Milan M. Petrov*, Ljubiša D. Andrić*, Mašan M. Grujić*

FLOTATION OF BLUE WATER**

Abstract

Flotation of ions and molecules represents a promising method of separating components from solution, or in our case, gelled copper salt from blue water. The method of flotation of ions and molecules is basically the flotation extraction process which produces different concentration gradients of multicomponent condensed phase system. Different concentration gradients in the flotation extraction are due to the driving forces of participating molecules driven by molecular interactions. Multicomponent condensed phase system, i.e. flotation pulp, consists of water molecules of solute, and a suitable reagent which has the role of connection the liquid and gaseous phases dispersed in a biphasic system. Such a system leads to the interaction of solute with reagent to the formation of coagulated component in water as solvent. Separation in the polyphased system is in accordance with the Van't Hoff equation, and spontaneously occurs in two-phase systems like gaseous-fluid, such as the system of flotation pulp. Using the osmotic pressure in a column flotation machine comes to separation of flotation pulp into heavy and light phase. This allows the water molecules to form their natural distances which are only valid for molecules of pure water or heavy phase. Also, the solute forms its light phase, copper – surfactant salt as insoluble product. For some polyphase systems such as colloidal systems like in the flotation process are sufficient atmospheric pressure conditions, and for others solutions should be applied overpressure while being aerated. This paper presents the results of research the flotation extraction of blue water, i.e. copper solution content of 0.2 g/l. It is concluded from results that there is a possibility of purifying the blue water from the copper mine tailing dump using the flotation extraction technology.

Keywords: concentration gradient, condensed phase, coagulation, osmotic pressure, xerogel

INTRODUCTION

Flotation was first applied in 1877 to enrich the graphite ore, but immediately afterwards it was abandoned. Since the first patented process (Elmore, 1898) [1], it was applied and constantly improved. The use of flotation in wastewater treatment is considered to be a revolutionary innovation because it runs 6-8 times faster than sedimentation and ends in 15-30 minutes [2]. In addition, it provides a very high degree of removal the suspended material, significantly reducing the con-

centration of surface active materials in waste water and increases the oxygen content, all in a great extent the later stages of processing. Today, the flotation process is applied in many areas of industry: in the enrichment, separation of various metals in ores and fuels, separation of valuable components from the solutions, while in the wastewater treatment it is used for removal the suspended and emulsified pollutants and biological sludge buildup. The solid particles, droplets, ions or mole

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cules from the liquid phase, "glued" to the air bubbles pumped to the liquid phase in various ways, are carried to the surface by the driving force of the osmotic pressure, and concentrated to a foam which is removed from there.

FLOTATION PROCESS

Flotation process is based on the fact that particles with hydrophobic surface in aqueous dispersions have the ability to stick with a gas bubble. During the process of mutual mixing the dispersion and bubbles, some particles are concentrated on the surface of bubbles, while particles without a hydro-

phobic surface remain in the volume of dispersion. Separation based on these natural capabilities of particles is used as an opportunity of getting separate particles based on their different abilities to concentrate on the surface of bubbles. Flotation is a process of molecular "attaching" of particulate materials on the boundary surface of phases, usually gas (usually air–water). Flotation is used as an alternative method to the other separation processes: sedimentation, centrifuge separation, filtration and similar, and it is often more efficient or economically justified [2]. Figure 1 illustrates differences between these processes, and Figure 2 shows the types of flotation process.

Figure 1 Illustration the similarity of flotation of ions and molecules with the flotation of minerals

- a) Flotation active mineral particles are adsorbed on surface of bubbles while inactive mineral particles remain in the bulk;
- b) Surface active components of solution are adsorbed on surface of bubbles, while other ones, eg. surface inactive, remain in the bulk;
- c) Onto surface of bubbles are adsorbed mineral particles covered with collector;
- d) On surface of bubbles is adsorbed surfactant (individual chemical compound), which consists of colligend (indicates the ion to be removed) and the collector;
- e) Ba^{2+} ions are attracted by fatty acid anion collector (RCOO^-) adsorbed on surface of quartz particles
- f) UO_2^{2+} ion is a binder between CO_3^{2-} ion and four ions of alkyl ammonium collector ($\text{R(R}_2)_3\text{N}^+$).

