 0.074 mm includes the main, two or four perechistnye and control operations.

Each of which is characterized by its own set and consumption of reagents (baritone, oleic acid, tallow oil, oxalum P-80, pine oil, liquid glass, soda ash, lime).

Complex fluorite-barite ores are also enriched by flotation technology both with sequential selection of fluorite and barite, and vice versa (barite suppressants - starch, sodium fluoride, lignosulfonates, potassium bichromate).

Iron barite ores are processed using a combined magnetic flotation technology of enrichment. Other additional processing methods are sometimes used to improve the quality of the final product. For example, chemical bleaching of enrichment concentrates is carried out with fine grinding of the material in a weak solution of sulfuric or hydrochloric acids followed by repeated washing.

When enriched with decripitation, barite cracks at a temperature of 400-450 ° C and turns into a powder state, unlike impurity minerals. By subsequent screening, a high-quality barite product is released. Promising methods of processing barite-containing ores of various types are the combined technology of radiometric enrichment, which includes the processes of large-batch sorting in transport tanks to a DS (distribution silo) and large-batch separation after crushing the ore.

The question of a rational scheme for the enrichment of iron-fluorite-rare-earth barite ores has not yet been finally resolved. To increase the extraction of barite, a combined processing scheme with flotation enrichment of industrial products and gravity tailings is used, which allows to additionally obtain up to 10% of the concentrate.

The flotation scheme (basic, control and several per-cleaning operations) is carried out with the fineness of the grinding of the material up to 90% -0.074 mm.

Technogenic waste containing barite in insignificant quantities (no more than 8-10%) can be used in the production of special cements or as raw materials for the re-extraction of barite. Barite is supplied in the form of ore-picking products, gravity and flotation concentrates.

The quality of concentrates should be regulated in each specific case by the contract between the supplier (mine) and the consumer or must comply with existing standards and specifications.

The granulometric composition of barite concentrate is determined at the request of consumers. Barite concentrates of all grades of class A are suitable as fillers of paints, varnishes and enamels, grades KB-1 and KB-2 of this class - for the production of barium salts, in the production of electrovacuum glass and lithopone. For the latter purpose, a KB-3 class A concentrate with a restriction on the content of fluorine (0.03%) can also be used.

For raw materials used in the production of lithopone and white-tone paints, the brightness coefficient is additionally normalized (for the KB-1 brand at least 90%, for other brands - at least 80%), as well as by size (the residue on the sieve No. 0056 is not more than 1%).

From concentrates of grades KB-3, KB-4 and KB-5 of class A, ground bleached barite is obtained by chemical bleaching, used as a filler in paint and varnish, electric lamp and other industries (the residue on the sieve No. 016 is not more than 0.1%), and as a result of additional enrichment of these concentrates by decripitation, bleaching and grinding at jet mills – bleached microbarite used in the production of enamels and paints for special purposes (size -20 microns at least 85%).

Barite concentrates of all grades of class A are used in the production of asbestos products, class B - in the cement industry, and grades KB-5 and KB-6 - in the production of other building materials.

When drilling for oil and gas used powdered modified barite weighting derived from gravity and flotation concentrates of barite class B.

For weighting normalized density (4-4,2 g/cm), the content of water-soluble salts of calcium (not more than 0.05 %), a measure of hydrophilicity (not less than 80 %) and fineness (residue on sieve № 0071 not more than 6 %).

Barite ores with an iron sulfide content of more than 1% as a feedstock for the production of a weighting agent are unsuitable.

1.5 Flotation properties of barite

The ores of the Karagailinsky deposit are classified by M.A. Eigeles as sulfide -barite, fine-grained.

Flotation properties have been studied in detail both in the CIS and abroad. The first systematic studies on the flotation of minerals of this type by fatty acids were conducted by Godin [84]. It was found that the flotation of a number of salt-like minerals is determined by the solubility of soaps formed by fatty acids and metal cations entering the crystal lattice.

M.A. Eigeles [8, 9] investigated the flotation of barite with oleic acid and a mixture of carboxylic acids from oxidized paraffin. In the works of M.A. Eigeles and I.D. Chogoshvili [10] it was shown that the most effective and selective collector for barite is tallow oil soap with 57% fatty acids and 36% resin acids. P.N. Fedorov [11] used the oxidation products of salt oil for barite flotation.

For the first time, alkyl sulfate was proposed for the flotation of barite by Helbich [35]. At the same time, it is noted. That collectors of this type floats barite more intensively than other minerals.

The possibility of barite flotation by cationic collectors was shown in the works of Taggart and Arbeiter using the example of dodecylamine [36]. At the same time, it was noted that free barium ions have a depressing effect on the flotation process.

According to the data of most researchers, multilayer coatings of collectors are formed on the surface of non-sulfide minerals [8].

As a result of studies of energy heterogeneity and active centers on the surface of minerals, confirmed by radiographic studies [15, 16, 17, 18], it is assumed that the collector's polylayers exist on the surface of minerals even in the case when the collector is fixed on them in an amount smaller than necessary for the formation of a monolayer. However, for barite, it has been observed that in the tested concentration range there is saturation of the surface by the collector. At the same time, a coating of 2.17 monolayers is formed on the surface of the barite.

M.A. Eigeles [8] points out that oleates of various metals have a collective effect, and barium oleate for barite and calcium oleate for fluorite are the most effective, dramatically reducing the time of adhesion of barite grains to the air bubble. Collectors are fixed on the surface of mineral grains with different strength and coating density. According to M.A. Eigeles, at low concentrations, the fixation of the collector on the surface of minerals with alkaline earth cations is quite stable.

Sodium oleate is most firmly fixed on celestine and barite. When oleate is adsorbed from the surface of these minerals, only the first washing gives a small effect. In the future, the amount of the fixed collector remains unchanged – for barite 8.8×10-10g-mol/l [12]. After five times washing, 15% is removed from the surface of the barite, celestine - 30% of the fixed sodium oleate. In an acidic environment for oleates, the molecular form of fixation prevails, in an alkaline one – ionic [20, 21].

A.S. Peck and M.E. Wadsworth, using the example of barite, calcite and fluorite by IR spectroscopy, showed that as a result of chemisorption of sodium oleate, anions were replaced on the surface of minerals, and the reactions were chemically reversible [22]. In the works of I.N. Plaksin and V.I. Solnyshkin, it was shown that after treatment of the barite surface with oleic acid, the nature of spectral lines in the IR spectrum "indicates the predominant removal of ions from the surface layer of the crystal lattice" [23]. According to various authors, complete extraction complete extraction of the pure mineral barite into foam in distilled water is achieved at a consumption of sodium oleate - 80 g/t, sodium alkyl sulfate - 100 g/t, tall oil - 180 g/t [24, 25, 26].

A. N. Grebnev and L.K. Stefanovskaya, floating barite with alkyl sulfates with different lengths of the hydrocarbon chain (from 10 to 18 links - CH_2 -), showed that the most effective collectors for barite are alkyl sulfates with 14 and 12 hydrocarbon links.

M.A. Eigeles established a sharp improvement in the flotation of barite with oleic acid at values of the hydrogen index greater than 6 [27, 28]. Barite is floated with alkyl sulfates in a wide pH range of the medium [29].

In the work of D.L. Talmud and N.M. Lubman, the improvement of barite flotation is achieved in a slightly alkaline medium and a slight decrease in the flotation activity of barite at pH = 13 [102]. S.I. Mitrofanov and G.E. Sokolova studied the effect of various concentrations of hydrogen ions on the flotation of barite with alkyl sulfates [26, 34]. It was found that for barite, the maximum flotation and sorption of hexadecyl sulfate do not coincide. The maximum of adsorption corresponds to the minimum of flotation.

Recently, the question of the relationship of the flotation properties of minerals with their electrokinetic potential has been widely discussed.

A.N. Dolzhenkova, G.S. Streltsin and I.N. Fokin show possible ways of using data on the zeta potential - potential in the study of the mechanism of interaction of flotation reagents with minerals. The study was conducted on a pure mineral - barite containing 99% $BaSO_4$. The set of surface properties of this mineral was studied: the electrokinetic potential in a wide range of pH values both in the absence and in the presence of collectors, the adsorption of the reagents used and the floatability of barite. Anion – and cation - active substances were used as collectors: alkyl sulfate, sodium oleate, laurylamine.

The conducted research allows us to state the absence of an unambiguous relationship between the floatability of barite and the value of its zeta potential, as well as the floatability of barite and changes in its zeta potential under the influence of introduced collectors. However, at the same time, the results on the zeta potential allow us to deepen the understanding of the processes on the surface of minerals during flotation. In particular, based on the data on the zeta potential, a characteristic of the state of barite at different values of the medium is given and possible variants of the mechanism of fixing sodium oleate, alkyl sulfate and laurylamine on barite under flotation conditions are considered.

When studying the flotation of barite from ores, the following two main points should be taken into account:

1. Barite is the main mineral;
2. Barite accompanies more valuable minerals, for example, scheelite, fluorite or galena.

In the first case, it is necessary to isolate barite from the minerals of the waste rock, calcite, dolomite and quartz. For this purpose, direct selective flotation is used by anionic collectors in the presence of depressors. In the second case, barite is released during the refinement of scheelite and fluorite concentrates or from the tailings of sulfide flotation. Quartz has the greatest difference from barite in terms of floatability. As noted by a number of studies, the activation of quartz by metal cations, always present in the ore pulp, significantly shifts the optimum floatability of quartz by anionic collectors to the region of more alkaline media [35, 36, 37]. This makes it necessary to use sodium silicate as a quartz depressor.

The most difficult task is to separate barite from calcite and dolomite. Fatty acids do not provide sufficient selection, more effective in this case are alkyl sulfates, which are a universal collector for the flotation of barite ores and ensure the selection of all minerals of the waste rock.

The issues of selection of barite and fluorite were studied in detail by M.A. Eigeles [38, 39]. The selection of these minerals was achieved by various effects of sodium silicate, aluminosilicate, dextrin and sulfite – cellulose extract depressing barite on them.

For flotation enrichment of barite-fluorite ore with a small barite content (22% $BaSO_4$), the following scheme is recommended: first, barite is floated with a small amount of alkyl sulfate, and then fluorite is floated with oleic acid in the presence of liquid glass [87].

Dobiash P.R. described the effect on barite and fluorite of all the main types of collectors: fatty acids, technical mixtures - oxidized kerosene, alkyl sulfonates - RSO_3Na, where R is an aliphatic radical with 10, 12 and 16 hydrocarbon atoms and cationic collectors – salts of N - substituted alkylpyridinium. The positive effect of increasing the pulp temperature to 40-500 C. was also noted. At the same time, the floatability of barite increases, and fluorite decreases, which is explained by an increase in the differences in the solubility of barium and calcium sulfonates [88, 89, 90].

V.I. Maksimov carried out work on the extraction of barite from siderite ores [40]. It was found that barite can be selectively floated by oleic acid at pH = 9, and octadecylamine by hydrochloride in an acidic medium at pH = 2.5.

Sodium silicate is used to depress the waste rock during barite flotation [41, 8, 26,34]. Haman proposed citric acid as a depressor in the separation of barite from iron–containing minerals [91]. Oxalic acid is used in the separation of scheelite-barite concentrates [42, 43]. M.A. Eigeles also emphasizes the ingenuity of the action of oxalic acid. However, the issue of barite depression during flotation of a number of other minerals has not been sufficiently developed.

The study of the floccular flotation of barite was carried out by O.S. Myakota, a mixture of oleate and sodium alkyl sulfate was used as a collector in the ratio of 1.25:1 - 1.5:1. Barite concentrate after three times cleaning without reagents contained 92-93% barium sulfate when 93-94% was extracted.

The beginning of the industrial flotation of barite dates back to the 30 years of the XX century.

The Salair processing plant processed lead-zinc-barite ores according to the scheme of direct selective flotation to obtain three products: lead, zinc, barite and concentrate gold [44, 45,46].

As a collector, acidol was proposed at a consumption of 0.4 - 0.5 kg/ton of ore. At that time, the factory processed ores containing from 45 to 60% barite. The subsequent gradual depletion of rich barite sections of the deposit led to a change in the reagent regime of barite flotation.

The Vniitsvetmet Institute has introduced a new technology of barite extraction at the factory, including two main flotations and two cleaning operations. The barite content in the finished concentrate increased from 65-73% to 83-86%, which corresponds to a weighting density of 4.08 - 4.18 g/cm^3.

The Mirgalimsay processing plant processes the ores of the Mirgalimsay deposit.

The barite of this deposit is located in thin accretions with calcite, dolomite and belongs to the number of hard-to-enrich ores. Initially, the factory produced Grade III barite weighting with a content of 65 - 70% barite at low extraction.

Then the factory switched to barite flotation using the DSSAM reagent at a flow rate of 100 g/t, which allowed to obtain richer concentrates with the same extraction as with alkyl sulfates. At the same factory, lead–barite ores of the Karagailinsky deposit were processed according to the same technological scheme and using the same reagents in the barite cycle.

1.6 Flotation of barite from ores, reagent mode

Flotation of barite from ores. Barite refers to easily flotation minerals. Its floatability with oleic acid and a mixture of carboxylic acids improves in an alkaline environment (at pH > 7). Salts of divalent (copper, lead, zinc) and trivalent (iron, aluminum) metals have a depressing effect on barite flotation. A mixture of liquid glass and potassium chromate depresses barite at low costs. Organic reagents (tannin, starch, dextrin, glucose, sulfitcellulose) depress barite only in a highly alkaline and acidic environment, being activators of its flotation at pH 7-9.

Barite is usually floated in an alkaline medium with oleic acid, tallow oil mixed with kerosene, sulfate oil, naphthenic acids or alkyl sulfates at a flow rate of 0.5-1.5 kg/t. Alkyl sulfates with a polar chain containing 15-17 carbon atoms have the greatest selectivity.

The easiest way to extract barite is from ores, the empty rock of which is represented by quartz and silicates, which are easily depressed even at low costs of liquid glass, somewhat activating the flotation of barite.

The consumption of the depressor increases sharply (up to 1.5-4 kg/t) with an increase in the content of calcium and magnesium carbonates in the ore. The consumption of all reagents is reduced if dithiophosphate (100-150 g/t) is used as a collector, which also provides the possibility of flotation in hard water without prior desalination. Since the increased concentration of liquid glass has a depressing effect on the flotation of barite, with a significant content of calcium and magnesium carbonates in the ore, it is advisable to process either industrial products in a separate cycle, or rough barite concentrate according to the method of N. S. Petrov. N. S. Petrov's method consists in steaming a pre-condensed (up to 50-60%) solid concentrate for 30-60 minutes in a solution of liquid glass (0.3-2%) at a temperature of 80-85 ° C, dilution with cold water to 25-40 °C and subsequent flotation of barite. During steaming, the collector is desorbed from the surface of the calcium mineral particles polluting the concentrate and their flotation is almost completely depressed.

If the ore contains a significant amount of oxidized iron minerals, then barite flotation is carried out in a soda medium (at pH 11) with a carboxyl collector; iron oxides of sodium metasilicate (0.5 -1 kg / t) are used as a depressor.

In most cases, barite is extracted from polymetallic ores. The resulting barite concentrates are used either in the chemical industry or as a weighting agent when drilling oil wells. High-grade concentrates for the chemical industry contain up to 95% barite. The density of the concentrate for the oil industry should be 4.1-4.3 g / cm^3, and the content of the class -10 microns should not exceed 5-7%.

The schemes of flotation extraction of barite are relatively simple. They usually provide for the main, control and two or three cleaning operations. Sometimes the concentrate of the last flotation is classified in hydrocyclones, the sands of which are a concentrate for the oil industry. A concentrate suitable for the chemical industry is obtained from the discharge of the hydrocyclone after two or three cleaning operations.

Flotation of fluorite from ores. Fluorite is extracted from silicate and carbonate fluorite, barite-fluorite, as well as sulfide ores and ores of rare metals. It is quite easily floated by oxyhydryl collectors: oleic acid, sodium oleate, OF and MA aerosols (dialkyl-sodium sulfosuccinate), alkyl sulfate. The maximum adsorption of the collector and the floatability of the mineral are observed at pH 6. Liquid glass reduces the adsorption of the anionic collector. Citric acid depresses fluorite flotation. Aluminum salts, especially in a mixture with liquid glass and organic reagents (dextrin, lignin sulfonates, etc.), depressing barite and calcite, even somewhat activate fluorite flotation. According to the results of laboratory studies, the separation of fluorite and quartz can be carried out using a cation collector; moreover, at pH 1-3 fluorite is floated, and at pH 11-14 quartz.

Either the initial ore, or the tails of gravity enrichment (in order to isolate coarse fluorite and barite), or the tails of sulfide flotation are received for flotation.

If the rock is represented by silicate minerals, high fluorite extraction is achieved at low costs (0.2-0.3 kg/t) of an oxyhydryl collector and liquid glass.

To increase the selectivity of fluorite flotation from carbonate ores, calcite depression is usually carried out in a highly alkaline medium created by caustic soda (0.4- 0.6 kg /t), with a sequential supply of liquid glass with a modulus of 2.6-2.8 (0.45-0.6 kg /t) and aluminum salts (0.6 - 0.8 kg /t). An additional supply of dextrin (0.6 kg/t), lignin sulfate or other similar organic reagents enhances calcite depression and activates fluorite flotation. The selectivity of flotation can be increased by heating the pulp to 40-50 ° C and some complication of the scheme as a result of the introduction of additional list operations or the allocation of industrial products for processing in a separate cycle.

The greatest difficulties arise during the flotation of barite-fluorite ores. In this case, a scheme of direct selective flotation of barite and fluorite is possible, as well as a scheme with preliminary collective flotation of both minerals and further release of fluorite into the foam product.

Variants of selective flotation schemes are shown in Figure 1.1.

According to the first of them (see Figure 1.1, a), barite is first floated at low costs (less than 0.4 kg / t) of alkyl sulfate, and then fluorite with oleic acid (0.2 kg /t) in the presence of liquid glass (0.8- 1 kg /t).

According to the second variant of the scheme (see Figure 1.1, b), fluorite is first floated when barite is depressed with chromatic and organic reagents (starch and dextrin), and then barite is floated when minerals of waste rock are depressed with citric acid.

The collective barite-fluorite concentrate is separated when barite is depressed by tannin and ferric oxide salt, dextrin and potassium bichromate, CMC (carbomethylcellulose) and aluminum sulfate, ligninsulfanol, dextrin or starch. The selectivity of separation can sometimes be improved by using a slightly acidic medium (pH 4.6-4.8) and heating the pulp to 40-45 °C. Flotation fluorite concentrates contain 92-98% CaF_2 and are used to produce hydrofluoric acid and fluoride salts. Harmful impurities in them are silica (no more than 1.5-3%) and calcite (no more than 2-3%). Extraction of fluorite into concentrate varies from 78 to 91% depending on the composition of ores. Together with fluorite, the rare earth elements associated with it pass into the concentrate.

