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Significance of the Flotation Process and the Study of Flotation Reagents

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ABSTRACT: Today, flotation is becoming increasingly important, since using this method it is possible to enrich various metal ores, purify wastewater from various oil and fat and suspended solids, as well as in other industries to solve a number of important processes. Available data show that flotation processes are based on different wettability properties of the surface of materials. In this regard, this review is aimed at the study of flotation reagents, their purpose and classification. The mechanisms of adsorption of flotation reagents on the surface of minerals are analyzed.

KEYWORDS: flotation, flotation reagent, surfactant, adsorption, flocculation.

I. INTRODUCTION

At present, the term flotation is often found in the scientific and technical literature, which is used to purify water from organic substances and solid suspensions, separate mixtures, and accelerate settling in the chemical, oil refining, food, and other industries. Flotation is one of the main technological processes for the enrichment of most minerals, due to the separation of mixtures of fine particles [1, 2]. Flocculation processes have been successfully used in ore dressing processes for a long time and probably the greatest theoretical and practical experience has been collected in this direction. Selective flocculation is the most promising method for concentrating and enriching minerals, separating especially valuable substances from natural raw materials [3].

The method of flotation enrichment of minerals is one of the most common processes that obey the laws of colloidal chemistry. Today, the method is becoming increasingly important, since it is its use that contributes to the enrichment of non-magnetic and finely disseminated ore with a complex material composition, which is not enriched by other classical methods [4].

Flotation contributes to the solution of a number of important problems related to: the expansion of mineral resources due to the possibility of bringing into operation a deposit of low-grade complex ores; complex use of polymetallic ores; sludge enrichment [5].

The use of the flotation process is continuously expanding. In terms of the quantity and variety of processed raw materials, flotation ranks first among other technological enrichment processes. The first data on the use of flotation in enrichment processes are given in a Persian manuscript dating back to the 15th century. These instructions provided for the mixing of raw materials with oil, followed by mixing with water, which promotes the separation of particles coated with oil and particles that are selectively wetted with water [6]. This type of flocculation was known as oil flocculation, and W. Hynes (Great Britain) was issued patent No. 488 for it in 1860 [7, 8]. However, the efficiency of this flotation method was underestimated due to the consumption of significant amounts of oil substances.

A. Nibelius (USA, 1892) and A. McQuisten (Great Britain, 1904) developed another type - film flotation, based on the ability of hydrophobic mineral particles to stay on the water surface, while hydrophilic particles sink in it [9]. At present, the above methods of flotation are practically not used.

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II. SIGNIFICANCE OF THE SYSTEM

Currently, the most common flotation method is probably froth flotation, with the help of which more than 1 billion tons of rock mass and more than 20 types of ores are enriched worldwide every year. According to literary sources, the first patent for this method is known, which was issued to Adolf and Arthur Bessel (Germany, 1877). According to this, the graphite particles fixed on the gas bubbles formed during the boiling of the suspension (pulp) float to the surface, due to which it is released from the separation zone. Today, froth flotation is carried out by supplying gas to flotation plants. There are numerous theoretical data explaining the nature of the formation of foams and their stability from the size of the components of the system [10], from the presence of reagents of the so-called foaming agents [11], etc. This type of flotation has been described as the single most important operation used to extract and enrich sulfide ores . The development of froth flotation has improved the recovery of valuable minerals, since copper and lead from natural minerals. It not only ensured the complete mechanization of mining, but also made it possible to cost-effectively recover valuable metals from ore with a lower content of the main element than before. To date, such modifications of froth flotation as vacuum, flotation gravity, ionic, electroflotation, flotation with CO_2 release, froth separation, etc. are known [12].

The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

The flotation process is used to separate large quantities of oxide, sulfide and carbonate minerals before further purification. Phosphate minerals and coal containing raw materials are also cleaned using flotation technologies. Despite the advances made in these areas of production, numerous scientific studies continue to improve flotation processes for the treatment of minerals. Thus, the problems and prospects for the processing of fine particles are studied, methods for optimizing the processes of enrichment of sulfide mineral raw materials and their stability, as well as the state of their surface in aqueous solutions and pulps, the mechanism of oxidation and formation of chemical compounds for various flotation conditions are given [13].