Figure 2 Scheme of foam separation (a), ion flotation (b), flotation extraction (c) and nucleate fractionating (d)

Where: 1. air, 2. bubbles prunger, 3. water solution, 4. surfacing bubbles, 5. foam layer, 6. upper product, 6' 6'' or the upper product which is returned to the wet foam and upper product which is returned under the foam, 7. starting solution, 7' i 7'' added to the starting solution, i.e. the initial solution added above and below the level of foam, 8. bottom product, 9. foam, 10. organic liquid phase

ADSORPTION ON SURFACE OF BUBBLE

Adsorption on surface of bubble is the basis of the flotation of ions and molecules [3].

Thermodynamics of adsorption: The basic thermodynamic equation of interfacial boundaries liquid-gaseous was given by Gibbs:

(1)

Where:

σ - surface tension

η_s - excess entropy in the system

T - absolute temperature

- the excess weight of i-th component per unit of surface of interfacial area

μ_i - chemical potential

n - number of components

From the expression given in the form of equation 1, the adsorption isotherm equation is derived:

(2)

Or

$$\text{---} \quad (3)$$

When

$$\text{---} \quad (4)$$

Where:

- standard chemical potential

- activity of the i-th component in solution

- universal gas constant

i (5)

$$\text{---} \quad (6)$$

In very dilute solution where

, - concentration of i-th component in the solution, instead of equation 6, there is:

$$\text{---} \quad (7)$$

or

$$\text{---} \quad (8)$$

Figure 3 Structure of adsorption layers at the interphase boundary liquid – gas, systems for water - dissolved surfactant

From equation 8 it follows, if the components of the solution reduce the surface tension (—) then adsorption on the interphase boundary () and vice versa. In the first case the substance is called surfactant, and contrary.

If the adsorption layer is considered as a single surface phase thickness δ , then for the i -th component of solution can be written:

(9)

If Γ_i is adsorption extent, C_i^0 equilibrium concentration in the solution, while C_i^a concentration in the adsorption layer () then from equations 8 and 9 it follows:

$$\Gamma_i = \delta (C_i^a - C_i^0) \quad (10)$$

Presented equation shows that in the case of highly active surface active substance — ratio can attain the value of 10^4 to 10^6 or more. Figure 3 illustrates the structure of adsorption layer.

- nonionic surfactant;
 - ionic surfactant (symmetric binary electrolyte unassociated with surface-active cation);
 - concentration in bulk
 - concentration on adsorption layer
 - i - concentration of anions and cations
- 1 – surface active molecules
2 – surface active ions
3 – opposite charged ions

Based on the review of the structure of the adsorption layer is obvious that calculations based on equation 10 are illustrative only. More artificial is the notion of homogeneity thickness of adsorption layer in case of ionic surfactants

Driving forces and theoretical aspects of flotation extraction of ions and molecules

The osmotic pressure Π from the Van't Hoff equation is

(11)

In this equation, c is the molar concentration of solute, R is the gas constant and T is the absolute temperature at which they are dissolved. The chemical potential of water must be in equilibrium and the same on both sides of the semi permeable membrane

(12)

In case of the solution the following is applied:

(13)

Changes in chemical potential related to changes in pressure are given by the equation:

(14)

Combining equations 2, 3 and 4 assuming that the molar volume of water varies very little at a given pressure range, the following is applied:

(15)

Therefore

(16)

Where k_p is piezoscopic constant (—),

When — is low, the following approximation is:

(17)

and it is

(18)

For small values of

—

(19)