1.7 The current state of the technology of circulating water supply during ore flotation

Generalization of the experience of operating factories in the conditions of recycled water supply allows us to draw some conclusions and identify the factors determining the use of recycled water supply in processing plants.

The use of a large range of flotation reagents, different degrees of dissolution of ore minerals leads to contamination of process water. The total mineralization of wastewater is 2-3 times higher than that of industrial waters [51]. At the same time, the hardness of water increases significantly, there is an accumulation of depressor ions, etc. All this creates difficulties in the introduction of recycled water supply.

Let's consider some examples of the features of the introduction of recycled water supply.

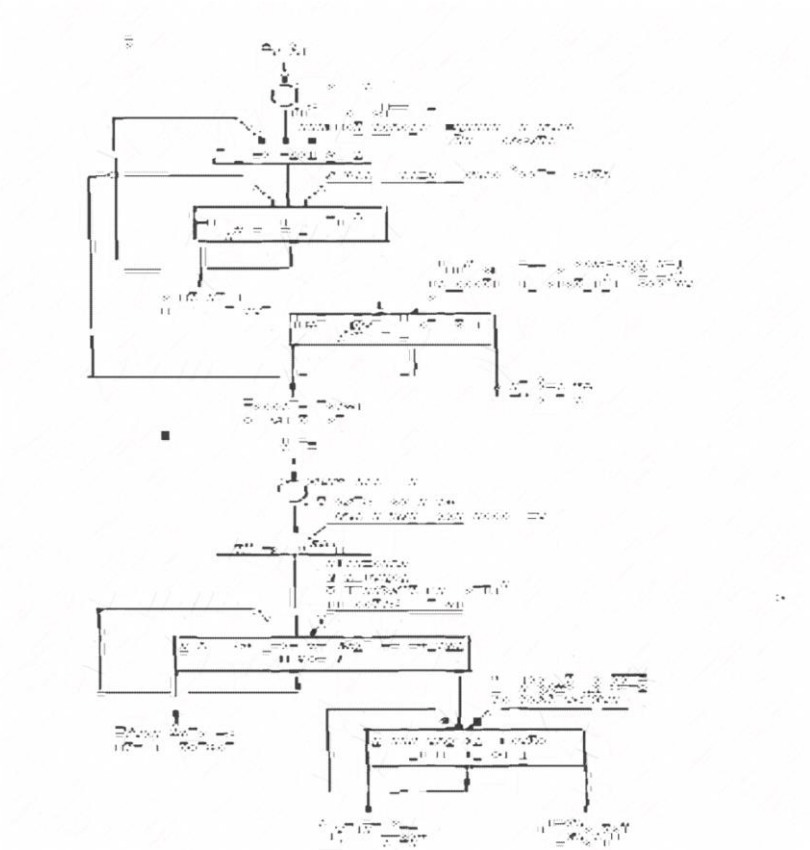


Figure 1.1 - Schematic diagrams of selective flotation of barite-fluorite ores

The Gaia processing plant operates according to a collective - selective flotation scheme with the production of copper, zinc and pyrite concentrates from interspersed sulfide ores from solid copper-zinc ore [52]. It was found that the pH of the aqueous phase of the tail pulp decreases in the tailings of the factory, the content of Cu^{2+} ions decreases from 0.75 to 0.1 mg / l and Fe_{gen}, purification from xanthogenate occurs (as a result of its decomposition and sorption on slurries), but there is an increased water hardness and an increase in the content of SO_4 ion to 1094 mg/ l. When using tail waters, the reagent flotation regime was adjusted, which made it possible to reduce the consumption of reagents in the conditions of circulating water supply without reducing technological indicators: butyl xanthogenate by

14.3%, sodium sulfide by 50.0%, activated carbon by 29.7%. This example shows that the study of recycled water supply is an appropriate measure.

Uchalinskaya concentrating Plant processes solid sulfide copper - zinc ores to produce copper, zinc and pyrite concentrates using cyanide-free technology.

The successful introduction of recycled water supply at the Uchalinsky factory was facilitated by the mutual neutralization of the alkaline effluents of the factory and the acidic mine waters of the Uchalinsky quarry in the tailings pond, followed by their secondary purification in the reservoir. The composition of recycled water during industrial tests was quite stable, the amount of suspensions was insignificant - 20-100 mg/l. The factory switched to using 69% of recycled water for enrichment [53].

Circulating water supply is most easily achieved in factories processing monometallic ores, where the presence of residual concentrates does not harm the technological process, but it is necessary to regulate the dosage of reagents when reusing water.

Some difficulties may arise when the reagent mode of the cleaning operations involves the use of depressors, the presence of which in the main flotation cycle may reduce extraction.

At the same time, it is more expedient to use recycled water only during the main flotation, and to supply fresh water or recycled water from the corresponding cycle of re-cleaning. Another difficulty may be the presence of finely dispersed sludge in the ore, while it is necessary to use such coagulants that, remaining in clarified water, would not worsen the enrichment process.

Relatively easy to solve question in the collective scheme of flotation and returns from the tailings pond to the collective flotation and subsequent breeding cycles can be used fresh water.

I. A. Beltyukov, T. S. Rovnaya and G. L. Venediktova held various options for the use of waste water as the circulating water in the collective flotation of lead and zinc ore flotation Altyn-Topinkova deposits and oxidized lead ore Kurganinskogo field [54]. The possibility of reducing the amount of fresh water to 30% without deterioration of technological indicators has been established.

Successful work was carried out at the «Kazmehanobr» Institute [55]. The introduction of recycled water supply in polymetallic factories requires preliminary purification of wastewater from many dissolved impurities [56]. At the same time, wastewater treatment according to the nomenclature and degree of impurities removed, as well as secondary salt contamination due to chemical cleaning, is regulated in each case by the requirements of the production technology.

The situation is more complicated with direct selective flotation of polymetallic ores. The percentage of recycled water use in this case is lower than in collective flotation.

The first study in relation to the scheme of direct selective flotation was carried out by N.S. Petrov on the barite-lead ore of the Mirgalimsay deposit.

The developed flotation mode was tested on a semi-industrial installation, where the possibility of circulating water supply was confirmed. The lead flotation received recycled water from the preliminary thickening of the final tails.

The recycled water used in the barite flotation cycle can be obtained from tailings waste water by pretreating them with lime and subsequent clarification in a thickener. The introduction of recycled water supply should reduce the consumption of fresh water to 35% of the total amount of water consumed.

The introduction of circulating water supply at the Zyryanovskaya concentrating plant in the ore washing operation turned out to be possible when water was conditioned with a dosage of sodium sulfide with automatic stabilization of the redox potential in the range of 130 - 150 Mv. Due to this, zinc losses in copper-zinc concentrate were reduced by 0.8% of the ore [57]. The consumption of fresh water supply has been reduced by 20%.

A brief analysis of the technological developments of recycled water supply in relation to the conditions of flotation of polymetallic ores, including lead – barite, for example, Karagailinsky. However, there is no information in the publications about the features of barite flotation under these conditions and, accordingly, recommendations for improving the technology when using saline waters during barite flotation.

A fundamentally important task to be solved in the development and improvement of water circulation schemes is to maintain the optimal ion-molecular and dispersion composition of circulating waters, which does not lead to a deterioration in the technological indicators of the enrichment process. At the same time, due to the significant volumes of recycled water flows returned, the task of minimizing the costs of cleaning and conditioning is urgent.

The improvement of water circulation regimes is also largely due to the tightening of requirements for the composition of wastewater entering environmental management facilities.

This task is especially relevant in connection with the removal of natural water sources previously used for the water supply of mining and processing enterprises.

An important task in improving water circulation is also the additional extraction of valuable components, the implementation of which improves the economic performance of Mining and processing plants.

The effluents of mining, processing and metallurgical enterprises, as a rule, are characterized by significantly increased concentrations of heavy metals. At the same time, the total salinity can be at the level of natural waters and is up to 50 mg/l (dump tailings of gravity-flotation schemes) or, on the contrary, can increase to 5 g/l (thickener drains, electrolysis baths, leaching tanks, etc.)

Such differences in ionic composition and mineralization determine the need for separate (cycle-by-cycle) conditioning of circulating waters.

Closed water circulation schemes have become most widespread in factories located in areas with a significant shortage of water (processing plants of Yakutia, Central Asia, Kazakhstan, Mongolia) or with a large number of agricultural and other consumers of water resources (processing plants of Ukraine, Chernozem region, Urals).

Currently, processing plants use partial closed water circulation to the greatest extent (from 35 to 85%). This is due to the fact that there remains a need to use clean water in certain operations of the technological process, such as ore crushing, preparation of reagents. On the other hand, incomplete water circulation is caused by natural water losses resulting from drainage and drying out of the tailings and sewage treatment plants.

In this regard, the task was set to study the flotation behavior of barite in the presence of certain soluble salts and to develop on this basis the technology of barite flotation in relation to the conditions of circulating water supply.

The features of barite flotation in salt solutions are considered in the aspect of the structural features of water and aqueous solutions.

1.8 Ideas about the structure of water and aqueous solutions

Water has a number of abnormal properties. The anomalous properties of water are explained by the peculiarity of the structure of its molecules.

The electron cloud of the H_2O water molecule is a truncated four-bladed screw that can be placed in the wrong cube.

At the same time, an oxygen atom is in the center, and two hydrogen atoms are in opposite corners of one of the faces of the cube. The $H\text{-}O\text{-}H$ angle is 104^0 31. Two of the eight electrons of an oxygen atom are located near its nucleus, the other two are connected to oxygen atoms, and two unshared pairs of electrons form branches stretching to opposite corners of the face occupied by oxygen atoms.

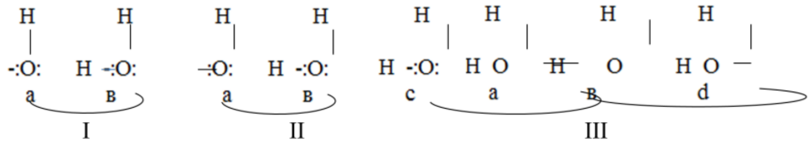
These branches of the electron cloud are of particular interest because, being areas of concentration of negative charges, they attract positively charged hydrogen atoms of neighboring molecules and provide a connection between water molecules.

Models of the structure of liquid water are divided into two types – in some theories the structure of water is considered as a homogeneous continuum, in other models the existence of a mixture of different structures is assumed, but in both cases the solid state structure is used as a starting point.

The structure of ice I_h according to the results of its study by X-ray diffraction analysis and neutron diffraction is a hexagonal system [92, 93].

Each oxygen atom in the ice structure is connected by hydrogen bonds with four other oxygen atoms, which are arranged along a tetrahedron at a distance of 2.76 A from the central oxygen atom.

The strength of the H_2O hydrogen bond is due to the Coulomb interaction of polar molecules and increases due to an increase in charge separation at various resonant interactions, such as:



Thus, the hydrogen bond in a certain sense has a collective character and the structure of water is hardened in a wide area.

What happens when the ice melts? The low melting heat of ice (1.44 kcal) indicates that no more than 15% of the hydrogen bonds present in the ice are broken during melting. The X-ray radial distribution curve for each liquid water indicates that the tetrahedral order in the arrangement of molecules is preserved during melting in water.

This leads to the idea that the structure of liquid water is very similar to the structure of ice - I_h, but at the same time it is necessary to remember the obvious differences between liquid and solid. An increase in the level of thermal motion leads to a weakening and rupture of bonds, and as a result, it is possible to melt a more "liquid" structure.

A.I. Samoilov emphasizes that the ice lattice - I_h is openwork and contains cavities inside the frame in which water molecules can be placed. The density of melting ice therefore increases [59]. As a result of the effect of thermal motion, the water molecule, having descended from the equilibrium position, performs a translational movement in the form of a jump to another equilibrium position in the cavity of the ice-like frame and remains there for some time until it again receives energy to jump to a new equilibrium position.

Cavity molecules are not energetically equivalent to molecules located in the nodes of an ice-like framework. They correspond to broken hydrogen bonds.

In another important type of models, improbable water is considered not as "free", but as forming a special structural form.

Of particular interest among them is the theory of Bernal and Fowler, the appearance of which marked the beginning of modern theories of ice structure [60]. They found, based on the data of X-ray diffraction analyses, that there are three types of arrangement of molecules for water.

Water *I* (ice–tredimite structure) forms a tetrahedral coordinated ice-like lattice resembling a distorted tredimite lattice due to hydrogen bonds.

Such a grid exists up to a temperature of 4^0. The process of melting ice is accompanied by the appearance of a second type of lattice - water *II*, representing a quartz-type structure.

The structure of water *II* has a higher density equal to 1.08 g/cm^3 compared to the density of 0.91 g/cm for water *I*.

The fruitful idea of Bernal and Fowler about the ice-like structure of water and the existence, therefore, of a high degree of order in the arrangement of its molecules made it possible to understand many anomalous properties of water that had previously defied strict explanation [61].

There are models of a different type of water structure that are not based on the statement that liquid water consists of an ice - I_h structure.

Such a water structure was proposed by Pauling and appears to be a clathrate structure [94]. The lattice consists of polyhedral cells connected to each other, formed by hydrogen bonds between water molecules, and inside the cells there are water molecules enclosed in them, but not forming bonds. The structure of Pauling water was quantitatively developed by Frank and Quist.

The two-structure model with tetrahedrally bound and monomeric water molecules also includes the model of "shimmering clusters" considered by Frank and Van, further developed by Nemeti and Shiraga and, according to P.A. Privalov, is "the most developed model of water, although perhaps not without drawbacks" [62].

Clusters are destroyed and reappear. The lifetime of cluster associates is about 10^{-10} - 10^{-11} seconds. 2/3 of the total number of water molecules participate in the formation of clusters at any given moment at room temperature, the remaining molecules are free of water-soluble bonds. Clusters are in equilibrium with monomeric molecules, connecting due to the latter and disintegrating again. The dissolution of the electrolyte changes the structure of liquid water. The dissolution of the electrolyte in water is accompanied by a change in the heat content, which serves as proof that the dissolution process is accompanied by the formation and destruction of chemical bonds.

Dissolved ions strongly interact with water molecules and hydration leads to the formation of a shell consisting of water molecules surrounding these ions.

Due to the fact that the forces of Coulomb attraction decrease proportionally to the square of the distance, the shell in question can effectively shield the ion charge.

Many electrolytes retain hydration water so firmly that when these solutions are evaporated, the resulting solid phase crystallizes with a certain number of water molecules, for example: $CuSO_4 \cdot H_2O$ (copper sulfate), $FeCl_3 \cdot 4H_2O$, $MgSO_4 \cdot 7H_2O$. The higher the charge density, the more hydrated it is.

As a result of the study of ion hydration, the following conclusions were made [63].

1. Cations have stronger hydration than anions;

2. The higher the charge of the ion, the more hydrated it is. For a double-charged Mg^{2+} ion, the primary hydration number is from 6-12, and for the Li^+ ion -4.

3. With the same charge, ions with a smaller crystalline radius hydrate more strongly. The values of hydration numbers for Li^+ - 3.2; Na^+ - 2.1; K^+ - 1.1.

Electrolytes are characterized by the phenomenon of electrostriction. Coulomb fields of ions interacting with water dipoles attract them to themselves, as a result, solvent compression occurs around the ion (Fig. 2).

Layer *A* is a denser layer, due to electrostriction, layer *C* is removed from the ion, water molecules remain "normal".

Layer *B* is an area of comparative disorder, disturbed arrangement of water molecules, destroyed structure.

The ordering or disordering action of the ion will depend on which of these layers prevails.

When considering hydration, the most significant is the interaction of hydrating particles and water molecules. This interaction is divided into two components. His approach is based on preferential consideration of the water–water interaction and kinetic stability of the ion–water molecule aggregate.

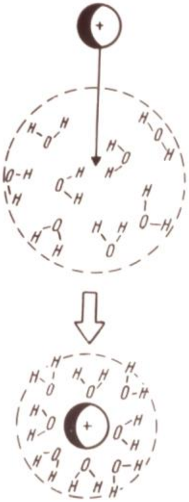


Figure 2 – Electrostriction

Consider how Frank-Van represents the effect of a dissolved substance on the structure of water. The ion in the solution is surrounded by two layers (Fig. 3).

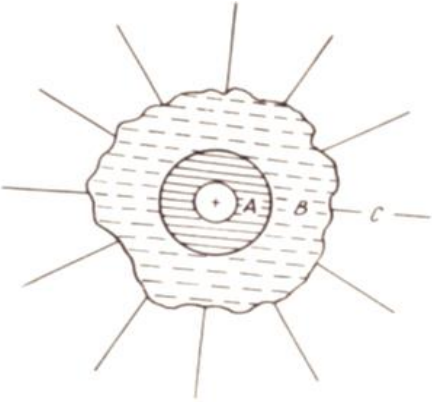


Figure 3 - Ion hydration model in an aqueous solution

Kinetic stability is determined by the activation energy of the exchange process of water molecules in the immediate environment of the ion to water molecules in the volume of liquid, i.e. the action of ions on a potential barrier separating neighboring equilibrium positions of water molecules. Hydration, in this case, is considered not as a strong binding by ions of a certain number of water molecules, but as the influence of an ion on the translational movement of nearby water molecules.

The kinetic approach to the phenomenon of ion hydration makes it possible to better understand the processes of hydration, since the kinetic properties of solutions and the mechanism of a number of processes in them are associated with near hydration.

The main quantitative characteristic of this phenomenon is the frequency of exchange of water molecules near the ion. According to O.Ya. Samoilov, the frequency of exchange depends on the magnitude of the energy barrier separating the equilibrium position of water molecules closest to the ion from the neighboring one. It turned out that some ions reduce the mobility of the nearest water molecules, and near other ions, the mobility of water becomes greater. The latter phenomenon is called negative hydration by Samoilov. For this case, the terms "near" and "far" hydration are accepted [64].

Negative hydration is accompanied by a violation of the water's own structure. Under the influence of the ion, the value of the energy barrier E, separating the neighboring equilibrium positions of the water molecules of the solution, decreases, the translational movement of the latter accelerates. The energy effect of the violation of the structure of water by ions is not compensated by the energy of the interaction of ions with the nearest water molecules interacting also with molecules in the volume of liquid.

With positive hydration of ions, the value of the energy barrier E separating the neighboring equilibrium positions of the water molecules of the solution increases, the translational movement of water molecules slows down. In this case, the effect of ordering the structure of water prevails.

G.A. Krestov noted that temperature affects the attribution of ions to ions with positive or negative hydration. A "limit temperature" has been established at which the strengthening or destructive effect of ions on the solvent structure becomes the same [65].