The results of the redox interaction of the components of sulfide pulps are analyzed. The kinetics of oxygen uptake by sulfides and their mixtures in solutions of modifiers has been studied. The concentration influence of iron on the processes of pyrite and sphalerite flotation was determined. The activating effect of copper cations on sphalerite was established [14].

The authors of [15] study the effect of pulp oxidation with live steam on the parameters of zinc flotation. As a result of the research conducted by the author, it was found that heating the pulp before the operations of the main and first refining flotation allows increasing the extraction of zinc into the final concentrate from 73,9 to 78,5%.

The results of enrichment by means of flotation of mineral copper-zinc [16], copper-lead-zinc [17], copper-molybdenum [18], copper-iron [19], gold-bearing [20], containing precious metals [21] are presented.

One of the flourishing areas of flotation methods can be seen in wastewater treatment plants of various industries, where fats, oils and suspended solids are removed from wastewater using this method. These units are called dissolved air flotation units [22]. In particular, flotation in this case is used to remove oil from wastewater from oil and gas processing plants, petrochemical and chemical industries [23, 24].

As another industry that cannot do without flotation enrichment, the paper processing industry can be shown. Froth flotation is one of the processes used to recover already recycled paper. The goal is to release and remove hydrophobic contaminants from recycled paper. The pollutants considered are mainly printing inks and some sticky materials [25].

It is well known that flotation is carried out due to the adsorption of air molecules on the mineral particles of the components under the influence of substances called "flotation reagents". The course of the flotation enrichment process and its result are largely determined by the reagent regime of flotation, i.e. assortment, type and method of their application. This mode is mainly determined by the physicochemical characteristics of the mineral, the degree of its dispersion, as well as the conditions for finished products [26].

In the flotation process, for the best enrichment result, several flotation reagents are usually used, the actions of which are interconnected and depend on the concentration of each of them. Therefore, the excess consumption of one reagent necessitates an increase in the consumption of other reagents, and in excess of an increase (or decrease) in their concentration can lead to a deterioration in the technological performance of the entire process. Experiments have

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shown that the lowest possible consumption of reagents provides lower costs for the processing of mineral raw materials and better results of the enrichment process. Despite the accumulated theoretical and practical experience, the required amount of reagents is always determined using laboratory flotation experiments, and is specified under industrial conditions for each mineral raw material [27].

The activity of flotation reagents is influenced by various physical processes, since supply of a reagent (in a vapor state or in the form of an aerosol) ultrasonic, thermal treatment and chemical processes, because electrochemical oxidation, bacterial treatment, mixing of different reagents, etc. Basically, these measures are used to improve the technical and economic indicators of the process as a whole [28].

The intended purpose of flotation reagents predetermines their compliance with one of three large classes: collectors, foam concentrates and regulators.

Collectors are organic in nature, anchoring mostly at the solid-liquid interface. Foaming agents are surface-active organic substances that are adsorbed predominantly at the liquid-gas interface. Regulators are used as an adjunct to collectors and frothers to increase flotation selectivity or mineral recovery. Representatives of this class are substances of both inorganic and organic origin [29].

The main purpose of the collectors is to hydrophobize the mineral surface, increase the speed and strength of adhesion of particles to air bubbles [30].

Recently, selective collectors have been mainly produced on the basis of chelate-forming organic compounds containing electron-donating atoms, since nitrogen, oxygen, sulfur, phosphorus and of course halogens. As a rule, the nonpolar part of anionic sulfhydryl collectors (the polar part contains S-2) contains 2–6 carbon atoms, while the oxyhydryl collectors (the polar part contains O–2) contain 12–18 carbon atoms [31].

Of the nonionic collectors, nonpolar oils and water-insoluble sulfur-containing oily reagents are used in flotation practice [32].