Where n_s is the number of moles of solute n_w number of moles of water

(20)

Where —, is molar concentration of solution

At low osmotic pressure up to 0.5 MPa, the ideal colligative equation has the form:

—

(21)

V is volume (in liters) of solution containing one liter of water. [4]

Description of equipment and processes

Flotation extraction device consists of three functionally incorporated wholes [5]:

- Worm pump
- Injector or sprinklers
- Column container

Figure 4 Schematic view of the flotation extraction device

Functional connection of the device is shown in Figure 1. The mobile worm pump (Mozly) has a basket (1) for the incoming pulp, engine (2), worm wheel (3) and three outlet orifices from valves (4), (5) and (6). In the pump basket the pulp is conditioned with reagent (usually a flocculant) so that the output from the pump is returned into the basket through the return line (5). At the moment when the prepared pulp is put into the column through the injector (7) discharge valve of clean water is closed (11) and valve of return line (5). Batch filling of the column (8) is carried out through injector element that sucks in the air (9) or to the air being blown through the compressor. In a higher part of column above the condensed phase (10) is formed a two-phase system characteristic for isobaric and isothermal macroscopic flow of the pulp. The two-phase system increases its volume by continuously full column injector, a meniscus condensed phase, which is actually a semi permeable membrane is moved upward. Dynamic equilibrium of the water molecule as a solvent is established on the semi permeable membrane or meniscus of condensed phases. Mass transfer of substance or flocculated gel in the case of larger quantities of dispersion is found in the nature of osmotic pressure.

MATERIALS AND METHODS

Tailing dumps resulting in exploitation of copper ore contain dissolved copper salt, i.e.

the so-called blue water. In order to inhibit precipitation of copper salts, it is necessary to form a compound with sodium-stearate from soap. Sodium stearate is a salt of sodium and stearic acid. This is one of the basic raw material in the manufacture of soap. The process of obtaining has been known since the ancient times [5] obtained by reacting vegetable oils with sodium hydroxide. In addition to the manufacture of cleaning stuffs, it is also used as an emulsifier in various creams, shampoos and foodstuffs. It is obtained by saponifying the ester with sodium hydroxide, thus obtaining sodium stearate, and glycerol. In the reaction of sodium stearate and copper from blue water in the process of flotation extraction, is formed a gel-like structure, i.e. copper stearate, which is collected on surface and removed mechanically.

Osmosis is a colligative property and depends on the amount of solute particles [6]. This feature is used to calculate the required weight of soap as a reagent, for the successful flotation extraction of blue water. The osmotic potential of pure water is defined as zero. Osmotic potential of solution has a negative value in units of pressure. At low concentrations of solution, the osmotic potential is expressed by the Van't Hoff equation:

(22)

Table 1 Values for calculation the osmotic pressure of blue water, and soap as a collector which was added to the flotation extraction process

1	2	3	4	5	6	7	8
n, mol	R, Jmol ⁻¹ K ⁻¹	T, K	P, Pa	V, m ³	M, g/mol ⁻¹	m, g	h, m
Blue water, solution of copper sulphate							
Amount of salt in solution	Molar gas constant	Temperature	Osmotic pressure	Volume of dissolved salt	Molar mass of CuSO ₄	Weight of dissolved salt	Foam height
0.00414	8.314	293.0	10073.0	0.00100	159.610	0.660	1.027
Soap							
Amount of soap in solution	Molar gas constant	Temperature	Osmotic pressure	Volume of dissolved soap	Molar weight of soap	Weight of dissolved soap	Foam height
0.000424	8.314	293	10333.4	1E-04	306.46	0.13	1.053
9.79E-05	8.314	293	2384.65	1E-04	306.46	0.03	0.219
4.89E-05	8.314	293	1192.32	1E-04	306.46	0.015	0.118
1.63E-05	8.314	293	397.442	1E-04	306.46	0.005	0.040