Ions with negative hydration with an increase in temperature at $T > T_{limit}$ they become ions with positive hydration. And from T to T_{limit} ($T < T_{limit}$) with increasing temperature, the negative hydration of ions decreases, above T_{limit}, only positive hydration is observed, which increases with increasing temperature.

Consideration of the floatability of minerals in suspension, changes in the hydration of the surface of particles, taking into account the properties of the liquid phase and its changes during the process does not give a complete and satisfactory explanation. The hydration of the surface, i.e. the interaction of the mineral surface with water, should be influenced, along with the physicochemical state of the solid phase, by the structural state of the water. The study of the properties of water and the effect on its structural properties of electrolytes, as well as the study of hydrophobic interaction in water should highlight the unscientific aspects of the phenomenon of salt flotation. When studying the hydration of ions and mineral particles in aqueous solutions, it should be borne in mind that an aqueous solution of electrolytes and a mineral suspension are complex systems in which forces between particles act differently in nature.

The phenomenon of solvation (hydration in the case of aqueous solutions) of ions in the region of dilute solutions has been sufficiently fully studied and theoretical provisions on these issues have been developed from the thermodynamic and kinetic points of view [66, 67, 68, 69]. In the area of highly concentrated up to saturated solutions, they have not been fully elucidated.

The results of the X-ray examination performed by Beck is the idea that the structure of highly concentrated solutions is similar to the structure of the corresponding aqueous salt - hydrate [95]. Based on the study of the raman scattering spectra of concentrated aqueous solutions of a number of nitrates, Metier and Lounsbury conclude that the division of ions tends to a distribution characteristic of crystallohydrates [96].

The available data allow us to conclude that the near ordering in concentrated aqueous solutions of electrolytes is similar to the ordering of the corresponding crystallohydrates.

1.9 The theory of "salt" flotation

Taking into account the development of flotation schemes with circulating water supply in non-ferrous metallurgy and the possibility of formation of solutions with a high concentration of salts (50 g/l or more) during water circulation, the study of the behavior of mineral grains in brines acquires a certain importance.

For the first time, the possibility of effective flotation in electrolyte solutions without reagent additives was established on coals [68].

The first explanations of the mechanism of "salt" flotation were based on the high foaming ability of brines [74]. In the future, the attention of researchers was drawn to the possible effects of hydrophobization of the solid-liquid surface.

Yu.M. Glebov, V.V. Konyshin, T.A. Kalacheva investigated the activating effect of inorganic salts during flotation of volcanogenic native sulfur. The maximum extraction of sulfur is observed at 0.5 - 1*N* concentration of electrolytes [69]. Hydrophobization of the surface of naturally hydrophobic minerals by inorganic salt ions is associated with a decrease in the surface charge and structural changes in water and the hydrate layer [70].

The enhancement of hydrophobization by inorganic electrolytes of such naturally hydrophobic minerals as some grades of coal, graphite, sulfur and others is considered in a number of works [70, 71, 74, 75].

Hydrophobization in electrolyte solutions of naturally hydrophilic or weakly hydrophobic minerals has not been studied sufficiently. The first studies in this area were made by M. Kusakov and A. Titievskaya [71]. They noted the dehydration of the surface of glass and mica during the adsorption of aluminum ions on them, while the surface from wetted becomes non-wettable.

B.V. Deryagin established the difference between the properties of the surface hydrate layer and the properties of the bulk liquid [72]. From his point of view, this difference lies in the fact that hydrate layers have a special oriented structure, a different viscosity and are separated from the bulk liquid by the interface.

B.V. Deryagin and Z.N. Zorin explain the change in the properties of the surface of hydrophilic bodies in electrolyte solutions by the peculiarity of the structure of the hydrate layer on their surface.

V.I. Klassen, considering the phenomenon of hydrophobization of coals in electrolytes, explains it by the compression of the ionic atmosphere of the double electric layer with a simultaneous decrease in the zeta potential, while the particles approach to a distance at which the forces of attraction exceed the forces of electrostatic repulsion.

V.S. Kharlamov expressed a different idea about the hydrophobization of coals in electrolyte solutions [74]. He suggests that the hydrophobization of coal particles occurs due to their ejection from the electrolyte medium, since the molecules of this medium interact with each other more strongly at a certain concentration of electrolyte than with the surface of solid phase particles.

Conclusions are drawn from the following provisions. Firstly, the electrolyte ions, hydrating, reduce the number of free water molecules in the solution, disrupt the established equilibrium in the system and contribute to the transition of water molecules from the surface to the volume, i.e.

dehydration of the surface. Secondly, electrolyte ions create strong electric fields that interact with each other and with solvent molecules and, when a certain salt concentration is reached, the forces acting on the water molecules of the hydrate layer from the electric fields of the ions become greater than the forces acting from the solid, and the water molecules from the surface pass into solution and the surface is dehydrated.

G.S. Streltsin conducted experiments on flotation of naturally hydrophobic minerals in electrolyte solutions of concentrations from 0.1 *N* to saturated. He showed that high extraction of minerals such as quartz, microcline, beryl can be obtained in these solutions [75]. He explained the results of the experiments by analogy with the point of view expressed earlier by B.V. Deryagin. Namely: at a high value of the zeta potential due to a strong uncompensated electric field on the surface of the body, the water molecules are oriented by the poles of the dipoles to the surface. This orientation extends deep into the liquid until it is interrupted by thermal motion.

Consequently, with a high value of the zeta potential, there is a hydrate layer of one-sided oriented water molecules on the surface, which is more strongly bound to the surface of a solid body than to each other in volume. At high concentrations of the electrolyte in the solution (low values of the zeta potential), the structure of the hydrate layer should be different. Hydrophobization of the surface at low values of the zeta potential according to G.S. Streltsin is determined by the closure of the bonds of neighboring antiparallelly arranged water molecules on the surface of the particles, which leads to a weakening of the interaction between them and water molecules in the volume. In both cases, the water molecules interact with the surface of the particles equally strongly. The difference lies in the extent to which it is possible to close the bonds of neighboring water molecules adsorbed on the surface with each other. This depends on the degree of ordering of the arrangement of ions on the surface of the particles and determines the thickness and properties of the resulting hydrate layer.

Depending on the properties of the water surface and the concentration of the solution, the formation of hydrate layers with two different types of orientation of water molecules is possible. One type of orientation determines hydrophilic, and the other hydrophobic properties of the surface of the hydrate layer (Fig.4, 5).

From the considered list of the theory of the hydrophobic effect of high concentrations of electrolyte, it immediately follows that the mechanism of "salt" flotation has not yet been reliably established.

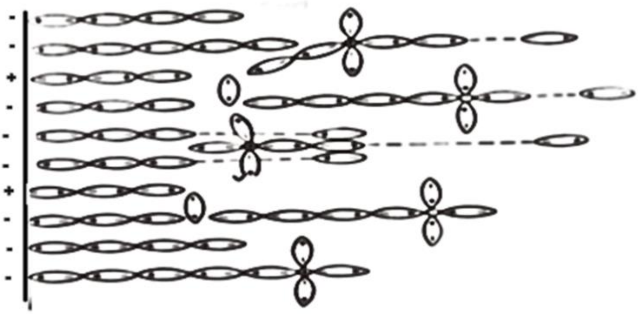


Figure 4 - Schematic picture of the formation of parallel orientation of water molecules

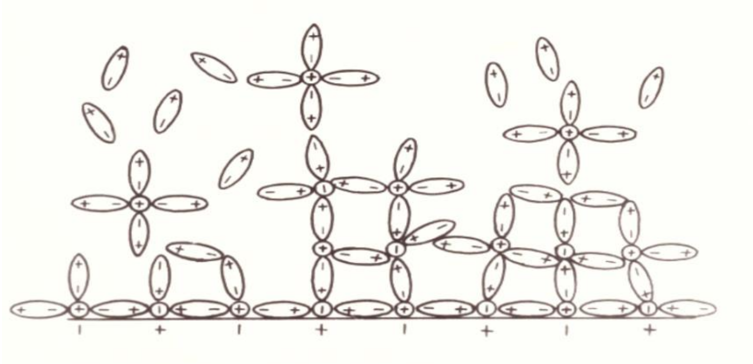


Figure 5 - Schematic picture of the formation of antiparallel orientation of water molecules

1.10 Definition of research goals and objectives

This chapter discusses the technology of flotation enrichment of barite-containing ores, the organization of circulating water supply during flotation of non-ferrous metal ores, ideas about the structure of water and aqueous solutions, as well as the theory of "salt" flotation.

Summarizing the materials in Chapter 1, the following conclusions can be drawn:

1. The production of flotation barite concentrate is an important task and research aimed at improving flotation technology is relevant.
2. Taking into account measures to improve environmental protection, non-ferrous metallurgy is developing to organize circulating water supply at flotation factories. The organization of circulating water

supply causes the emergence of new conditions for the flotation of minerals, namely, the transition from flotation in weak solutions to flotation in brines.

3. The study of the features of barite flotation in brines requires consideration of the properties of aqueous solutions of inorganic electrolytes, as well as scientific ideas about the structure of water and aqueous solutions.

The published articles clearly indicate that water is a structured system and that concentrated aqueous solutions of inorganic electrolytes are structured somewhat differently than weak electrolyte solutions.

According to some authors, the structure of brines should resemble the structure of crystallohydrates. The existence of the concept of "salt" flotation in the theory of flotation is associated with discussion, mainly with changes on the mineral–water or water–air interface, with an increase in the concentration of inorganic electrolytes in solution. The features of structural changes in the volume of water were practically not used in the construction of the theory of "salt" flotation.

4. The well-known theories of "salt" flotation do not explain the observed phenomena of changes in the results of flotation with an increase in pulp temperature.

The most modern theory put forward by G.S. Streltsin determines the special nature of the structure of the hydrate layer on the surface of the mineral - the parallel arrangement of hydrating dipoles in solutions of low concentration and antiparallel in brines. However, this theory does not explain the reasons for the increase in the flotation activity of minerals in brines with an increase in pulp temperature.

5. The following research directions have been identified:

a) study of the structural features of aqueous solutions of inorganic electrolytes of high concentration;

b) determination of the role and significance of structural changes in water and the forces of hydrophobic interaction in the processes of flotation adhesion;

c) determination of the features and optimal conditions of barite flotation in the conditions of circulating water supply with appropriate adjustment of the water turnover scheme and the reagent regime of barite flotation.

CHAPTER 2. INVESTIGATION OF CHANGES IN THE PROPERTIES OF AQUEOUS SALT SOLUTIONS

The section performed in chapter I allowed us to determine the main directions of studying the features of mineral flotation in solutions of high concentrations of inorganic salts. It was noted that the main attention of researchers was paid to the change in the state of the mineral-liquid and liquid–gas interface. The question of changing the state of the liquid in the volume to a certain extent escaped the attention of researchers of "salt" flotation.

In this chapter, in relation to brines, the results of determining changes in both the phase interface (in the processes of foaming and wetting) and the actual structure of water in the volume are presented. From the whole complex of issues of changes in the properties of water in volume, changes in viscosity and optical characteristics (in the infrared region of the spectrum) have been studied within the framework of this work, which, it seems to them, to some extent allows us to judge structural changes in water.

2.1 Study of foaming in brines

The role of foaming in the "salt" flotation of coals was studied by V.S. Kharlamov [74]. The concentration of the solutions studied by him reached 0.5*N*. We have investigated the foaming ability of brines. Foaming was assessed by the volume of foam formed and by the time of its destruction. The experiments were carried out on the installation according to the method described in [76]. For research, chemically pure brand salts were used.

The measurement results are shown in figures 6, 7.

With an increase in the concentration of the electrolyte in the brine, the foaming ability increases. The formation of foam depends on the nature of the anion and the salt cation, moreover, the change in foaming ability corresponds to a lyotropic series of cations and anions:

$$Na^{+}>K;\ SO^{2}_{4}>Cl^{-}>NO^{-}_{3}.$$

These results are in accordance with the data [74]. When studying the foaming ability of brines, it was noticed that with an increase in the concentration of the electrolyte, the foam becomes more finely dispersed. To determine the size of the formed bubbles, the P.A. Rebinder installation was used [76]. The air bubble was squeezed out of the capillary and sat on the horizontal surface of the barite strip in the electrolyte solution.

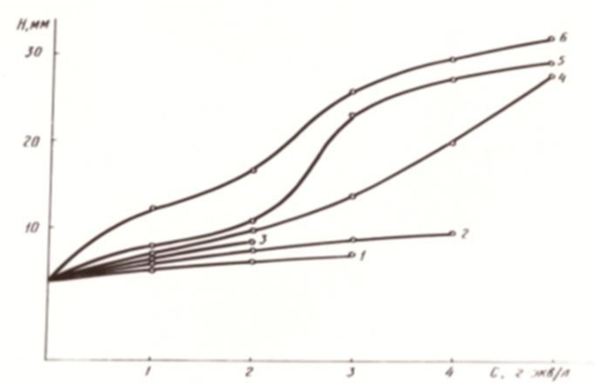


Figure 6 - Dependence of the height of the foam column on the brine concentration and its nature: KNO_3 (1); KCl (2); K_2SO_4 (3); $NaNO_3$ (4); $NaCl$ (5); Na_2SO_4 (6).

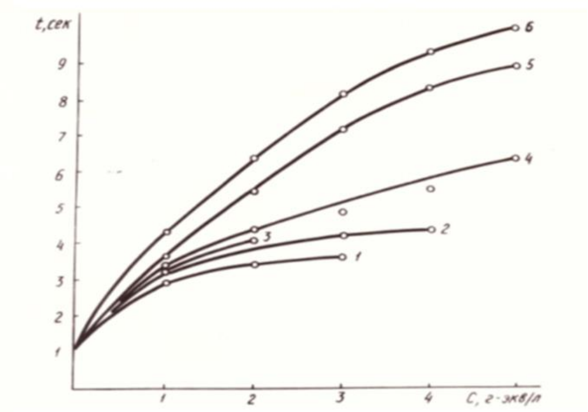


Figure 7 - Dependence of foam lifetime on brine concentration and its nature: KNO_3 (1); KCl (2); K_2SO_4 (3); $NaNO_3$ (4); $NaCl$ (5); Na_2SO_4 (6).

To maintain constant conditions for the formation of an air bubble in solutions of different densities, the height of the solution column was changed so that the hydrostatic pressure was constant. Given the difficulties of visually determining the volume of bubble V, its value was calculated using the Frumkin-Kabanov equation [8].

$$\pi \times a \times \sin\theta = \vartheta \times g \times \rho + \pi \times a^2 / 4 \times (2\,\sigma_{гж} / R - Hg\rho),$$

where a – diameter of the bubble base, cm;
θ – wetting edge angle;
ρ – density of the liquid medium, g/cm3;
R – radius of curvature of the bubble at the vertex, cm;
σ $_{г\text{-}ж}$- surface tension at the gas-liquid phase interface, din/cm;
H – bubble height, cm.

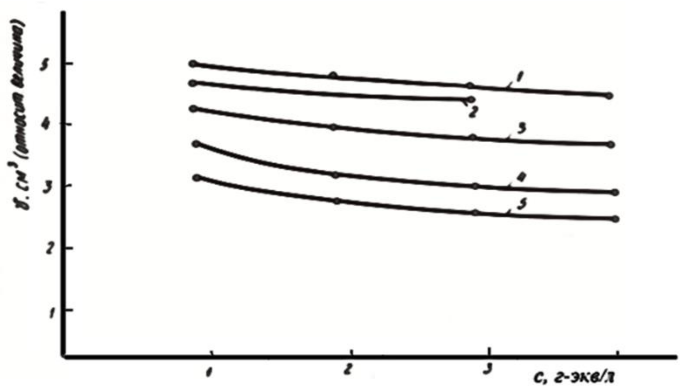


Figure 8 - Dependence of the volume of the air bubble on the concentration of brines for salts: KNO_3 (1); KCl (2); $NaNO_3$ (3); $NaCl$ (4); Na_2SO_4 (5).

The values of *α*, *Θ*, *R* and *H* were determined experimentally with an error of ± 10% (P = 0.95), and *ρ* and *б* - according to tabular data [77]. The results of the experiments are shown in figure 8. With an increase in the concentration of the electrolyte, the volume of bubbles formed under the same conditions decreases, which in turn may cause an increase in the foaming ability of more concentrated brines.

Increased foaming by itself cannot serve as a basis for improving the flotation of minerals in salt solutions. This was convincingly shown by V.S. Kharlamov [74]. At the same time, foaming undoubtedly contributes to the flotation process, ensuring the formation of a larger specific surface area in the pulp, this contributes to the intensification of flotation, and the formation of a foam layer above the pulp, which ensures the spatial separation of the fluted grains from the pulp volume.

Thus, an increase in salinity in circulating waters in this sense will be useful for the intensification of mineral flotation.

2.2 Study of the process of wetting barite in salt solutions

The wetting characteristics of the barite surface were determined by the value of the edge angle of the surface, determined at the Rebinder installation according to the method described in the previous section [76].

The table shows the obtained values of Θ and cosΘ.

As can be seen, starting from the salt concentration of 2N, an increase in the concentration leads to an increase in the value of Θ and, accordingly, a decrease in the value of cos Θ.

In Na_2SO_4 solutions, the Θ value reaches 66°.

Table 1 - Values of Θ and cosΘ depending on the concentration of the electrolyte solution

№	Name of the salt	Concentration	Θ, grade	$\cos\Theta$
1	Na_2SO_4	1	60	0,5000
		2	62	0,4695
		3	64	0,4384
		4	66	0,4067
2	*NaCl*	1	55	0,5736
		2	56	0,5592
		3	58	0,5299
		4	60	0,5000
3	*KCl*	1	57	0,5446
		2	58	0,5299
		3	60	0,5000
		4	61	0,4848
4	KNO_3	1	50	0,6428
		2	53	0,6018
		3	54	0,5878
		4	58	0,5299
5	$NaNO_3$	1	50	0,6428
		2	51	0,6293
		3	52	0,6157

The data obtained indicate that in solutions of high salt concentration, the wetting ability of water is weakened.

2.3 Investigation of the peculiarities of ion hydration in concentrated salt solutions

The literature review presented the results of studies of the nature of ion hydration in concentrated solutions.

It is necessary to pay attention to another feature of concentrated salt solutions.

According to M.A. Klochko, the existence of a maximum of electrical conductivity in solutions is explained by the fact that at a certain salt concentration, a sharp increase in viscosity begins and the mobility of ions decreases [78].

A sharp change in the viscosity of electrolyte solutions starting from a certain concentration of dissolved salt is evidence of significant changes in its structure. The dependence of the viscosity of aqueous solutions on the concentration of clusters was determined by A. Einstein in the form: [97]

$$\eta = \eta_0 \times (1 + 2{,}5V_c + 7{,}17V_c^2 + 16{,}2V_c^3),$$

where Vc – volume fraction of clusters.