For flotation of sulfide and sulfidized ores of heavy nonferrous metals, sulfur-containing collectors—sulfhydryl and thiocarbamic acid derivatives—are most effective [33]. Oxygen-containing (carboxylic acids and their derivatives), nitrogen-containing (amines, quaternary ammonium bases, ammonium salts) and some sulfur-containing collectors are effective in the flotation of oxidized minerals ores of rare, ferrous, and some non-ferrous metals [34].

As flotation reagents that are selective with respect to gold due to the formation of sparingly soluble complex compounds, the use of modified solutions of sulfhydryl collectors—xanthate and diethyldithiocarbamate—consisting of nonionic components with a hydrophobizing ability and complexing properties with respect to noble metals [35] was proposed.

In the flotation of quartz, sylvinite, and some oxidized minerals of non-ferrous and rare metals (smithsonite, calamine, wolframite, etc.), nitrogen-containing (amines, quaternary ammonium bases, ammonium salts) and oxygen-containing (carboxylic acids and their derivatives) collectors are used [36].

The possibility of increasing the selectivity of the flotation separation of copper and zinc sulfides by using a composition of reagents - sodium dialkyldithiophosphate and butyl xanthate has been established. The influence of the ratio of the main collector Kx and the additional collector BTF on the technological parameters of flotation and the selectivity of the separation of copper and zinc sulfides was determined [37]. For flotation of sulfide ores of heavy non-ferrous metals, oxyhydryl and cationic collectors are also effective; however, in this case, they are significantly inferior in selectivity to sulfhydryl collectors and thiocarbamic acid derivatives [38].

Foaming agents are used to effectively disperse the air delivered to the flotation cell into bubbles of the required volume and stability. Their molecules have a heteropolar structure, i.e. contain hydrophobic and hydrophilic groups of atoms [39], the nonpolar part of which includes one or more aliphatic or cyclic hydrocarbon radicals. Foaming agents owe their polar nature to hydroxyl, carboxyl, carbonyl, amino or sulfo groups.

The intensity of the flotation process is determined by the size of the liquid-gas interface, which, with the same amount of gas, will increase with increasing bubble dispersion. However, this process is accompanied by a sharp increase in the free surface energy, which makes the pulp more unstable in terms of thermodynamics [40], i.e. merge into larger ones, their total surface and the value of the free energy of the system decrease in this case. Pure liquids cannot form stable foam because air bubbles coalesce upon collision, reducing the total surface area and free energy values of the system. Foaming agents slow down the process of coalescence, because as a result of adsorption on the liquid-gas interface, an oriented layer of molecules is formed, the polar ends of which are hydrated by water dipoles.

Depending on the foaming ability of the pH, blowing agents are classified into three main groups: acidic, basic and neutral. Acid and neutral foaming agents are practically not used in the flotation of non-ferrous and rare metal ores,

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because they are toxic (phenolic reagents, heavy pyridine bases) and wastewater treatment from them is a great difficulty [41].

Neutral blowing agents containing aromatic alcohols include terpinel-containing substances and some synthetic reagents containing ether bonds, including monoethers of polypropylene glycols, polyalkoxyalkanes, dialkyl phthalates, dimethyl phthalates, OPSB reagents (propylene oxide, butyl alcohol), E-1, etc. The OPSB blowing agent has a very strong foaming properties and is used in the flotation of copper-molybdenum and other ores, in the cycle of collective flotation of sulfides from polymetallic ores [42].

Foaming agents with ether bonds include oxal (T-80), T-66, OPSB, OPSM, E-1. T-80 is an improved version of the T-66 foam concentrate. It is less toxic and less volatile than T-66 and its consumption is 10-20% lower. Oxal is a by-product of dimethyldioxane production; it contains over 60 compounds, of which only 15 have been identified [43].

A foaming agent for the flotation of non-ferrous and precious metal ores was obtained on the basis of fusel oil by modifying it with the use of sulfuric acid as a catalyst and air oxygen as an oxidizing agent [44]. The product with the most pronounced foaming quality is designated MFS - modified alcohol fraction, tested in the flotation of gold-bearing ore.