Blue water with 0.662 CuSO₄ g/l has an osmotic potential of about 10000 Pa, Table 1, which is enough to hold the water column of about one meter. The experimental procedure is clear in a sense that it is obvious that when frothier was added surface tension of liquid is decreased and the foam is formed. Above the surface of water, upgraded gaseous liquid two-phase system (foam) is formed which can potentially carry copper compound. It certainly creates a copper stearate scum in the form of gel that is necessary to add in a soap solution. Calculating the amount of soap is done by equalizing the osmotic pressures of blue water and soap as a collector as shown in Table 1, Column 4. Four different doses of soap in four separate experiment were used, but the best results gave the experiment in which the osmotic pressure of soap coincided with the osmotic pressure which produces a solution of blue water. Ordinary laboratory flotation cell with a height of h=30 cm would not meet the conditions of set height of foam, so this account evidence that there is at least one reason why the column is used in flotation ex

traction process. A device that is used for flotation extraction of blue water has an important characteristic that highly aerate (in our case) solution, which is only possible to achieve increasing the inlet pressure in ejector. With the help of worm pump is realized the flow of materials and required excess pressure of 5 bar in order to effectively and efficiently carry out the necessary flotation extraction.

ANALYSIS THE ACHIEVED RESULTS

After treatment the blue water with major soap compound (sodium-stearate), a chemical analysis of the product was carried out and is shown in Table 1. The FTIR analysis was performed on the device - **Thermo Fisher Scientific Nicolet IS-50by ATR** (attenuated total reflectance) technique in the range of 4000 to 400 cm⁻¹ at resolution 4. Upon completion of e measurement baseline correction was done - atmospheric (for elimination of signal gases CO₂ and H₂O)[7].

Table 2 Distribution and chemical analysis of flotation extraction of blue water

	M %	Cu %	Fe %	S %	M*Cu	M*Fe	M*S	R Cu	R Fe	R S
Concentrate	0,74	2,65	0,13	8,23	1,961	0,096	6,1	94,5	33,8	9,9
Output	99,26	0,00115	0,0019	0,56	0,114	0,188	55,6	5,5	66,2	90,1
Feed	100,00	0,0208	0,0028	0,62	2,075	0,284	61,7	100	100	100

(infra-red) spectroscopy is used primarily as a contribution to the structural analysis of organic molecules (as well as inorganic anions) in a manner that is based on the position of absorption bands by which the functional groups that are present in molecule can be identified. spectrum are vibration spectrum, i.e. absorption of radiation comes from the vibrational transitions in molecule. When the absorption of radiation occurs there is a change in oscillation frequency of chemical bond between two atoms. Based on the radiation energy that is required for a given vibration transi-

tion, (spectrum is ordered sequence of such energies), i.e. From the vibration frequency change of chemical bond, it can be concluded that between two atoms linked by chemical bond the vibration transition occurred.

In case of gel which during ionic flotation of blue water comes to the surface and for which it is assumed that it is the insoluble salt of copper and organic acid soap (mostly stearic, although they are always present to some extent, palmitic, oleic etc., since the commercial soap was used), in addition to the standard AAS analysis to

determine the percentage of copper in sample ("solid" phase which floated up), analysis is done to unequivocally shows that the gel is actually insoluble salt containing Cu(II) cations, and organic nature anions (originating from the water-soluble sodium and potassium salts of higher fatty acids in soap). Therefore, if one looks at the spectrum of the dried gel, where one should have in mind that the in drying air all the trapped water cannot evaporate completely, the following can be concluded:

The intensive band at (~ 1100) probably originates from the bond (valent vibration of bond) of sulphate anions that are co-precipitated with the formation of "solid phase".

Band at (~ 1450) comes from the bonds (- deformation vibrations, i.e. change in the angle of chemical bonds; the band is in nature of medium intensity, but

since the number of groups in the molecule is high in this case it is clearly visible).