By G. Jones and M. Dole, in relation to electrolyte solutions, this expression was given in the form [98]:

$$\eta = \eta_0 (1 + A\sqrt{C} + BC),$$

Where η and η_0 - corresponding viscosities of the solution and solvent;

C – solute concentration g-mol/l;

A and B – constant characteristics of the solute.

The viscosity coefficient B quantitatively takes into account the change in the structure of water depending on the properties of ions [99].

Table 2 shows the viscosity coefficients for some ions in aqueous solutions at 25° C according to [63].

Table 2 Viscosity coefficient in individual ions at water 25 ° C

Ions	Viscosity coefficient	Ions	Viscosity coefficient
Li^+	+ 0,147	Cl^-	- 0,007
Na^+	+ 0,086	Br^-	- 0,032
K^+	- 0,007	I^-	- 0,080
Rb^+	- 0,0029		
Cs^+	- 0,045		

Ions that strengthen the structure of water have a positive value of coefficient B, and ions that destroy the structure of water are characterized by negative values of this coefficient.

Viscosity coefficient *B* for salt (cation+anion) is determined additively. Given the small values of the viscosity coefficient of the chlorine ion (- 0.007) for chlorine salts ($NaCl$. $MgCl_2$, $CaCl_2$, etc.), the experimentally determined value of the viscosity coefficient B can be attributed entirely to the cation.

In weak solutions of a number of electrolytes, ion hydration, according to many authors, has a Coulomb character (63.96), when water molecules are strongly bound to the ion by electrostatic forces. The hydrophobic character of hydration has been traced for a homologous number of hydrocarbon compounds, in particular, containing NR_4+ type cations, where R is a hydrocarbon radical. In the work, the values of the coefficient *B* for solutions of high concentrations, up to saturated, are calculated. The values of the viscosity of the brines determined in the Ostwald viscometer and the coefficient *B* are given in table 3.

The experimental data were processed graphically in the coordinates $\frac{\eta/\eta_0 - 1}{C}$ and $\frac{1}{\sqrt{C}}$, in which, in accordance with the Jones-Dole equation, straight lines are obtained with Coulomb hydration, cutting off a segment equal to *B* along the ordinate axis, and the angle of inclination of the straight line satisfies the condition tg α = A. The corresponding data are shown in figure 9.

Table 3 - Values of brine viscosity and coefficients B

№	Name of the solution	Concentration, g-mol/l	Viscosity, sdr	Tabular data at 20^0C	Coefficient values *B*
1	$NaCl$				
	for weak solutions	1	1,103	1,1	0,103
	A = 0,02	2	1,157	1,16	0,08
	B = 0,08	3	1,301	-	0,10
		4	1,414	1,5	0,104
		5	2,546	-	0,31
2	$CaCl_2$				
	for weak solutions	1	1,168	1,11	0,168
	A = 0,082	2	1,240	1,27	0,12
	B = 0,086	3	1,41	1,46	0,137
		4	1,74	1,70	0,185
		5	2,85	-	0,38
3	$MgCl_2$				
	for weak solutions	1	1,23	1,2	0,23
	A = 0,124	2	1,39	1,4	0,195
	B = 0,106	3	1,61	1,7	0,203
		4	1,82	2,0	0,205
		5	2,14	-	0,228

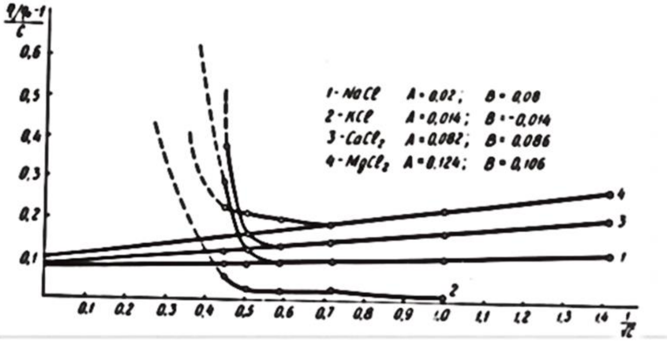


Figure 9 - Graphical processing of viscosity data according to the Jones-Dole equation

The results of the studies lead to the fact that the Coulomb character of hydration is observed for electrolyte solutions at $C \leqslant 2$ g-mol/L.

Higher concentrations lead to a significant deviation from this type of hydration.

Figure 10 shows the values of coefficients *B* for weak solutions of *Ca* and *Mg* chloride salts depending on the ionic radius of the cation (curve 1). According to the available data, values for a number of other cations are plotted on the same curve.

As can be seen, with the Coulomb character of hydration, the values of B_c decrease with an increase in the ionic radius. Curve 2 has a different character, reflecting the dependence of the coefficient *B* on the radius of NR_4^+ ions. As already noted, in this case, hydrophobic hydration takes place.

Curve 3 (figure 10) characterizes the dependence of the B_c coefficient on the ionic radius for Mg^2+, $Na+$, Ca^2+ cations according to the viscosity of 5M solutions of their chloride salts.

The nature of curve 3 is similar to curve 2 and indicates a change in the hydration of cations from Coulomb in weak solutions and hydrophobic in high concentration solutions. This circumstance allows us to assume that the structuring of water in concentrated solutions sharply increases and electrolyte ions act as analogues of hydrocarbon radicals.

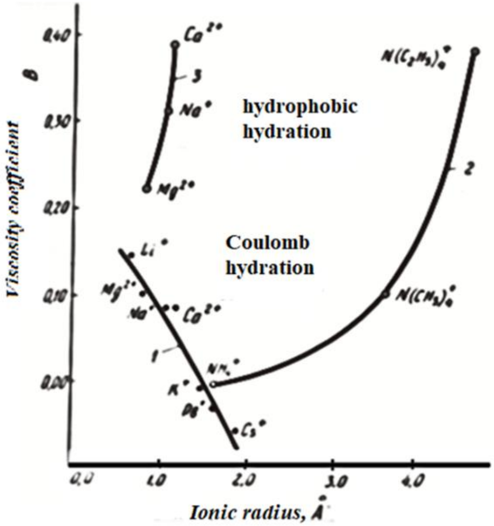


Figure 10 - Dependence of the viscosity coefficient B on the radius of ions

2.4 Research in infrared spectra

The statement made in the previous section about the change in the nature of ion hydration during the transition from weak solutions to brines, from our point of view, must be confirmed by the presence of corresponding structural changes in water. One of the methods most sensitive to structural changes at the molecular level is infrared spectroscopy. For these purposes, it was used by G.V. Yuknevich when studying the features of the structure of water [79].

The technique of removing the IR spectra of water assumes the need to prepare its thin strips in the preparation. Removal of X-ray spectra in cuvettes is impossible due to the large absorption of infrared rays by water. That is why we applied the technique of removing the spectra of water and its salt solutions "on optical contact" between two plates of KRS, the material of which, as is known, does not interact with water. The spectra obtained by us are shown in fig. 11, 12, 13, 14.

As can be seen, in all cases, in 1N salt solutions, there is a narrowing of the absorption bands in the region of 3400 cm^{-1}. It is known [79] that this is the region of oscillations of groups of OH^{-} water. The narrowing of the absorption band indicates the quantitative predominance of oscillations of a certain frequency. Such a change in the IR spectrum is interpreted as an increase in the volume of water H – bonds of a certain energy. Indeed, with a high concentration of salt in the solution, its ions should enter the framework of the water structure and enhance its structuring. The choirs note that any separation of charge leads to an increase in the hydrogen bond [63]. In this case, there is a large number of ions of different signs, which causes an increase in the binding of frame formations in water according to the scheme: frame element - cation - frame element - anion - frame element, etc..

It is known that "concentration" compression of the double electric layer occurs on the surface of a solid at high concentrations of electrolytes in solution. The structural change in water at a high salt concentration can be considered by analogy with this "concentration" compression of the double electric layer.

Thus, according to IR spectroscopy data, it can be assumed that in solutions of high concentrations of inorganic electrolytes, there is an increase in the structuring of water. This conclusion confirms the conclusion made in the previous chapter on the basis of ion hydration data.

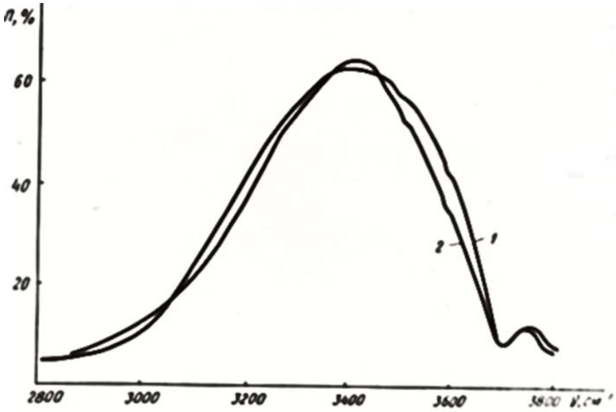


Figure 11 - Comparison of infrared (absorption) spectra of pure water (1) and 1N MgCl2 solution (2)

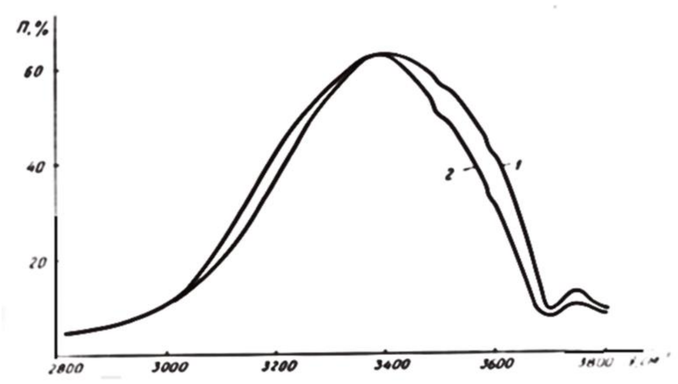


Figure 12 - Comparison of infrared spectra (absorption) of pure water (1) and 1N solution of KCl (2)

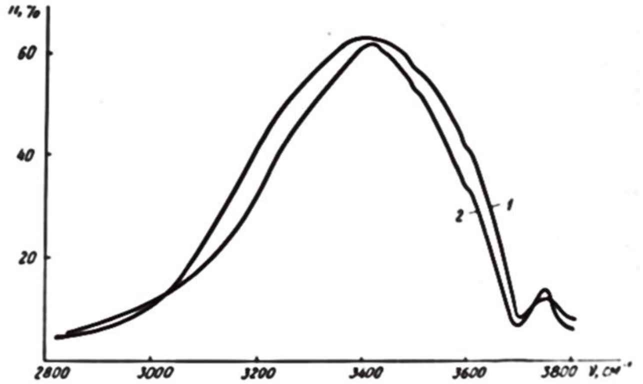


Figure 13 - Comparison of infrared (absorption) spectra of pure water [1] and 1N NaCl solution (2)

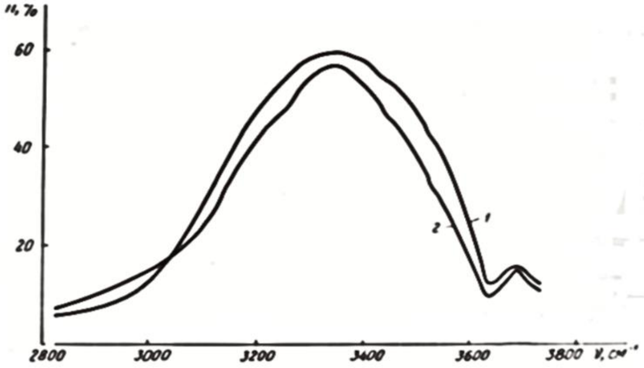


Figure 14 - Comparison of infrared (absorption) spectra of pure water (1) and 1N CaCl2 solution (2)

The increased structuring of water as a result of the dissolution of substances introduced into an aqueous solution causes, as is known, the occurrence of hydrophobic interactions [OHI] caused by the desire of water to maintain its equilibrium structure at a given temperature.

Hydrophobic interactions lead to the ejection of ions, molecules and particles from the volume of the aqueous solution, which contribute to the strengthening of water structuring. The result is ion association, micelle formation, flocculation and flotation.

2.5 Chapter conclusions

The experimental data presented in this chapter and their discussion allow us to draw the following brief conclusions.

1. In accordance with the available results of previously performed studies, the increase in foaming in solutions of inorganic salts has been confirmed.

For the first time, the study of foaming in brines showed that in this case, an increase in the concentration of the solution leads to increased foaming and to a decrease in the size of air bubbles during aeration.

According to the measurement of the wetting edge angles, it is shown that the wetting abilities of water decrease with an increase in the concentration of salts.

2. The nature of ion hydration in salt solutions varies significantly from weak solutions to brines. It was shown for the first time that ion hydration becomes hydrophobic in solutions of high concentrations. This

thesis is confirmed in studies of infrared spectra, according to which it is established that the structuring of water in brines is enhanced.

It was suggested, confirmed later, that strong hydrophobic interactions should occur in brines causing flocculation and flotation of minerals.

CHAPTER 3. INVESTIGATION OF THE MECHANISM OF "SALT FLOTATION" OF BARITE

3.1 Mineralization of bubbles during flotation

Many processes are described by the most general laws. One of them are two principles of thermodynamics. The first principle of thermodynamics is the law of conservation of energy. In nature, there is a constant transformation of one type of energy into another in strictly equivalent relations.

At the same time, energy is not created and is not lost. All types of energy pass into each other. Otherwise, we can say that in an isolated system the sum of all types of energy is constant. The first principle of thermodynamics does not allow us to determine whether the transformation of one type of energy into another (or the exchange of energy between bodies) will occur and in which direction.

All real processes are non-equilibrium (unsteady) and tend to bring the system to an equilibrium state. Nonequilibrium processes proceed in the direction of achieving equilibrium spontaneously. A necessary condition for their flow is the presence of energy potential or intensity (intensity) of energy.

The second principle of thermodynamics states: spontaneous energy transfer is possible only from a system with a higher energy potential to a system with a lower potential and continues until thermodynamic equilibrium occurs.

The direction of energy transitions is determined by the "quality" of energy — its potential. For example, thermal energy spontaneously passes from a body with a higher temperature to a body with a lower temperature. Here the potential is the temperature. At the same time, the total energy reserve in one or the other body does not matter.

According to the second principle of thermodynamics, the internal energy of the system cannot be completely converted into work. The internal energy of the system is considered as the sum of two terms. $E = P + T$. Here P is a part of the internal energy that can be turned into work (free energy P). Free energy is in the system in the form of potential energy, and its amount decreases as the system performs work. T is a part of the energy that cannot be turned into work (bound energy T).

The bound energy can only pass into thermal energy dissipating in space (energy dissipation). Any isolated system in a spontaneous process tends to reduce the level of free energy to a minimum and go into a state of stable thermodynamic equilibrium. Consequently, only such spontaneous processes can occur in an isolated system, as a result of which the free energy of the system decreases.

This is the principle of minimum free energy. It allows you to determine the direction of processes, find out in advance the conditions of thermodynamic equilibrium and establish the most probable state of the system.

The main form of phase interaction during flotation is adsorption processes and heterogeneous chemical reactions. The reagents are fixed on the surface of the phases interacting during flotation by adsorption.

Adsorption is the process of concentrating a substance (adsorbate, adsorbent) from the volume of phases on the interface. It occurs spontaneously under the action of the surface forces of the adsorbent and is accompanied by a decrease in the free surface energy of the system and the release of a certain amount of heat – the heat of adsorption. Adsorption processes always take place at the interface of the phases.

The adsorbate molecules are attracted not only to the adsorbent, but also to each other. As the surface fills, this attraction increases due to a decrease in the average distance between the molecules.

With a very dense filling, attraction turns into repulsion. The attraction of molecules of two different phases, which manifests itself on the surface of their interface, is called adhesion (stickiness). The adhesion is based on the forces of molecular attraction, as in physical adsorption. When separating these phases, it is necessary to expend energy characterized by the work of adhesion (erg / cm^2).

The adhesion work is equal to the sum of the surface energies of these phases minus the interfacial surface energy at their interface: $A = U1 + U2 - Us$, where U1, U2 is the surface energy of phases 1 and 2, Us is the interfacial energy at the interface of phases equal to:

$$Us = S\ \zeta,$$

where ζ – specific surface energy of the interface, often referred to as surface tension, erg/cm2, din/cm (n/m);

$$\zeta = Us / S.$$

The main types of adsorption are physical and chemical. During physical adsorption, the adsorbate molecules retain their individuality, and during chemical (chemisorption) they form chemical compounds with the adsorbent.

3.2 Физическая адсорбция. Химическая адсорбция

The adsorbed substance and the adsorbent crystal lattice are independent systems The adsorbed substance and the adsorbent crystal lattice are energetically one.

The connection with the lattice is carried out due to the Van der Waals forces of intermolecular attraction, which is not accompanied by processes at the electronic level. The addition of an atom to the crystal lattice is caused by the transition of electrons from the atom to the lattice (or vice versa) or by the socialization of electrons by them.

The thermal effect and binding strength of molecules or ions are small. The thermal effect and binding strength of molecules or ions are significant.

Uniform distribution of the reagent over the surface of the adsorbent (mineral), the reagent is fixed primarily on the most active areas of the surface. As they fill, an adsorption layer may form on other parts of the surface.

Many minerals are crystals that have heterogeneous surface properties. This is due to the origin and structure of ores. The atoms of the crystal lattice on different sides of the crystal have different levels of free surface energy. Therefore, the ability to adsorb different compounds from the solution is different. An atom or ion 1 located inside a crystal expends all its bonds to interact with neighboring atoms. The atom on the surface of the face has one unsaturated bond, the atom on the edge of the face has 2, and the atom on the top of the crystal has 3 unsaturated bonds.

Therefore, these atoms have different ability to interact with water and reagents. The mineral surface is energetically unequal and has an adsorption heterogeneity.

First of all, the interaction with water and reagents begins at the most active sites, where there are more unsaturated bonds. Deviations in the structure of real crystals from idealized ones are called defects in the crystal lattice.

Interstitial metal ions Me and empty metalloid nodes M are defects with a plus sign). These are the places most favorable for fixing the reagent anions. Interstitial metalloid ions M and empty metal nodes Me are defects with a minus sign. Here the fixation of the reagent is unlikely.

In addition, different areas of the mineral surface have different microrelief - protrusions, depressions, microcracks, inclusions of other minerals and isomorphic substitutions of lattice atoms. (Isomorphic substances are those whose atoms or ions can be mutually substituted in crystal lattices, forming solid solutions.

A prerequisite is the proximity of the sizes of ions, atoms or groups of ions and the equality of charges.) There is another type of volumetric and surface heterogeneity caused by the mosaic-block structure of the crystal.

The crystal consists of a set of numerous and disoriented blocks relative to each other. Blocks are small formations (microns), each of which can be a perfect crystal. The mosaic structure affects the activity of the surface areas of the mineral when it interacts with reagents.