During the flotation of non-ferrous metal ores, reagents based on acetylenic alcohols DMIPEK and DK-80 act as selective additional collectors with foaming properties, and at a flow rate of 3–35 g/t, they can reduce the flotation time, as well as increase the recovery of copper up to 3.5% , zinc up to 12%, gold up to 8-10%. The use of DMIPEK and DK-80 as additional selective foam collectors in the flotation of various types of non-ferrous and precious metal ores will increase the extraction of valuable components by 1.5-12.0%, almost double the flotation speed, improve the quality of the resulting concentrates, improve the stability of the flotation process and reduce the environmental burden on the environment in the area of operation of flotation plants by reducing the content of heavy metals in tailings [45].

AKA-9 foaming agent was synthesized on the basis of hydrocarbon feedstock processing products to improve the process of flotation of polymetal feedstock [46].

Compositions based on the foaming agent T-80 with aqueous solutions of sodium sulfur-containing inorganic salts have been created, which help to reduce the consumption of the foaming agent, increase the extraction and content of valuable components in concentrates [47].

Very interesting complex selective reagents have been synthesized: composite xanthate (XC) and composite aeroflot (CA) with the preparation of mixtures KS-1, KS-2, KS-3 based on them at various ratios for the flotation extraction of sulfide minerals with fine inclusions of gold from refractory ores [48].

There are data on the synthesis of a foaming agent based on monohydric secondary alcohols [49], a mixture of methyl esters of benzenecarboxylic, isoamyl, succinic, and glutamic acids obtained as a result of methylation of a coal oxidation product [50].

As noted, regulators are flotation reagents used in addition to collectors and frothers to increase flotation selectivity or increase mineral recovery. For the flotation of mineral raw materials, about four hundred regulators have been proposed. Depending on the intended purpose in the process of flotation, in each case, regulators of an activating, depressing, or suppressing action and regulators of the environment are distinguished [29].

IV. EXPERIMENTAL RESULTS

Before studying the mechanism of adsorption of flotation reagents, it is necessary to consider the basic principles of natural flotation and hydration of minerals. Inherent surface hydration is possible when the interrelation of molecules of one phase is less than the interrelation of molecules between different phases [51]. Typically, air molecules will attach to more hydrophobic particles. This process is determined by the interfacial energies between the solid, liquid and gas phases, which is determined by the Young-Dupré equation [52], which characterizes the relationship between the work of adhesion and the contact angle of wetting:

$$W_a = \sigma_{12}(1 + cos\theta), \quad (1)$$

where,

σ_{12} - surface tension at the interface of two phases (liquid-gas),

$cos\theta$ - wetting angle,

W_a - inverse work of adhesion.

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Under the conditions of having a mineral with good wettability, it is possible to form multilayer coatings from water molecules. If the contact angle is equal to 90°, the adhesion and cohesion energies are characterized by the same values (W_a/W_k=1). In the case when θ=180° (W_a<W_k), the liquid does not wet the surface of the mineral at all. However, as practice shows, minerals with a wetting angle of more than 105° have not been found, and for minerals such as quartz and hematite, these indicators do not exceed 25°. This is due to the formation of unsaturated bonds during the destruction of the mineral, and the formation of unsaturated bonds can be associated with the breaking of bonds between atoms, molecules and ions in the composition of the original mineral.

Today, using the possibilities of modern programming, it is possible to adequately simulate the collision velocities of small particles (less than 0.08 mm), but there is no theory that accurately models the collision of bubbles with particles up to 300 µm in size, which are commonly used in flotation processes [53].

The efficiency of the adsorption medium is affected by the ratio between the surfaces of both materials. There are many factors that affect the efficiency of physical or chemical adsorption. Among such factors, starting with surface energy and polarity, ends with the shape, size and roughness of the particle. In froth flotation, adsorption is a consequence of free surface energy, since finely dispersed particles, having a high surface area to size ratio, form attraction with adsorbates. The air bubbles must selectively adhere to the necessary particles to lift them to the surface of the suspension, wetting the particles of another mineral and leaving them in the aquatic environment of the system.

The adsorption of flotation reagents is based on complex physical and chemical interactions of the sorbent with the adsorbate. Basic information about the adsorption properties of a mineral and the nature of adsorption on it can be obtained based on the analysis of adsorption isotherms and their description by the corresponding models of isotherm equations [54].