Poor visible band at (~ 1650) originates from -group—it is a valent symmetric vibration of resonance structures of carboxyl anion).

The band, which should be the highest intensity at (~ 1720), i.e. valent vibration, lacks because separated gel does not contain the fatty acids but the fatty acids salts.

Band at (3000 - 3500) originates from the bond (valent vibration, extended due to hydrogen bonds between water molecules—at 3600 there is a small peak of bond which belongs to the water molecules that are not connected by hydrogen bond). Therefore the spectrum clearly shows that the sample contains molecules with hydrocarbon chain (bond), carboxyl group (), and water molecules (Figure 5).

Figure 5 IR spectrum dried gel

The second spectrum is the spectrum of residue which was crystallized upon evaporation of the solution. Based on the appearance of deposits, it is assumed that the sediment is mostly blue stone (). spectrum confirms this (Figure 6). It is certain that in the solution of

"blue water" there are other salts that were deposited during evaporation together with clearly present (copper(II) sulphate), but those in the spectrum are not visible, i.e. spectrum indicates the sulfate (sulfite), water, and optionally nitrate (nitrite).

Based on the spectrum of the sample obtained by evaporating the solution (figure 6), the following can be concluded:

The intense band at (~ 1100) comes from the bond (valent vibrations) of sulphate anions. Broad band at (~ 3600-2700) comes from the bond. Everything that was said regarding the presence of

water in the sample is also applied to residue.

The medium intensity band at (~ 1680) probably comes from nitrate () valent vibrations. Therefore the spectrum clearly shows that the sample contains molecules with hydrocarbon chain (), carboxyl group (band and band), and water molecules.

Figure 6 IR spectrum of evaporated solution

CONCLUSION

Any physical system contains the energy of a certain amount. The amount of energy of the system is not an absolute value, but relative to the reference condition or reference level. At the beginning of the twentieth century W. Nernst performed various fields of chemistry classification based on the type of energy introduced into the system: thermochemistry, electrochemistry, photochemistry, etc. The name mechanochemistry referred to the reactions initiated by mechanical energy, eg. reactions initiated by the process of friction, breaking, during the mechanical treatment of solid components. The activation energy of mechanochemical treatment system is required to enable the

external force to increase the surface of material, to affect the reagents in the flotation of various pneumatic suspensions. The processes of enrichment the mineral resources in the flotation systems are based on electrochemistry, adsorption and catalytic functioning of the individual reagents to separate the components of such systems. In order to achieve solute transport to form the gel on surface in the flotation extraction process, the activation energy must have such an impact on system and the energy barrier that resists that transport should be overcome by the external force. Adsorption extent refers to the gaseous fluid, and in a solid there is a change of intermolecular and intramo-

lecular forces. Intramolecular forces are the forces that hold together the atoms and thus form a molecule or compound. Intramolecular forces include all types of chemical bonds. They are stronger than the intermolecular forces that occur between the atoms or molecules which are not bound. The activation energy of the reacting system in one device (reactor) plays a very important role in the physical characteristics of the system in terms of selective separation the components of the system. It is shown that one can calculate the intensity of the intramolecular force as the force of osmotic pressure, and it can be used to calculate the necessary amount of reagents for successful flotation extraction.