A special place in the issue of heterogeneity of minerals is occupied by dislocations – large distortions of the crystal structure. Previously, it was believed that liquids are similar in properties and motion of molecules to gases.

The modern theory of the liquid state brings it closer to the solid (crystalline) state in the temperature range close to the crystallization point.

Solids are characterized by a long-range order in the arrangement of molecules, i.e. the presence of discrete (discontinuous) distances between the particles of matter.

X-ray studies have shown that the arrangement of molecules and their associates in liquids has a short-range order, i.e. at short distances in liquids there is an order of the same type as in crystalline bodies.

In water, this short-range order is more pronounced than in other liquids. In the region of high temperatures, water has properties approaching the properties of gases; in the region of low and at low specific volumes, it has properties of solids.

In this case, the structure of water is called quasi-crystalline. Water belongs to the number of highly associated liquids, hydrogen bonds play an important role here. Being a typical liquid, water has many anomalous features. For example, the melting of ice is accompanied by its compression, not expansion (as is the case for the vast majority of substances). With an increase in temperature from 0 ° to 4 °C, the density of water increases, and only when heated above this temperature begins to decrease. The water molecule has a significant dipole moment (1.87 debye), which occurs due to a sharp asymmetry in the arrangement of positive and negative charges. Two hydrogen atoms are located in a water molecule at an angle of 104.50 with respect to an oxygen atom. There is a covalent bond between the H and O atoms. It is formed by a pair of electrons from oxygen atoms O and hydrogen H, i.e. these electrons pass into joint possession of both atoms.

In ice, each molecule is surrounded by four molecules, and in liquid water, a similar arrangement of molecules in the form of tetrahedra is observed. This structure is called openwork.

Water consists of two types of molecules. The molecules of the first type are connected by hydrogen bonds with their neighbors, form a stable tetrahedral framework and do not rotate. The voids in the associated tetrahedra are filled with the second type of molecules that rotate freely.

These molecules are devoid of hydrogen bonds. The peculiarity of the hydrogen bond is that in a water molecule, a hydrogen atom can be attracted to a neighboring molecule. Due to the absence of hydrogen bonds, molecules of the second type are energetically unequal with molecules of the first type and interact weakly with them.

The movement of water molecules occurs mainly through voids in the frame. In most cases, water acts on the solid phase as a solvent, some amounts of the mineral are transferred to the volume. Therefore, during flotation, minerals react not with pure water, but with a solution saturated with mineral matter and gases. Sometimes the composition of such a solution is quite complex.

The dissolving effect of water is associated with the hydration of solid phase ions and their separation from the crystal lattice, which is due to the significant dipole moment of water molecules.

Therefore, large forces of electrostatic interaction arise between the water molecules and the solute.

The gas phase in the flotation process is more often represented by air. Air composition by volume: nitrogen 78.1%, oxygen 20.9%, argon 1%. In addition, there is carbon dioxide, helium, neon, krypton. It can be sulfur dioxide, ammonia, etc. industrial gases.

In addition to air, there are also water vapors in the volume of air bubbles. As a result of interaction with water, the composition of the air changes. For example, dissolved air contains 65% nitrogen, 35% oxygen. Air bubbles play a positive role, being carriers of particles of the floated mineral. The adsorption of gases from the atmosphere on the surface of mineral particles forms gas films that hydrophobize the mineral.

The adsorption of gases can change the surface properties of minerals, for example, the oxidation of sulfides with oxygen worsens the floatability.

Of great importance for flotation is the solubility of air in water and its change depending on temperature and pressure.

At atmospheric pressure and a temperature of 20 °C, 1 liter of water dissolves: nitrogen 0.016 liters; oxygen 0.031; carbon dioxide 0.88; hydrogen sulfide 2.58; ammonia 702 liters.

The solubility of gases that do not chemically interact with water is very low. Gases that actively interact with water (carbon dioxide and sulfur dioxide, hydrogen sulfide, ammonia, etc.), dissolve in significant quantities. The solubility of gases decreases with increasing temperature and increases with increasing pressure.

When a mixture of gases (for example, air) is dissolved, the solubility of each of the components depends on its partial pressure in the mixture (Henry's law). In places of pressure drop in flotation machines, air bubbles are actively released from the solution. The use of such bubbles is based on the use of a number of types of flotation machines. Initially fixed on the surface of mineral particles, microbubbles released from the solution activate the adhesion of large bubbles to these particles.

3.3 Investigation of the features of barite flocculation in solutions of inorganic salts

In order to clarify the effect of high concentrations of salts on the flotation of barite, studies were conducted to determine the flocculation of barite minerals in solutions of the collector (sodium oleate).

The dissolution of hydrocarbon compounds in water leads to the emergence of hydrophobic interactions (HI) due to a decrease in entropy due to the structuring of water.

Hydrophobic interactions cause the "ejection" of hydrophobic or hydrophobic mineral grains collected by reagents from the liquid volume, resulting in flocculation, and in the presence of air bubbles in the pulp, flotation itself.

As noted by Nemeti and Chirac, one of the most characteristic features of HI is their temperature dependence, unlike the London-Van der Waals forces, the HI increases with increasing temperature [100]. A.A. Pchelin decided to study the HI in aqueous suspensions based on the temperature dependence of the fluff of the grain sediment [80].

The fluff of the sediment during the formation of the sediment column is associated with an increase in the interaction forces in point contacts when a falling grain collides with a grain lying in the sediment and corresponds to an increase in the degree of flocculation [81].

The fluff of the sediment can also occur for grains of an isometric shape, for example, spherical, since the coupling of several balls forms anisometric aggregates, the behavior of which is similar to anisometric single grains.

The height of the grain sediment column was determined on a device consisting of upper and lower storage tanks connected by a narrow measuring tube with an inner diameter of 2.5 mm. In the lower storage tank, a Schott filter is soldered for filtration changes in the composition of the solution.

The device was filled through the upper channel with a vacuum suspension. The suspension of mineral grains was selected in such a way that in the initial measurements the meniscus of the sediment column was fixed in the middle of the height of the measuring tube. The outer jacket of the device is used for thermostating the suspension and was connected to a water thermostat that maintains the set temperature with an accuracy of ±0,02^0 C.

The sensitivity of measurements on the device depends on the ratio of the volume of the storage tank and the diameter of the measuring tube.

The minerals were prepared by crushing large minerals of pure samples followed by dry sieving on sieves of 0.25 and 0.1 mm. Processing of the mineral powder sample with a grain size of - 0.25 + 0.1 mm was carried out in a separate glass with subsequent transfer of the suspension into the device. After processing the powder in the collector's solution, it was washed with a tenfold volume of distilled water. Previously, the powder, solution and water were evacuated to remove dissolved gases. Additionally, flushing was carried out in the device by filtering water through a Schott filter until a constant and reproducible value of the sediment height was obtained.

In some experiments, fluff (or compression) of the sediment was observed to such an extent that the sediment meniscus went beyond the scale. In these cases, sprinkling or, conversely, grain sampling was carried out and the value of the height of the sediment column was taken into account the value in this solution.

Barite, which is a naturally hydrophobic mineral, is characterized by compression of the sediment of its grains with an increase in the temperature of the suspension. At a concentration of sodium oleate of 10^{-6} g-mol/l, the nature of changes in the height of the sediment column (compression) with a change in temperature is preserved. At higher concentrations of the collector, the sediment of barite grains fluffs up and to a greater extent, the higher the concentration of the solution.

With an increase in the concentration of salts, the precipitate fluffs, flocculation of barite grains in high-concentration salt solutions with an increase in the temperature of the suspension. Also, in high-concentration solutions, the nature of the change in sediment sediment height from temperature is similar to the change in collector solutions. This circumstance allows us to assume that responsible for the changes in the degree of aggregation of barite in this case is a structural change in oxen, causing the occurrence of hydrophobic interaction forces.

3.4 Investigation of the features of the floatability of barite and quartz in salt solutions

In order to clarify the causes of changes in the degree of hydrophobicity (hydrophilicity) of the surface in solutions of inorganic salts, flotation experiments were conducted with monominerals of barite and quartz with a size of -100+63 microns. The experiments were carried out in the Hallimond tube.

The conditions for all experiments were the same: the flotation time was 5 minutes, the weight was 200 mg, the agitation time of the mineral with salt was 5 minutes.

For research, salts of the brand " chemically pure " dissolved in distilled water were used.

The results showed that all the studied salts significantly activate the flotation of barite and quartz by increasing the concentration.

The greatest hydrophobization is observed in solutions of $CaCl_2$ and $NaCl$, and quartz in a solution of KCl. Thus, in 5N solutions of $CaCl_2$ and $NaCl$, the yield of barite is 60% and 52%, respectively, and the yield of quartz in 3N KCl is 42%. Quartz is the main accompanying mineral of barite. Its depression is carried out by sodium silicate. The possibility of quartz depression in KCl solution with the addition of 0.5 kg/t Na_2SiO_3 was investigated and almost complete depression of quartz with sodium silicate in saline solution was established.

3.5 Calculation of the energy of hydrophobic interactions in aqueous solutions of hydrocarbons

Studies of the flocculation of barite in brines of inorganic salts and the floatability of quartz and barite in the same solutions in the absence of a collector have shown that the changes caused by the salts introduced into the water are to some extent similar to those changes inherent in the reagents of collectors. It was previously noted that a change in the structure of water can cause hydrophobic interaction forces in aqueous solutions. It should be shown that hydrophobic interactions can contribute to the activation of flotation.

The aim was to calculate the energy of hydrophobic interaction and its change with temperature change and comparison with the results of mineral flotation during pulp heating.

– membranous.

The results obtained are shown in figure 15.

An increase in temperature invariably leads to an increase in the extraction of galena, chalcopyrite, sphalerite and chalcosine. These data cannot be explained by a decrease in the viscosity, density or surface tension of water with an increase in temperature, since under analogical conditions, grains of pyrite (possibly oxidized surfaces), quartz and calcite were not floated.

To explain the data obtained, calculations of the energy of hydrophobic interactions (E_{HI}) with temperature changes were carried out.

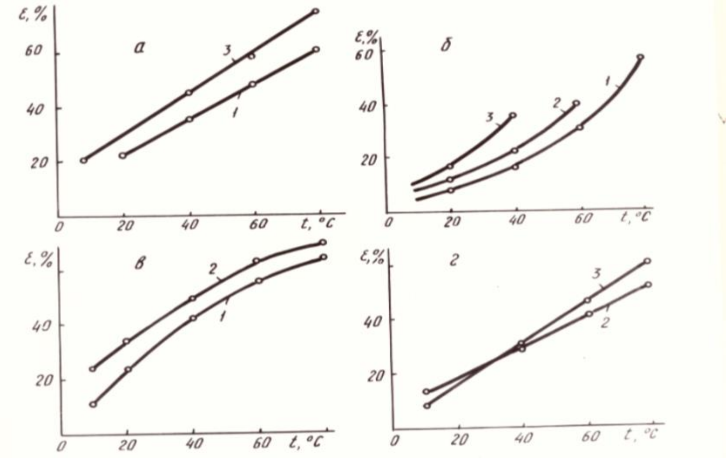


Figure 15 - Results of flotation of minerals without a collector when the pulp is heated: a - galena; b - chalcopyrite; c - sphalerite; d - chalcosine at a pH equal to 6 (1), 8 (2), 10 (3)

The calculations were based on experimental data from Nemeti and Shirag, which determine the molar fraction of hydrogen bonds in pure water at different temperatures and the same value in solutions of apolar compounds, for example, aliphatic and aromatic hydrocarbons [101]. The value of the molar fraction of hydrogen bonds in water at a given temperature characterizes its structure, the change of which, when introduced into a hydrocarbon solution, meets a certain resistance, causing the occurrence of hydrophobic interactions. The value of the corresponding energy can be estimated by changing the energy of the hydrogen bond. Accordingly, the data is unknown. The calculation is based on the heat capacity of the water.

Assuming that in the temperature range 0 – 70^0 C, the heat capacity of water varies slightly (from 75.2 to 75.9 J/mol^{0}C, at 760 mmHg), averaging 75.5 J/mol ^{0}C, based on the equality:

$$C_S = \Delta E_{kin} + \Delta E_{V-D-W} + \Delta E_{HB} + A,$$

where ΔE_{kin} - the change in the kinetic energy of molecules when heated $1 \cdot {}^0$C, equal to 12.5 J / mol$\cdot {}^0$C;

ΔE_{V-D-W} - the change in the energy of the van der Waal attraction is a value that, on average, for the temperature range 0 – 70^{0}C can be assumed to be equal to 3 J/mol^{0}C;

ΔE_{HB} - energy spent on breaking hydrogen bonds;

A – the work of water expansion, which, due to the smallness of the volume change, can be neglected.

It turns out that when heated by one degree:

$$\Delta E_{HB} = 75{,}5 - (12{,}5 + 3) = 60 \text{ J/mol}^0\text{C}.$$

To calculate the value of the hydrogen bond energy in different temperature ranges, it is necessary to know the molar fraction of bonds that break when heated.

In accordance with the data for different temperature ranges, the calculated values of the molar energy of the hydrogen bond are given in table 4 [101].

Table 4 - Calculated data of hydrogen bond energy and hydrophobic interactions

Temperature range	Broken hydrogen bonds, fraction of a mole by [101]	Energy $H_B \cdot 10^3$ J/mol^{0}C	Broken hydrogen bonds, fraction of a mole according to [101]		$E_{HI} \cdot 10^3$, J/mol^{0}C	
			in solution. aliphatic. carbohydrate. (bhutan)	in solution. aromatic carbohydrate. (benzene)	in butane solution	in benzene solution
0 -10	0,035	17,00	0,141	0,103	2,40	1,70
10 - 20	0,031	19,40	0,134	0,097	2,60	1,90
20 - 30	0,028	21,40	0,126	0,091	2,70	1,90
30 - 40	0,025	24,00	0,119	0,085	2,90	2,00
40 - 50	0,021	28,60	0,108	0,077	3,10	2,20
50 - 60	0,018	33,40	0,098	0,069	3,30	2,30
60 - 70	0,014	42,80	0,080	0,059	3,40	2,50

The increase in the value of E_{HB} with an increase in temperature should be explained by an increase in the dissociation of water, and, accordingly, an increase in the separation of charges leading to the strengthening of the hydrogen bond [63].

The value of the energy of hydrophobic interactions in a given temperature range can be obtained by multiplying two values: the change in the molar fraction of hydrogen bonds in a hydrocarbon solution and the value of the hydrogen bond energy.

The E_{HI} values calculated in this way are given in table 6 and shown in figure 23. With a decrease in the proportion of broken hydrogen bonds in the range of higher temperatures, the energy of hydrophobic interactions increases with an increase in temperature, which corresponds to the available concepts [83].

Different energy values for butane and benzene solutions indicate the dependence of hydrophobic interactions on the structure of the hydrocarbon compound, which in turn means that different flotation reagents – collectors and minerals will be characterized by different values of E_{HI}. As a result of increased hydrophobic interactions, flotation adhesion processes such as flocculation and mineralization of air bubbles with an increase in temperature, despite a decrease in van der Waals attraction, under other constant conditions, should be activated, which was observed in the above experiments.

Accordingly, hydrophobic interactions should occur in salt solutions due to structural changes in water, as noted above. These forces may be responsible for increasing the flotation activity of minerals during flotation in concentrated salt solutions.

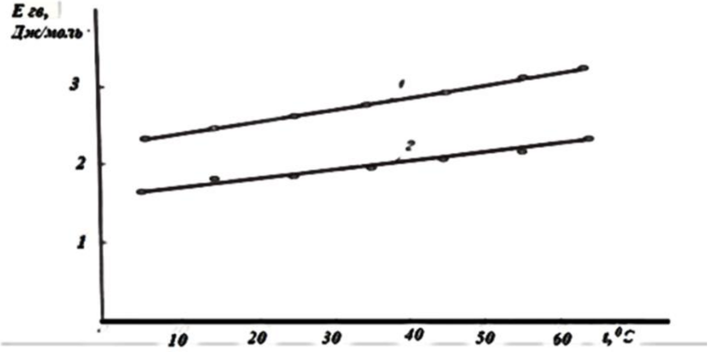


Figure 16 - Change in the energy of hydrophobic interactions with temperature changes in a solution of butane (1) and benzene (2)

3.6 New ideas about the mechanism of "salt" flotation

Of the existing theories of "salt" flotation, the hypothesis of G.S. Streltsin is of particular interest as the most probable and corresponding to the essence of the phenomena occurring. The hypothesis of G.S. Streltsin does not consider the changes occurring on the surface of air bubbles, which emphasizes the subordinate importance in the "salt" flotation of processes occurring at the gas-liquid interface. The materials presented in this chapter confirm the validity of this statement, since the phenomenon of sediment fluff with an increase in salt concentration increases, indicating an increase in the hydrophobic hydration of barite mineral grains in brines, which in itself is the basis for the assertion of an increase in the flotation activity of barite. The processes of increasing foaming in brines of inorganic salts can be considered as a phenomenon that promotes, but does not determine, the flotation of barite.

Thus, when considering the theory of "salt" flotation, the main attention is paid to the mineral – water salt solution system.

The available experimental data suggest that the hypothesis of G.S. Streltsin needs a significant addition. Indeed, if the hydrophobicity of the mineral surface in concentrated salt solutions is determined by the antiparallel arrangement of hydrated water dipoles, then with an increase in temperature, the degree of hydration should decrease, since an increase in temperature will cause "erosion" of the hydrate layer of any structure, including "antiparallel".

The given calculated data on the increase in the energy of hydrophobic interactions with an increase in the temperature of the suspension allow us to assert that the condition of "salt" flotation is met not only by a special "antiparallel" structure of the surface hydrate layer on the particles of mineral grains, but also by a special structure of water in the volume, which determines the growth of the forces of the HI with an increase in temperature and overrides the growth of hydrophilization of the liquid-solid surface due to the "erosion" of the hydrate layers of the hydrophobic structure. Thus, a new consideration of the mechanism of "salt" flotation consists in the assertion that, firstly, in concentrated salt solutions, the surface of mineral grains is hydrophobized due to the occurrence of hydrophobic hydration of ions both in the volume of the solution and on the surface of mineral grains (the structure of the hydrate layer on the surface of mineral grains at the same time probably corresponds to the antiparallel arrangement of the water dipole - according to G.S. Streltsin), secondly, in concentrated solutions of indifferent salts, forces of hydrophobic interactions arise, causing the expulsion of ions and mineral grains adsorbing these ions from the volume of water, which leads to increased flocculation in the presence of air bubbles of flotation, and thirdly, that with an increase in the temperature of the suspension, despite the inevitable "erosion" of the hydrophobic structure of hydrated ions on the surface of mineral grains, flocculation and flotation is activated due to the overlapping gain the energy of the HI.

An increase in foaming in brines is favorable for the "salt" flotation of minerals, but does not determine the observed effect as a whole.