During the adsorption of cationic collectors, the molecules of the dissolved adsorbate interact simultaneously with water molecules and with atoms of the surface layer of the mineral. In this case, the energy that keeps the adsorbate molecules on the surface of the sorbent is equal to the difference between the energies of these two interactions. Therefore, the greater the difference, the greater the adsorption energy and the amount of adsorbed substance [55].

Mirgorod Yu.A. and his colleagues, studying the thermodynamics and sorption kinetics of cationic and anionic surfactants in solutions, experimentally determined the area per surfactant molecule as a function of temperature and the Gibbs adsorption energy. It was established that the sorption kinetics of cationic surfactants is controlled by the equilibrium excess concentration on the surface of a solid, while that of anionic surfactants is controlled by the adsorption barrier [56].

Foams used in the flotation beneficiation of ores should have a fineness, which is characterized by air bubbles (dispersed phase), having sizes in the range of 0,6–1,2 mm [44]. It is the dispersity in the specified range that gives the foams lifting abilities, providing the floating of fine particles with valuable components into the surface foam layer.

The relationship between the structure and properties of adsorption foam films and their stability was considered in [57]. Unlike low molecular weight surfactants, their high molecular weight varieties create adsorption layers with a relatively higher viscosity and strength, which ensure the action of the structural-mechanical stability factor [58].

From the course of colloid chemistry, it is known that with a decrease in the surface tension of a solution, its foaming ability increases, tk. in this case, less work is expended to obtain the same volume of foam and the supply of free surface energy decreases [59]. At constant pressure and temperature:

$$\Delta G = -\sigma_{12}\Delta A, \qquad (2)$$

where,

ΔG - change in the Gibbs energy;

ΔA - change in the specific surface area of the system.

It can be seen from (2) that a decrease in ΔG is accompanied by a decrease in the value of ΔA, which contributes to the destruction of foam bubbles. To develop a thermodynamically stable foam, the solution must contain a surfactant. The criterion for evaluating the effectiveness of a surfactant as a foaming agent is the value of its adsorption at the solution–air interface and a decrease in surface tension [60].

The foaming ability of surfactants depends on the mutual influence of such factors as temperature, *pH* of the solution, the presence of additives of electrolytes and organic non-polar liquids, etc. It is shown that the foaming ability depends on the location of the hydrophilic group in the molecule: the closer this group is located to the middle of the molecule, the higher foaming ability of solutions of anionic surfactants [61].

An increase in the concentration of a surfactant in a solution leads to an increase in its adsorption and foaming ability [31]. It is shown that the time of liquid outflow from the foam film sharply increases in a narrow concentration range. Typically, maximum foaming occurs when the CMC is reached. In this region of surfactant concentration, the formation of the adsorption layer is completed, and the foam film acquires maximum strength. Exceeding the CMC leads to a weakening of the diffusion of surfactant molecules into the adsorption layer of the mineral, due to which the foaming ability decreases. Therefore, it is recommended to evaluate the foamability of aqueous solutions of surfactants during CMC [62].

It is well known that foams are not thermodynamically stable. However, their lifetime can be significantly extended by the action of the Marangoni and Gibbs effects, an increase in the relatively high surface viscosity or mechanical properties in the film, which determine the effect of the structural-mechanical factor of stability. Surface hydrated layers and double electrical layers, which prevent their thinning, have a significant effect on the film stability [63].

V. CONCLUSION AND FUTURE WORK

Today, flotation is becoming increasingly important, since using this method it is possible to enrich various metal ores, purify wastewater from various oil and fat and suspended solids, as well as in other industries to solve a number of important processes. Available data show that flotation processes are based on different wettability properties of the surface of materials. In principle, flotation is very similar to the sinking and floating process, where the density characteristics of the materials relative to the medium in which they are located underlie the separation. Flotation reagents interact with the surface of the particles of the enriched ore due to the mechanism of physical or chemical adsorption. Using the corresponding adsorption equations, it is possible to establish the nature of the processes of flotation interaction.

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