3.7 Chapter conclusions

Based on the results of the studies presented in this chapter, the following brief conclusions can be drawn:

1. Flocculation of barite grains in brines of high concentration salts increases with increasing suspension temperature. This circumstance allows us to assume that responsible for the changes in the degree of aggregation of barite, causing the occurrence of hydrophobic interaction forces.
2. According to the study of the behavior of barite and quartz grains in salt solutions, it immediately follows that the results of flocculation and flotation actually coincide and that it is the hydrophobic interactions in solutions of high concentrations of non-organic salts that determines the results of flotation of barite and quartz.
3. The performed calculation of the energy of hydrophobic interactions in aqueous solutions confirms that the value of the HI increases with an increase in temperature and that this additionally justifies the improvement of the flotation of minerals with an increase in the temperature of the suspension.
4. A new understanding of the mechanism of "salt" flotation, which is based on the theory developed by G.S. Streltsin and complements it with the statement about the essential role of structural changes in the volume of water and the determining significance of the forces of the HI in the processes of flotation adhesion in the conditions of "salt" flotation.

CHAPTER 4. INVESTIGATION OF BARITE FLOTATION FROM THE ORES OF THE KARAGAILINSKY DEPOSIT IN SALINE WATERS

4.1 Geological characteristics of the Karagailinsky deposit and the existing technology of barite enrichment from ores

The Karagailinsky barite-polymetallic deposit is located in the Karaganda region.

The deposit area is located on the northern slope of the Balkhash-Irtysh highlands and is composed of sedimentary-metamorphic rocks forming a synclinal fold extending from north-west to south-east along an azimuth of 100-150°.

The main ore body is confined to the northeastern wing of the syncline and is divided by the discharge shift into Large [western] and Small [eastern] lenses with an amplitude of displacement along the disturbance by 250 meters. The total length of the ore deposit is 1100 meters, of which the Large Lens accounts for 900 m.

An ore deposit is an irregular formation of wave-shaped ore bodies composed of baritized and scarred rocks interspersed with ore materials. Ore bodies are deposited according to the rocks containing them.

The following types of rocks take part in the geological structure of the deposit:

1 Quartz-barite
2 Baritized siliceous-clay shales
3 Hornfels
4 Siliceous-clay shales
5 Microquartzites
6 Skarny

These varieties of rocks form irregular-stratified and plast-Lenticular veins, mutually passing into each other, both in strike and in fall.

Quartz-barite rocks are of the greatest importance in the structure of ore deposits. The content of barite is 20-90% and quartz is 10-40%. These rocks form powerful interlayers and consist of fine and medium-grained barite, nests and veins of white coarse-crystalline barite and unstable fine-grained quartz. Mineralization is represented by galena, cerussite and sphalerite.

Baritized siliceous shales separate the lenses of quartz-barite rocks and are traced in the recumbent side of the ore deposit. These shales, along the strike and fall, turn into quartz-barite rocks, into baritized hornfels and siliceous shales.

Hornfels – the lenses of quartz-barite bodies are separated and have a significant distribution and a number of varieties in the western part of the main site.

Siliceous-clay shales at the western end of the deposit, the components of the ore deposit change: quartz-barite bodies are wedged out and they are represented by low-power interlayers of hardened siliceous-clay shales, similar in appearance and internal structure to the shales of the recumbent side. By stretching and falling, siliceous shales turn into cornea and baritized shales.

Microquartzes are dense, monolithic differences consisting of 95% fine-grained quartz [0.05-0.2 mm]. They are not marked on the surface in the contour of the Large Lens, they occur only at a depth where they contain nesting secretions of barite and rare fine inclusions of galena and a significant amount of chalcopyrite. By stretching and falling, microquartzites pass into cornea, and sometimes into quartz-barite ores.

Scarns have subordinate meanings and explanations in them are rare. According to the content of the main valuable components, ores are divided into the following types:

1 Lead-zinc barite
2 Lead-zinc
3 Lead
4 Zinc
5 Baritones
6 Copper

All the identified types of ores are interconnected and practically have no clear separation.

According to barite, four generation groups are distinguished.

The first generation rarely prevails over the others and occur in the form of irregular grains in accretions with quartz. The grain size ranges from 0.03 mm to 1 mm. It is often represented by a dense almost homogeneous mass with quartz relics and sulfide grains.

Fine-grained barite is observed in germination with quartz and saturated with frequent inclusions of sphalerite.

The second generation does not contain sulfide minerals, grain sizes from a few millimeters to 1-2 centimeters. The second generation barite is formed due to the recrystallization of the first generation barite.

The third generation is represented by low-power veins that secrete all the rocks of the deposit.

The fourth generation is expressed in the form of deposits and crusts, represented by a surface formation. They are rare.

Barite is the main ore-forming mineral. It is in close fusion with quartz. Fine-grained barite in germination with quartz composes a quartz-barite mass. The size of the barite inclusions in these areas is 0.03-0.1 mm. The coarser-grained barite [0.15-0.8 mm to 10.0 mm] forms independent sections.

In areas composed of fine-grained quartz, barite occurs in the form of veins and inclusions arranged in the form of veins and inclusions.

Quartz and barite in quantitative terms form a series of constant transitions from the sharp predominance of quartz to the predominance of barite. The grains of barite are finer-grained where there is a lot of quartz and where fine-grained baritone prevails.

Galena is a common sulfide mineral. It is in close fusion with sphalerite, forming a thin impregnation. The size of galena inclusions in the barite-quartz mass is 0.01-0.5 mm, less often up to 3.2 mm. In the case of oxidized galena, cerussite or chalcosine develops. The size distribution from 0 to 2 microns is 40%, 20-50 microns is 40%. above 50 microns – 20%.

Cerussite replaces galena, is often permeated and surrounded by a covellin rim. It is characterized by an independent inclusiveness among barite, is in fusion and malachite, covellin, smithsonite and limonite.

Anglesite - occurs in small quantities in association with cerussite and in the form of spots on the edge of galena and in the rock.

Sphalerite occurs in clusters of irregularly shaped grains included in the quartz-barite mass. In some veins, sphalerite has a quantitative predominance over galena. Most often, sphalerite is in fusion with galena.

Smithsonite is represented by dots and spots among the rocks, sizes range from 3 microns to 160 microns.

Pyrite is unevenly distributed throughout the ore and, in relation to sphalerite, galena and chalcopyrite, is an earlier mineral by the time of formation. The percentage of accretions: 15-20% with galena, 20-25% with sphalerite, 10% with other minerals. In some places it is completely or partially replaced by hematite, hydrohematite and limonite.

Chalcopyrite is in accretion with sphalerite and galenite, often forming an emulsion impregnation with a size of 0.005-0.015 mm. During the oxidation of chalcopyrite, covellin develops on the surface, forming edges with a thickness of 0.05-0.1 mm and bornite with a capacity of 0.015-0.3 mm.

Chalcosine is observed in irregularly shaped grains and has uneven boundaries of accretions. As a result of oxidation, chalcosine is impregnated inside with needle-like covelin crystals. The size of chalcosine secretions is 0.008-0.3 mm.

Pyrrhotite occurs as rare inclusions in idiomorphic crystals of pyrite with a size of 0.1 mm.

Covellin is observed in ore sites enriched with sphalerite, chalcosine, cerussite. Grain sizes 0.03-0.2 mm.

Iron hydroxides develop along pyrite, sometimes completely replacing it or forming edges around the grains. The capacity of the edges is 0.01-0.3 mm.

Malachite is in fusion with malachite and cerussite. The content is insignificant.

Azurite is observed in fusion with malachite and cerussite.

Viterite is noted in the quartz-barite mass in fusion with chlorite and epidote. Irregular viterite grains with a size of 0.14-0.03 mm, less often 0.3 mm.

Quartz is the main rock-forming mineral, is in close germination with barite.

Epidote is distributed throughout the ore fairly evenly. It is more often observed in the form of inclusions in thin veins in the quartz-barite mass in fusion with garnet. The size of its secretions is 0.02-0.8 mm.

Garnet is colorless or yellowish in passing light. Grain size 0.01-0.02 mm clusters 0.5-0.8 mm. Garnet is associated with quartz and epidote.

Apatite is marked as thin rare inclusions in quartz with a size of 0.003-0.01 mm.

The charge is observed in fusion with radially radiant barite. Grain size 0.08-0.4 mm.

Chlorite is marked as flakes in radially radiant aggregates. Chlorite together with epidote fills cracks in quartz-barite mass. The size of its secretions is 0.075-0.4 mm.

Muscovite rare scales in quartz. Their size is 0.08-0.15 mm.

Aragonite is found in quartz-barite mass in the form of corroded grains, the size of which is up to 100 mm.

Psilomelan forms polymineral comparisons with galena, covellin and sphalerite. It occurs in the form of spots up to 100 mm.

Based on the study of the material composition of ores and the conditions of their occurrence, the following types of ores can be identified:

a) sulfide barite-polymetallic;

b) sulfide-oxidized ores;

c) oxidized lead-barite ores containing more than 40% of oxidized lead differences.

Ore minerals are barate, sphalerite, galena, chalcopyrite, cerussite, anglesite, calamine and covellin. By the nature of mineralization, interspersed, sometimes striped textures with fine and fine-grained structures predominate.

The rocks are composed of quartz, sericite, epidote, garnet, calcite, viterite and chlorite. Galena and sphalerite are observed mainly included in the barite-quartz mass and most often in association with each other.

The Karagailinsky processing plant processes lead-barite ores with a barite content of 40-42%. Tails of zinc flotation with a size of 80-85% of the class - 0.074 mm (pH – 9-9.5) after contact with liquid glass (1.1-1.2 kg/t) and alkyl sulfate mixture (DSSAM: FAFTO - 1:1) – 150 g/t arrive at the first main, and then after additional loading of 25 g/t alkyl sulfate mixture - at the second main flotation; the concentrate of the third main is subjected to two re-cleaning, and tails - control flotation.

The concentrate of the first main one is subjected to two re-sweeps, the tails of the re-sweeps and the concentrate of the second main flotation go to pre-flotation with an additional loading of alkyl sulfate mixture - 25 g/t.

The combined barite concentrate contains about 93.4% barite with 76.50% extraction.

4.2 Results of barite flotation in salt solutions from ore samples under laboratory conditions

To study the effect of inorganic salts on the flotation of barite from ore, a sample of lead –zinc ore from the Karagailinsky deposit with a content of *1,45% Pb, 1,45% Zn, 47,22%* $BaSO_4$ was used.

The scheme and the main conditions of the experiments are shown in figure 25. The scheme includes the collective flotation of sulfides and the main flotation of barite.

The conditions for collective sulfide flotation are the same for all experiments, the flotation time is 7 minutes, flotation was carried out with ore crushed to 85% cl. - 0.074 mm.

The main rock in the ore is represented by quartz. Quartz depression is carried out with sodium silicate at a flow rate of 1200 g/t, agitation with it – 3 min. Various salts were used in the experiment, agitation with them – 5 min. The results of a series of experiments with various loads of inorganic salts (in the experiments, the salt of the brand "chemically pure" was used are shown in tables 8, 9, 10, 11 and are graphically depicted in figure 26.

The conditions for the flotation of barite at the optimal flow rate adopted at the factory, sodium alkyl sulfate - 200 g/t, as well as at a flow rate of 150 g/t are shown in table 5.

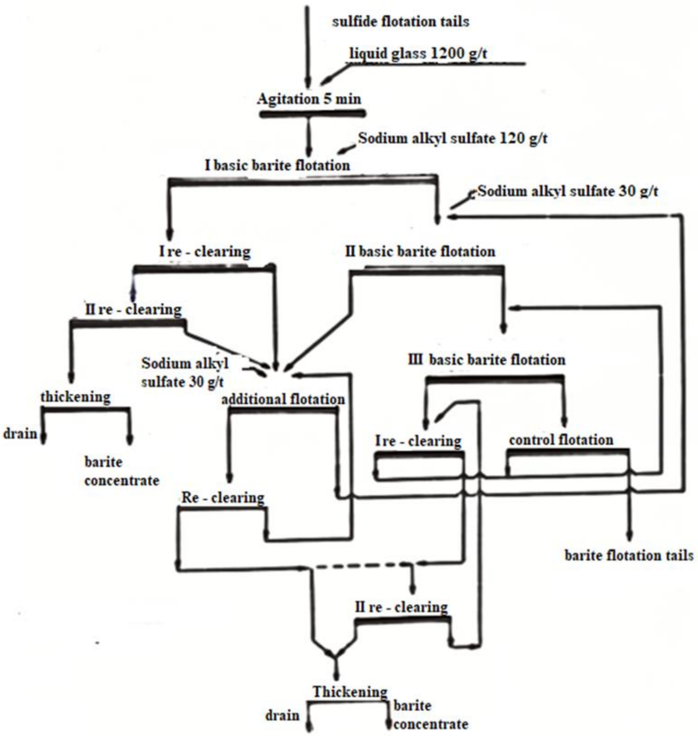


Figure 17 - Technology of barite enrichment from the ore
of the Karagailinsky deposit

As can be seen, according to the results of flotation, it can be concluded that the addition of salts leads to an increase in the extraction of barite. When flotation of barite only with sodium alkyl sulfate at a consumption of 150 g/t - extraction is 61.2% (table 7, item 2), and the addition of salts up to 3.2 kg/t leads to increased extraction, and a further increase in the loading of inorganic salts reduces extraction. Thus, at the expense of *NaCl* - 4200, 5000, 6000 g/t and sodium alkyl sulfate 150 g/t, the extraction of barite, respectively, is in %: 68.50; 66.12; 61.20. With an increase in the concentration of salts, the viscosity of the pulp continuously increases, this can explain the decrease in extraction at a consumption of more than 3.2 kg/t. At the expense of *NaCl - 3200* g/t and sodium alkyl sulfate 150 g/t, the extraction of barite is 72.25% (table.6), and with the consumption of sodium alkyl sulfate - 200 g/t, extraction - 72.30 (table 5). Flotation with the addition of salt reduces the consumption of the collector.

At the consumption of sodium alkyl sulfate 150 g/t with the addition Na_2SO_4, $NaNO_3$, $MgCl_2$ *-3200* g/t to the pulp, the extraction of barite is, respectively, %: 68.50; 66.12; 65.22 (Tables 7, 8, 9). Table salt has the most activating effect.

To clarify the reagent regime, it was recommended to conduct experiments on flotation with the addition of salt on the tailings of sulfide flotation at the current samples of the Kentau processing plant, where Karagailinsky ores are processed.

Table 5 - Results of barite flotation from ore at optimal sodium alkyl sulfate consumption of 200 g/t and 150 g/t (accepted at the factory)

№	Name of products	Y, г	Y, %	⇓, %	$BaSO_4$ content in ore, g	έ, %	Collector consumption, g/t
1	Ore	291,73	-	-	-	-	Alkyl Sulfate - 200
	Barite	279,58	-	47,22	132,02	-	
	lead.-zinc. k-t	12,15	-	-	-	-	
	barite k-t	180,00	64,38	53,02	95,45	72,30	
	tails	99,58	35,62	36,72	36,57	27,70	
2	Ore	287,99	-	-	-	-	Alkyl Sulfate - 150
	Barite	275,47	-	46,90	129,19	-	
	lead.-zinc. k-t	12,52	-	-	-	-	
	barite k-t	145,57	64,38	54,31	79,07	61,20	
	tails	129,90	35,62	38,59	50,13	38,80	

Table 6 - Results of barite flotation from ore at a sodium alkyl sulfate consumption of 150 g/t and with additional $NaCl$ loading

№	Name of products	Y, г	Y, %	⇓, %	$BaSO_4$ content in ore, g	έ, %	Collector consumption, g/t
1	Ore	298,12	-	-	-	-	Alkyl Sulfate-150, $NaCl$ - 1000
	Barite	237,46	-	46,84	134,65	-	
	lead.-zinc. k-t	10,76	-	-	-	-	
	barite k-t	168,25	58,53	49,07	82,56	61,32	
	tails	119,21	41,47	43,68	52,08	38,80	
2	Ore	292,90	-	-	-	-	Alkyl Sulfate-150, $NaCl$ - 2000
	Barite	280,90	-	47,12	132,36	-	
	lead.-zinc. k-t	12,00	-	-	-	-	
	barite k-t	170,70	60,77	50,49	86,19	65,12	
	tails	110,20	39,23	41,89	46,17	34,88	
3	Ore	293,30	-	-	-	-	Alkyl Sulfate-150, $NaCl$ - 3200
	Barite	281,95	-	47,10	132,79	-	
	lead.-zinc. k-t	11,35	-	-	-	-	
	barite k-t	179,20	63,56	53,54	95,95	72,25	
	tails	120,75	36,44	35,86	36,85	27,75	

4	Ore	291,73	-	-	-	-	Alkyl Sulfate-150, $NaCl$ - 4200
	Barite	280,78	-	46,92	131,74	-	
	lead.-zinc. k-t	10,95	-	-	-	-	
	barite k-t	175,62	62,55	51,38	90,24	68,50	
	tails	105,16	37,45	39,46	41,49	31,50	
5	Ore	292,66	-	-	-	-	Alkyl Sulfate-150, $NaCl$ - 5000
	Barite	281,30	-	47,30	133,05	-	
	lead.-zinc. k-t	11,36	-	-	-	-	
	barite k-t	179,18	63,70	49,09	87,97	66,12	
	tails	102,12	36,30	44,14	45,07	33,88	
6	Ore	293,14	-	-	-	-	Alkyl Sulfate-150, $NaCl$ - 6000
	Barite	280,15	-	47,27	132,42	-	
	lead.-zinc. k-t	12,99	-	-	-	-	
	barite k-t	170,25	60,77	47,60	81,04	61,20	
	tails	109,90	39,23	46,75	51,38	38,80	

Table 7 - Results of barite flotation from ore at a sodium alkyl sulfate consumption of 150 g/t and with additional loading of Na_2SO_4

№	Name of products	Y, г	Y, %	⇓, %	$BaSO_4$ content in ore, g	έ, %	Collector consumption, g/t
1	Ore	294,92	-	-	-	-	Alkyl Sulfate-150, Na_2SO_4 - 1000
	Barite	282,67	-	47,34	133,82	-	
	lead.-zinc. k-t	12,25	-	-	-	-	
	barite k-t	162,33	57,50	50,53	82,03	61,30	
	tails	120,34	42,50	43,03	51,78	38,70	
2	Ore	292,80	-	-	-	-	Alkyl Sulfate-150, Na_2SO_4 - 2000
	Barite	280,80	-	47,12	132,31	-	
	lead.-zinc. k-t	12,00	-	-	-	-	
	barite k-t	170,12	60,60	49,78	84,68	64,00	
	tails	110,68	39,40	43,03	47,63	36,00	
3	Ore	291,59	-	-	-	-	Alkyl Sulfate-150, Na_2SO_4 - 3200
	Barite	281,17	-	47,23	132,79	-	
	lead.-zinc. k-t	17,57	-	-	-	-	
	barite k-t	175,72	62,50	51,76	90,97	68,50	
	tails	105,45	37,50	39,67	41,83	31,50	
4	Barite ore	294,59	-	-	-	-	Alkyl Sulfate-150, Na_2SO_4 - 4200
	is lead.-zinc.	283,26	-	47,30	133,98	-	
	k-t	11,60	-	-	-	-	
	barite k-t	168,12	59,35	53,39	89,77	67,00	
	tails	115,14	40,65	38,40	44,21	33,00	
5	Ore	293,74	-	-	-	-	Alkyl Sulfate-150, Na_2SO_4 - 5000
	Barite	281,34	-	47,10	132,51	-	
	lead.-zinc. k-t	12,40	-	-	-	-	
	barite k-t	163,30	58,05	52,74	86,13	65,00	
	tails	118,04	41,95	39,29	46,38	35,00	
6	Ore	294,21	-	-	-	-	Alkyl Sulfate-150, Na_2SO_4 - 6000
	Barite	282,32	-	47,08	132,92	-	
	lead.-zinc. k-t	11,89	-	-	-	-	
	barite k-t	160,84	36,97	49,58	79,75	60,00	

	tails	121,48	43,03	43,76	53,17	40,00	

Table 8 - Results of barite flotation from ore at a sodium alkyl sulfate consumption of 150 g/t and with additional NaNO3 loading

№	Name of products	Y, г	Y, %	⇓, %	$BaSO_4$ content in ore, g	έ, %	Collector consumption, g/t
1	Ore	292,46	-	-	-	-	Alkyl Sulfate-150, *$NaNO_3$ - 1000*
	Barite	280,32	-	47,12	132,08	-	
	lead.-zinc. k-t	12,14	-	-	-	-	
	barite k-t	160,15	57,13	50,59	81,04	61,35	
	tails	120,17	42,87	42,48	51,05	38,65	
2	Ore	292,96	-	-	-	-	Alkyl Sulfate-150, *$NaNO_3$ - 2000*
	Barite	281,12	-	47,23	132,77	-	
	lead.-zinc. k-t	11,84	-	-	-	-	
	barite k-t	164,15	58,39	50,15	82,32	62,00	
	tails	116,97	41,61	43,13	50,45	38,00	
3	Ore	298,45	-	-	-	-	Alkyl Sulfate-150, *$NaNO_3$ - 3200*
	Barite	286,30	-	47,30	135,42	-	
	lead.-zinc. k-t	12,15	-	-	-	-	
	barite k-t	173,34	60,55	51,65	89,54	66,12	
	tails	112,96	39,45	40,61	45,88	33,88	
4	Ore	296,34	-	-	-	-	Alkyl Sulfate-150, *$NaNO_3$- 4200*
	Barite	284,27	-	47,24	134,29	-	
	lead.-zinc. k-t	12,07	-	-	-	-	
	barite k-t	170,84	60,10	51,17	87,43	65,11	
	tails	113,43	39,90	41,31	46,85	34,89	
5	Ore	297,12	-	-	-	-	Alkyl Sulfate-150, *$NaNO_3$ - 5000*
	Barite	282,34	-	47,26	133,43	-	
	lead.-zinc. k-t	14,78	-	-	-	-	
	barite k-t	167,41	59,30	50,61	84,73	63,50	
	tails	114,93	40,70	42,37	48,70	36,50	
6	Ore	292,84	-	-	-	-	Alkyl Sulfate-150, *$NaNO_3$- 6000*
	Barite	280,92	-	47,24	132,70	-	
	lead.-zinc. k-t	11,92	-	-	-	-	
	barite k-t	160,34	57,01	48,17	77,23	58,20	
	tails	120,58	42,92	34,99	42,20	31,80	

Table 9 - Results of barite flotation from ore at a sodium alkyl sulfate consumption of 150 g/t and with additional $MgCl_2$ loading

№	Name of products	Y, г	Y, %	⇓, %	$BaSO_4$ content in ore, g	έ, %	Collector consumption, g/t
1	Ore	294,36	-	-	-	-	Alkyl Sulfate-150, *$MgCl_2$ - 1000*
	Barite	281,81	-	47,10	132,73	-	
	lead.-zinc. k-t	12,55	-	-	-	-	
	barite k-t	162,34	37,61	49,81	80,86	60,92	
	tails	119,47	42,39	43,42	51,87	39,08	
2	Ore	295,34	-	-	-	-	Alkyl Sulfate-150, *$MgCl_2$- 2000*
	Barite	282,06	-	47,18	133,07	-	
	lead.-zinc. k-t	13,29	-	-	-	-	

	barite k-t	167,37	59,34	49,69	83,17	62,50	
	tails	114,69	40,60	43,51	49,90	37,50	
3	Ore	294,92	-	-	-	-	Alkyl Sulfate-150, *$MgCl_2$- 3200*
	Barite	281,30	-	47,32	133,11	-	
	lead.-zinc. k-t	13,62	-	-	-	-	
	barite k-t	171,22	61,87	50,70	86,82	65,22	
	tails	110,08	39,13	42,06	46,29	34,78	
4	Ore	296,31	-	-	-	-	Alkyl Sulfate-150, *$MgCl_2$ -4200*
	Barite	282,84	-	47,24	133,61	-	
	lead.-zinc. k-t	12,47	-	-	-	-	
	barite k-t	168,04	59,42	51,18	86,00	64,37	
	tails	114,80	40,58	41,47	47,60	35,63	
5	Ore	291,37	-	-	-	-	Alkyl Sulfate-150, *$MgCl_2$ - 5000*
	Barite	282,36	-	47,40	133,84	-	
	lead.-zinc. k-t	9,01	-	-	-	-	
	barite k-t	162,00	57,37	52,03	84,29	62,98	
	tails	120,36	42,63	41,15	49,53	37,01	
6	Ore	294,86	-	-	-	-	Alkyl Sulfate-150, *$MgCl_2$- 6000*
	Barite	283,72	-	47,37	134,39	-	
	lead.-zinc. k-t	11,14	-	-	-	-	
	barite k-t	159,03	56,06	48,18	76,63	57,02	
	tails	124,69	43,94	46,32	57,76	42,98	

4.3 The main conclusions based on laboratory research data

Based on the results of laboratory studies on the flotation of barite with the addition of salts, the following main conclusions can be drawn:

1. Having studied the material composition of the Karagailinsky ores, it can be concluded that the empty rock in the ore is represented by quartz. Its depression is carried out by sodium silicate. As described in chapter 3, inorganic salts noticeably activate quartz flotation, but with the addition of sodium silicate, quartz can be almost completely suppressed.
2. The addition of inorganic salts during the flotation of barite from ore activates flotation, but up to a certain salt concentration at a flow rate of up to 3200 g/t for all salts. Further loading from 3200-6000 g/t leads to a decrease in barite extraction. This is probably due to a significant increase in pulp viscosity.
3. The best results were obtained with table salt, with the consumption of sodium alkyl sulfate - 150g/t with the addition of *NaCl -3200 g/t*, the same results of barite flotation were obtained as with the optimal consumption of sodium alkyl sulfate accepted at the factory – 200 g/ t.
4. The addition of table salt during barite flotation reduces the consumption of an expensive collector by 50 g/t.
5. In order to clarify the reagent regime with the use of salt, experiments were conducted on current samples of Karagailinsky ores.

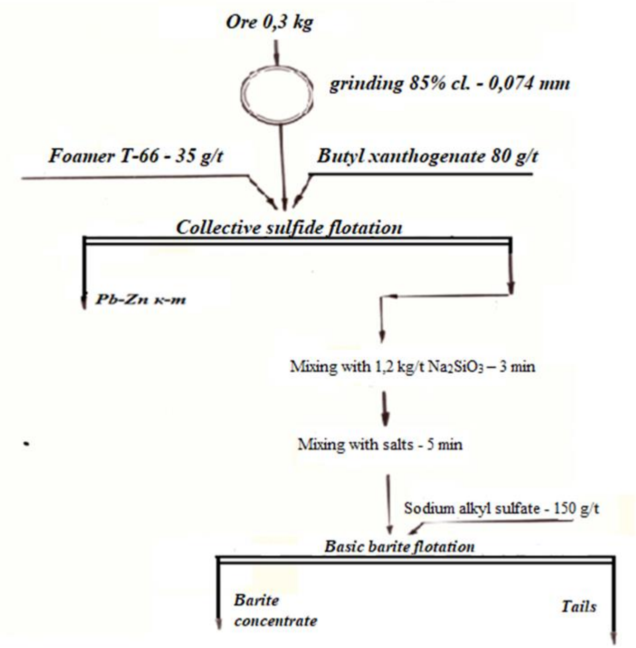


Figure 18 - Diagram of laboratory experiments on the ore of the Karagailinsky deposit

CHAPTER 5. TECHNOLOGICAL TESTS OF BARITE FLOTATION IN SALT SOLUTIONS AT THE KENTAU PROCESSING PLANT

5.1 Investigation of barite flotation from sulfide flotation tailings in a solution of table salt

The experiments were carried out in the central laboratory on the current samples of the Kentau processing plant processing Karagailinsky ores.

The sample was taken from the zinc flotation tails during the shift, then this sample was divided into ten equal parts for barite flotation experiments. The scheme of barite flotation from sulfide flotation tailings in a solution of table salt is shown in Figure 19.

As can be seen from table 12, the addition of table salt from 2500 to 3000 g/t leads to an increase in the quality of barite concentrate, but with a consumption of 4.2 kg/t or more, extraction decreases. Thus, with the consumption of alkyl sulfate paste 150 g/t with the addition of table salt 4200, 3600, 5000, 9000 g/t, the cure of barite, respectively, is, %: 75,66; 70,31; 69,10; 74,75; 72,41 (table 12). These results are similar to those obtained earlier (chapter 4, section 4.2), the decrease in extraction is explained by a sharp increase in pulp viscosity.

During flotation according to the reagent regime of the concentrator (table 12, experiments 1, 2), the quality of barite concentrate is 83.70%, extraction is 76%.

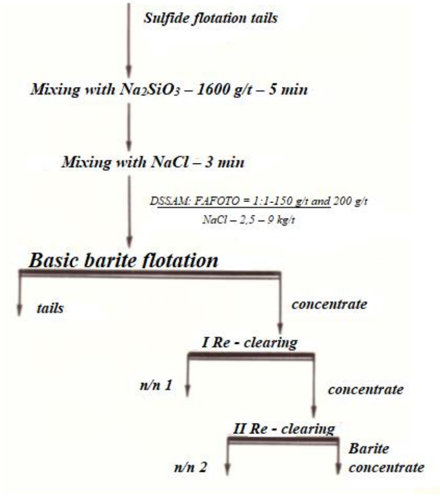


Figure 19 - Scheme of experiments on barite flotation with the addition of NaCl on the tailings of sulfide flotation

Flotation time: main flotation – 12 min., I re-cleaning of concentrate - 6 min., II re-cleaning of concentrate - 4 min.

Table 10 - Results of barite flotation from ore at the consumption of alkyl sulfate paste 200, 150, 124 g/t

№	Name of products	Y, г	Y, %	⇓, %	$BaSO_4$ content in ore, g	έ, %	Reagent mode, g/t
1	Ore	1150	100,00	50,47	580,500	100,00	Liquid glass-1600; DSSAM-100; FAFTO - 100
	Barit c-t	557	48,43	83,40	437,697	75,40	
	Pr.pr. 1	98	8,52	29,70	29,106	5,01	
	Pr.pr. 2	55	4,78	41,12	22,616	3,89	
	Coarse c-t	710	61,73	72,71	516,260	89,00	
	Tails	440	38,27	14,60	64,240	11,06	
2	Ore	1175	100,00	49,40	580,465	100,00	- // -
	Barit c-t	540	45,19	82,33	444,636	76,60	
	Pr.pr. 1	95	8,07	33,04	31,388	5,41	
	Pr.pr. 2	75	6,17	49,56	37,170	6,40	
	Coarse c-t	710	60,43	73,70	523,270	90,14	
	Tails	465	39,57	12,30	57,195	9,84	
3	Ore	1117	100,00	53,81	601,045	100,00	Liquid glass - 1600; DSSAM - 75; FAFTO - 75
	Barit c-t	515	46,11	86,44	445,166	74,07	
	Pr.pr. 1	87	7,79	38,60	33,582	5,59	
	Pr.pr. 2	90	8,06	49,38	44,352	7,37	
	Coarse c-t	692	61,96	75,58	523,100	87,03	
	Tails	425	38,04	18,34	77,945	12,97	
4	Ore	1179	100,00	52,18	615,214	100,00	- // -
	Barit c-t	535	45,38	84,06	449,721	73,10	
	Pr.pr. 1	100	8,48	36,80	36,800	5,98	
	Pr.pr. 2	54	4,58	44,68	24,127	3,92	
	Coarse c-t	689	58,44	74,11	510,648	83,00	
	Tails	490	41,56	21,34	104,566	17,00	
5	Ore	1140	100,00	49,83	586,098	100,00	Liquid glass - 1600; DSSAM - 62; FAFTO - 62
	Barit c-t	475	41,67	86,48	410,780	72,31	
	Pr.pr. 1	95	8,33	42,40	40,280	7,09	
	Pr.pr. 2	40	3,51	53,30	21,320	3,75	
	Coarse c-t	610	53,51	77,44	472,380	83,15	
	Tails	530	46,49	18,06	95,718	16,85	
6	Ore	1163	100,00	50,04	581,966	100,00	- // -
	Barit c-t	480	41,27	86,90	417,120	71,69	
	Pr.pr. 1	108	9,29	42,44	45,835	7,86	
	Pr.pr. 2	40	3,44	55,44	22,176	3,81	
	Coarse c-t	628	54,00	77,25	485,131	83,36	
	Tails	535	46,00	18,10	96,835	16,64	

The consumption of sodium silicate for quartz suppression is the same for all experiments – 1600 g/t.

Tables 10, 11, 12 present the results of experiments to determine the optimal consumption of alkyl sulfate paste, fatty acid fraction of tall oil and table salt.

Table 11 - Results of barite flotation from ore at the consumption of alkyl sulfate paste 200, 124 g/t and *NaCl* - 2500 and 3000 g/t

№	Name of products	Y, г	Y, %	⇓, %	BaSO4 content in ore, g	έ, %	Reagent mode, g/t
7	Ore	1277	100,00	37,57	479,803	100,00	Liquid glass-1600; DSSAM - 100; FAFTO - 100
	Barit c-t	528	41,35	77,40	408,672	85,17	
	Pr.pr. 1	138	10,81	12,50	17,250	3,60	
	Pr.pr. 2	91	7,13	20,81	18,937	3,95	
	Coarse c-t	757	59,28	58,76	444,859	92,72	
	Tails	520	40,72	6,72	34,944	7,28	
8	Ore	1284	100,00	37,60	482,824	100,00	- // -
	Barit c-t	524	40,81	78,28	410,187	85,00	
	Pr.pr. 1	137	10,67	12,28	16,824	3,50	
	Pr.pr. 2	96	7,48	20,48	19,661	4,01	
	Coarse c-t	757	58,96	59,00	446,672	92,51	
	Tails	527	41,04	6,86	36,152	7,49	
9	Ore	1248	100,00	37,78	471,567	100,00	Liquid glass-1600; DSSAM - 100; FAFTO - 100; *NaCl*-2500
	Barit c-t	505	40,46	78,12	394,506	83,66	
	Pr.pr. 1	140	11,22	13,42	18,788	3,98	
	Pr.pr. 2	96	7,70	25,00	24,000	5,10	
	Coarse c-t	741	59,38	59,02	437,290	92,73	
	Tails	507	40,62	6,76	34,273	7,23	
10	Ore	1297	100,00	37,20	482,481	100,00	Liquid glass - 1600; DSSAM - 62; FAFTO - 62; *NaCl*-3000
	Barit c-t	485	37,39	80,92	392,462	81,34	
	Pr.pr. 1	149	11,48	16,42	24,466	5,07	
	Pr.pr. 2	86	6,63	28,32	24,355	5,05	
	Coarse c-t	720	55,51	61,29	441,283	91,46	
	Tails	577	44,49	7,14	41,198	8,54	

Table 12 - Results of barite flotation from ore at the consumption of alkyl sulfate paste 150 g/t and NaCl - 2500 and 3000 g/t

№	Name of products	Y, г	Y, %	⇓, %	BaSO4 content in ore, g	έ, %	Reagent mode, g/t
11	Ore	1212	100,00	49,16	595,858	100,00	Liquid glass - 1600; DSSAM - 75; FAFTO - 75; *NaCl*-2500
	Barit c-t	521	42,99	85,80	455,455	76,73	
	Pr.pr. 1	120	9,90	32,58	39,096	6,56	
	Pr.pr. 2	74	6,11	49,00	36,260	6,09	
	Coarse c-t	715	59,00	72,34	520,811	37,41	
	Tails	497	41,00	15,10	75,047	12,59	
12	Ore	1225	100,0	49,52	606,620	100,00	- // -
	Barit c-t	535	43,27	85,90	459,565	75,75	
	Pr.pr. 1	122	9,96	31,50	38,430	6,33	
	Pr.pr. 2	65	5,31	49,16	31,954	5,27	
	Coarse c-t	117	58,53	73,02	523,534	86,30	
	Tails	508	41,47	16,36	83,109	73,70	
13	Ore	1215	100,00	49,20	597,785	100,0075	Liquid glass - 1600; DSSAM - 75; FAFTO - 75; *NaCl*-4200
	Barit c-t	535	44,03	84,80	453,680	,89	
	Pr.pr. 1	117	9,63	29,72	34,772	6,82	
	Pr.pr. 2	68	5,60	43,44	29,539	4,94	
	Coarse c-t	720	59,26	71,94	517,991	86,85	
	Tails	485	40,74	16,12	79,794	12,38	
14	Ore	1203	100,00	49,50	594,317	100,00	- // -
	Barit c-t	523	43,47	85,72	448,316	75,43	
	Pr.pr. 1	112	9,31	30,64	34,317	5,77	
	Pr.pr. 2	62	5,15	45,80	28,396	4,80	
	Coarse c-t	697	57,94	73,31	511,029	56,00	
	Tails	506	42,06	16,46	83,289	14,00	
15	Ore	1217	100,00	49,46	601,885	100,00	Liquid glass - 1600; DSSAM - 75; FAFTO - 75; *NaCl*-8400
	Barit c-t	533	43,80	84,30	449,319	74,65	
	Pr.pr. 1	121	9,94	29,20	35,332	5,85	
	Pr.pr. 2	73	6,00	43,80	31,974	5,33	
	Coarse c-t	723	59,74	71,06	516,625	85,83	
	Tails	490	40,26	17,40	85,260	14,17	
16	Ore	1218	100,00	50,07	609,891	100,00	- // -
	Barit c-t	463	38,01	86,90	402,347	65,97	
	Pr.pr. 1	105	8,62	31,50	33,075	5,42	
	Pr.pr. 2	62	5,09	47,34	29,351	4,82	
	Coarse c-t	630	51,72	73,77	464,773	76,21	
	Tails	588	48,28	24,68	145,118	23,79	

17	Ore	1190	100,00	49,82	592,838	100,00	Liquid glass - 1600; DSSAM - 62; FAFTO - 62; $NaCl$-4200
	Barit c-t	490	41,18	86,71	425,124	71,71	
	Pr.pr. 1	122	10,25	33,66	41,064	6,93	
	Pr.pr. 2	44	3,70	49,48	21,771	3,67	
	Coarse c-t	656	56,13	74,38	487,960	82,31	
	Tails	534	44,87	19,64	104,878	17,69	
18	Ore	1212	100,00	49,35	593,113	100,00	- // -
	Barit c-t	503	41,501	85,40	429,582	71,82	
	Pr.pr. 1	122	0,07	36,74	44,823	7,50	
	Pr.pr. 2	40	3,30	45,12	18,048	3,02	
	Coarse c-t	665	54,87	74,05	492,433	82,33	
	Tails	547	45,13	19,32	105,080	17,67	
19	Ore	1235	100,00	50,13	619,151	100,00	Liquid glass - 1600; DSSAM - 75; FAFTO - 75; $NaCl$-8600
	Barit c-t	518	41,96	85,14	442,061	71,40	
	Pr.pr. 1	130	10,53	34,50	44,350	7,24	
	Pr.pr. 2	47	3,81	45,60	21,432	3,46	
	Coarse c-t	695	56,28	73,14	508,344	82,10	
	Tails	540	43,72	20,52	110,808	17,00	
20	Ore	1209	100,00	49,53	598,325	100,00	- // -
	Barit c-t	463	38,30	86,20	400,032	66,30	
	Pr.pr. 1	121	10,01	34,40	41,624	6,95	
	Pr.pr. 2	42	3,47	49,12	20,603	3,45	
	Coarse c-t	626	51,76	73,85	462,286	77,20	
	Tails	583	48,22	23,42	136,539	22,80	
21	Ore	1210	100,00	49,20	595,320	100,00	Liquid glass - 1600; DSSAM - 75; FAFTO - 75; $NaCl$-5000
	Barit c-t	520	42,97	85,80	44,649	75,00	
	Pr.pr. 1	110	9,09	30,85	33,533	5,70	
	Pr.pr. 2	82	6,77	38,62	31,671	5,32	
	Coarse c-t	712	58,84	71,92	512,094	86,02	
	Tails	498	41,15	16,06	80,011	13,44	
22	Ore	1200	100,00	49,40	592,800	100,00	- // -
	Barit c-t	519	43,25	85,09	44,183	74,50	
	Pr.pr. 1	100	8,33	37,46	37,465	3,32	
	Pr.pr. 2	80	6,66	45,34	36,279	3,12	
	Coarse c-t	699	58,25	73,73	515,380	86,94	
	Tails	501	41,75	14,35	718,066	12,13	
23	Ore	1210	100,00	49,601	600,160	100,00	Liquid glass-1600; DSSAM - 75; FAFTO - 75; $NaCl$-9000
	Barit c-t	498	41,20	85,60	426,280	71,02	
	Pr.pr. 1	127	10,62	37,30	47,410	7,90	
	Pr.pr. 2	52	4,32	39,20	20,400	3,40	
	Coarse c-t	678	56,14	72,86	49,405	82,32	
	Tails	531	43,86	19,98	106,108	17,68	

24	Ore	1200	100,00	49,70	596,400	100,00	- // -
	Barit c-t	513	42,80	85,80	440,150	73,80	
	Pr.pr. 1	134	11,20	23,58	31,610	5,30	
	Pr.pr. 2	46	3,80	38,63	17,770	2,98	
	Coarse c-t	693	57,20	70,64	489,500	82,08	
	Tails	514	425,80	20,79	106,875	17,92	
25	Ore	1162	100,00	48,35	561,893	100,00	Liquid glass-1600; DSSAM - 75; FAFTO - 75; *NaCl*-3800
	Barit c-t	605	52,07	79,14	478,797	85,21	
	Pr.pr. 1	90	7,75	24,54	22,086	3,93	
	Pr.pr. 2	77	6,63	27,60	28,952	5,15	
	Coarse c-t	772	66,45	68,63	529,835	94,29	
	Tails	390	33,56	8,22	32,058	5,71	
26	Ore	1180	100,00	48,24	569,256	100,00	- // -
	Barit c-t	560	47,45	81,02	453,712	79,70	
	Pr.pr. 1	104	8,90	24,98	26,229	4,61	
	Pr.pr. 2	90	7,63	43,80	39,420	6,93	
	Coarse c-t	425	36,01	11,74	498,95	8,76	
	Tails	755	63,99	68,79	519,361	91,24	
27	Ore	1182	100,00	49,40	583,908	100,00	Liquid glass - 1600; DSSAM - 62; FAFTO - 62; *NaCl*-2500
	Barit c-t	492	41,62	85,80	422,165	72,30	
	Pr.pr. 1	96	8,12	32,80	31,531	5,49	
	Pr.pr. 2	94	7,95	31,00	29,195	5,00	
	Coarse c-t	682	57,69	70,80	482,892	82,70	
	Tails	500	42,30	20,20	101,016	17,30	
28	Ore	1179	100,00	49,30	581,247	100,00	- // -
	Barit c-t	520	44,10	81,20	422,566	72,70	
	Pr.pr. 1	84	7,12	23,53	19,762	4,40	
	Pr.pr. 2	24	4,49	35,09	18,599	3,20	
	Coarse c-t	657	56,73	70,15	460,928	79,30	
	Tails	522	44,27	23,04	120,318	20,70	
29	Ore	1189	100,00	50,00	594,500	100,00	Liquid glass-1600; DSSAM - 62; FAFTO - 62; *NaCl*-3800
	Barit c-t	524	44,10	83,60	438,146	73,70	
	Pr.pr. 1	92	7,74	26,49	24,374	4,10	
	Pr.pr. 2	92	7,80	36,96	34,005	4,72	
	Coarse c-t	709	59,64	69,99	496,288	82,52	
	Tails	479	40,36	20,45	97,974	16,48	
30	Ore	1077	100,00	49,70	470,649	100,00	- //
	Barit c-t	430	39,92	81,24	349,690	74,30	
	Pr.pr. 1	63	5,85	16,43	10,354	2,20	
	Pr.pr. 2	62	5,76	25,27	15,673	3,30	
	Coarse c-t	555	51,53	67,67	375,578	79,80	
	Tails	522	48,46	18,20	95,071	20,20	

With the consumption of alkyl sulfate paste 150 g/t with the addition of table salt 2.5 kg/ t (table 12, experiments 11,12), the quality of barite concentrate is 85.80% with the extraction of 76.20%, while with the flotation of barite from ore with the addition of only alkyl sulfate paste - 150 g/t, the content in the barite concentrate is 85.28% with the extraction - 73.50%, which is 3% lower (table 10, experiment 3.4).

According to the results of studies of barite flotation with an alkyl sulfate paste consumption of 124 g/t and 200 g/t with the addition of table salt of 2.5-3.8 kg/t (table 11.12), it can be seen that the addition of salt at such collector costs leads to a decrease in barite extraction. So, for example, at the consumption of an alkyl sulfate mixture of 200 g /t with the addition of salt of 2.5 kg /t, the extraction of barite into the concentrate is 88.66% versus the extraction of 85.08% during the flotation of barite with the addition of only alkyl sulfate paste of 200 g/t (tables 11, experiment 7, 8, 9).

The addition of salt 2.5 kg/t at the consumption of alkyl sulfate paste 124 g/t during barite flotation leads to a deterioration in the quality of barite concentrate. The quality of the concentrate at the consumption of alkyl sulfate paste 124 g/t is 83.50% (Table 12, experiments 27, 28), while at the flotation of barite only with alkyl sulfate paste 124 g/t, the quality is 86.60% with equal extraction.

Table 13 shows the averaged data of the barite flotation results.

Table 13 - Averaged data of barite flotation results

№ of experiments	The content of $BaSO_4$%			Y, %	έ, %	Reagent mode, g/t			
	in ore	in concent.	in the tails			Liquid glass	alkyl sulfate	tallow oil	*NaCl*
1+2	50,00	83,70	13,40	46,70	76,00	1600	100	100	-
11+12	49,20	85,80	15,50	43,50	76,20	1600	75	75	2500
13+14	49,30	85,30	16,00	43,60	75,60	1600	75	75	4200
15+16	49,50	85,50	20,50	41,50	70,00	1600	75	75	8400
19+20	49,40	85,60	20,02	41,70	71,00	1600	75	75	8600
23+25	49,70	85,70	20,60	42,00	72,00	1600	75	75	9000
29+30	49,80	82,00	19,70	42,02	74,00	1600	62	62	3800

The best results of barite flotation were obtained at the consumption of alkyl sulfate paste 150 g/t with the addition of table salt 2.5 kg/t, which allows to increase the quality of the concentrate by 2% without reducing extraction, to reduce the consumption of alkyl sulfate paste (DSSAM: FAFTO = 1:1) per 50 g/t.

As a result of flotation of barite with the addition of salt, it was found that the deposition time of barite concentrate decreases sharply. A series of experiments was conducted to determine the deposition time of barite concentrate with the addition of table salt and aluminum sulfate coagulant used to thicken the concentrate.

It was found that the deposition time of barite concentrate at an aluminum sulfate consumption of 4.5 kg/t is 15 minutes, while when salt is added 2.5 kg/t, the deposition time is 5 minutes, which reduces the consumption of aluminum sulfate coagulant by 2 kg/t.

5.1 Features of the circulating water supply scheme, taking into account the recommendations

According to the nature of the use of wastewater in the technological process of enrichment, the schemes of circulating water supply can be divided into the following types: full, partial and cycle-by-cycle turnover [60].

A complete water cycle is characterized by the use of all the drains of the enterprise without their discharge. It can be organized according to the scheme: concentrating plant - tailings dump - concentrating plant, i.e. all wastewater after settling in the tailings dump with or without pre-treatment is used as recycled water (Fig. 29).

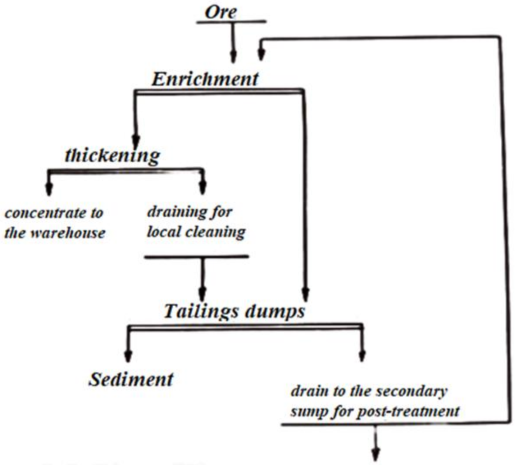


Figure 20 - Water flow diagram: factory - tailings dump – factory

In the scheme of partial water circulation, a part of the runoff is used without cleaning or with cleaning. The rest after cleaning up to sanitary and fishery standards is dumped.

The cyclic turnover can provide full or partial demand for water. The advantages of a cycle-by-cycle turnover include the fact that lines of a certain stage of the technological process are used in the turnover, containing practically residual concentrations of only those reagents that are used in this flotation cycle. However, the accumulation of salts in the recycled water of flotation reagents with an unstable concentration makes it impossible to timely and effectively manage the technological process, which is a significant drawback of this water circulation scheme. Nevertheless, such a scheme such a water circulation scheme is used in domestic and foreign practice (Fig. 21).

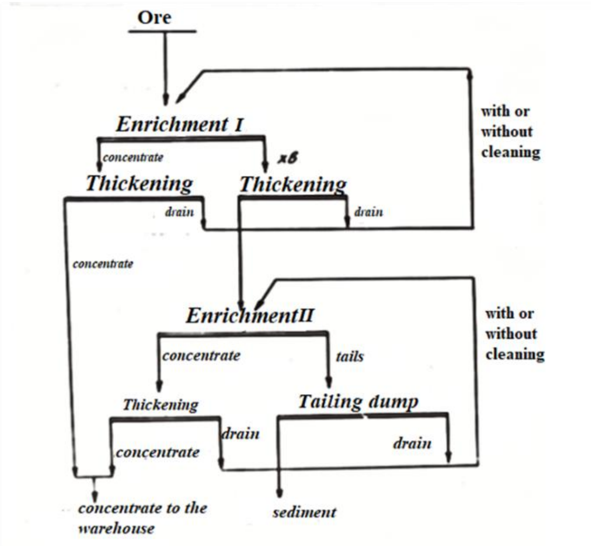


Figure 21 - Diagram of the water cycle turnover

At the Karagailinsky processing plant, the project provides for the full use of recycled water and ensuring the operation of the factory without wastewater discharge. Recycled water is used in the technological process and for plumbing purposes. To obtain a discharge from the tailings dump suitable for these needs, a solution of aluminum sulfate is fed into the tailings of the factory before dumping into the tailings dump, which helps to remove harmful impurities, complete solid deposition and create an appropriate *pH* drain. Two recycling water supply systems are provided: external - from the tailings storage and internal - with chemical purification from reagents (Fig.22). A cycle-by-cycle scheme of recycling water supply is provided at the factory, which allows using table salt to control only its concentration in recycled water and when the concentration of 2.5 kg/t is reached, stop the supply of salt in barite flotation.

The scheme of circulating water supply at the Karagailinsky concentrating plant is shown in Fig. 22.

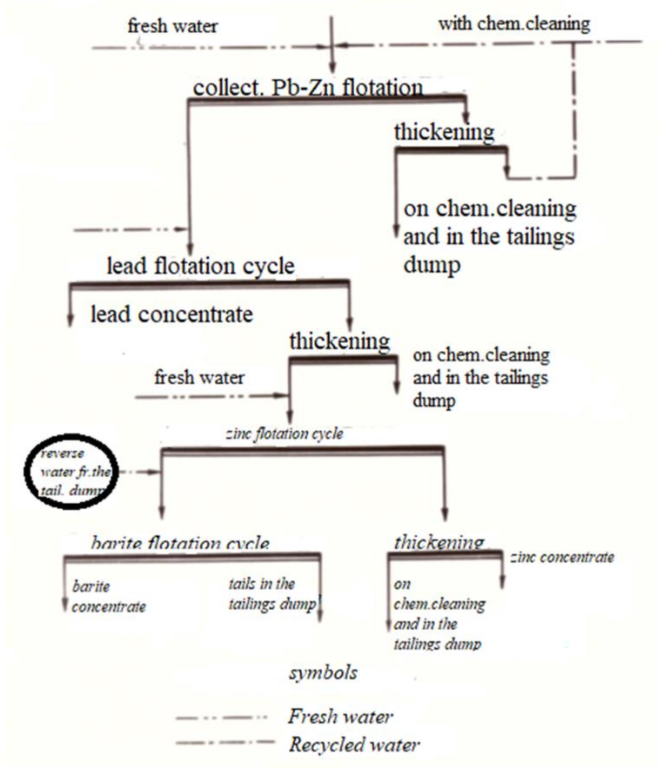


Figure 22 - Scheme of circulating water supply at the Karagailinsky concentrating plant

6 CONCLUSIONS AND RECOMMENDATIONS

As a result of the literature review, analysis of the results of previous studies, experimental study of foaming in brines, structural changes of water in various concentrations of salts, experiments to determine the degree of flocculation of barite in aqueous solutions of inorganic electrolytes, "salt" flotation of barite and quartz, as well as technological studies of barite flotation and recommendations.

1. Given the steady growth in the production and consumption of flotation barite concentrates, research aimed at improving the flotation of barite from polymetallic ores of the Karagailinsky deposit should be considered an urgent task.
2. The improvement of flotation technology in modern conditions should be accompanied by an ever-increasing use of wastewater in the circulating water supply. In this sense, studies of barite flotation technology should be considered reasonable and expedient, taking into account the features that arise when using highly saline circulating waters. Barite flotation in the case of circulating water supply can be considered as "salt" flotation of barite and the technological features of the process will be determined by the features of "salt" flotation.
3. It is shown that in solutions of high salt concentration there is an increase in foaming, a decrease in the size of air bubbles during aeration and a decrease in the wetting properties of water.

However, the change in foaming by itself is not responsible for the results of "salt" flotation.

The study of the viscosity and infocracy of salt solutions has shown that the nature of ion hydration in concentrated solutions is hydrophobic and that the structure of water is strengthened, resulting in hydrophobic interactions, the magnitude of which increases with temperature. These forces determine the strengthening of flotation and the increase in the flotation activity of minerals.

The results of flotation of monomineral fractions of barite and quartz in concentrated electrolyte solutions confirmed that the hydrophobicity of the mineral surface increases.

The greatest hydrophobicity of barite was observed in solutions of $CaCl_2$ and $NaCl$.

The hypothesis put forward about the mechanism of "salt" flotation consists in the statement that the flotation of minerals in high-concentration salt solutions is determined by hydrophobic interactions. At the same time, the possibility of a special (antiparallel) orientation of hydrating dipoles on the surface of minerals is not excluded.

4. Barite flotation is significantly activated in the presence of salts at a flow rate of up to 3.2 kg/t. Table salt has the most activating effect. Further loading of salt from 3.0 kg/t to 6 kg/t leads to a decrease in barite extraction. This is due to a significant increase in the viscosity of the pulp.

Concentrated solutions of electrolytes exhibit actions similar to the action of the collector. On this basis, it was recommended to conduct tests on the flotation of ores of the Karagailinsky deposit according to the regime with a reduction in the consumption of the alkyl sulfate mixture and the introduction of NaCl into the pulp, as the most effective of the studied salts.

5. Experiments conducted in the laboratory on current samples of the Karagailinsky deposit showed that under the conditions of using NaCl - 205 kg /t, it is possible to reduce the consumption of an expensive alkyl sulfate mixture by 50 g/t, reduce the consumption of coagulant during thickening by 2 kg/t and improve the quality of the concentrate by 2%.

When organizing recycled water supply at the factory, it is recommended to control the concentration of table salt in recycled water and, when reaching 2.5 kg/t, stop supplying salt to the barite flotation process.

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BARITE FLOTATION IN SALT SOLUTIONS

Subscribe to print 30/03/2022. Format 60×90/16.
Edition of 500 copies.
Printed by “iScience” Sp. z o. o.
Warsaw, Poland
08-444, str. Grzybowska, 87
info@sciencecentrum.pl, https://sciencecentrum.pl

ISBN 978-83-66216-62-4