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FLOTACIJA PLAVE VODE**

Izvod

Flotacija jona i molekula predstavlja perspektivan metod odvajanja komponenata iz rastvora, odnosno u našem slučaju geliranog bakar sulfata iz plave vode. Jedna od metoda flotacije jona i molekula je floto-ekstrakcija u kojoj nastaju različiti koncentracijski gradijenti višekomponentalnih kondenzovanih faza. Različiti koncentracijski gradijenti u floto-ekstrakciji nastaju usled pokretačkih sila učestvujućih molekula vodenih molekulskim interakcijama. Višekomponentna kondenzovana faza ili flotacijska pulpa sastoji se iz molekula vode rastvorka i pogodnog reagensa koji ima ulogu konekcije tečne i gasovite faze u dvofaznom disperznom sistemu. U takvom sistemu dolazi do sinteze rastvorka sa reagensom i do stvaranja koagulisane komponente u vodi kao rastvaraču. Separacija nastalih koagulisanih komponenata, saglasno Van't Hoff-oj jednačini, spontano se dešava u dvofaznim sistemima tečno gasovito, kakav je sistem flotacijske pulpe. Primenom osmotskih pritisaka u kolona flotacijskoj mašini dolazi do difuzije i razdvajanja flotacijske pulpe na tešku i laku fazu. Aeriranjem se omogućava molekulima vode da formiraju svoja prirodna rastojanja koja važe samo za molekule čiste vode odnosno tešku fazu. Takođe i rastvorak formira svoju laku fazu, kserogel bakar-sulfata, kao nerastvorni proizvod. Za neke kondenzovane faze kao što su koloidni sistemi u floto-ekstrakciji je dovoljan atmosferski pritisak a za druge pak (prave rastvore) je potrebno primeniti nadpritisak u delu aeracije. U radu su prikazani rezultati istraživanja floto-ekstrakcije plave vode sa ulaznim sadržajem bakra od 0,2 g/l. Iz prikazanih rezultata istraživanja zaključuje se da postoji mogućnost prečišćavanja plave vode iz jalovišta rudnika bakra primenom floto-ekstrakcijskih tehnologija.

Ključne reči: koncentracijski gradijent, kondenzovana faza, koagulacija, osmotski pritisak, kserogel

UVOD

Flotacija je prvi put primenjena 1877. godine u obogaćivanju grafitne rude ali je odmah zatim bila napuštena. Od prvog patentiranog postupka (Elmore, 1898.) [1] ona se sve više primenjuje i stalno usavršava. Primena flotacije u obradi otpadnih voda se smatra revolucionarnom inovacijom jer ona protiče 6-8 puta brže od sedimentacije i završava se za 15-30 minuta. [2] Pri tome se obezbeđuje veoma visok stepen uklanjanja suspendovanog materijala, značajno se smanjuje koncentracija površinski

aktivnih materijala u otpadnoj vodi i povećava sadržaj kiseonika, a sve to u znatnoj meri olakšava kasnije faze obrade. Danas se flotacija primenjuje u mnogim oblastima industrije: u obogaćivanju, u razdeljivanju ruda različitih metala i goriva, u izdvajanju visokovrednih komponenti iz rastvora, dok se u obradi otpadnih voda primenjuje za: uklanjanje suspendovanih i emulgovanih zagađivača, koncentrisanje bioloških muljeva. Čvrste čestice, kapljice, molekuli ili joni iz tečne faze, prilepljeni uz mehurove

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vazduha koji se formiraju u tečnoj fazi na različite načine, bivaju silom osmotskog pritiska iznošene na površinu tečnosti, gde se koncentrišu u obliku pene koja se odatle uklanja.

PROCESI FLOTACIJE

Proces flotacije zasnovan je na činjenici da čestice vodenih disperzija sa hidro-fobnom površinom imaju sposobnost da se prilepe uz mehurić gasa. Pri uzajamnom mešanju mehurića i disperzije podobne čestice koncentrišu se na površini mehurića, a čestice koje nemaju hidro-fobnu površinu ostaju u zapremini disperzije. Razdvajanje

zasnovano na tim sposobnostima mehurića koristi se kao mogućnost dobjanja odvojenih čestica na osnovi njihovih različitih sposobnosti koncentrisanja na površini mehurića. Flotacija je proces molekularnog „slepljivanja“ čestica materijala koji se flotira uz graničnu površinu faza, obično gas (najčešće vazduh) - voda. Flotacija se koristi kao alternativna metoda drugim separacionim postupcima: sedimentaciji, separaciji centrifugama, filtraciji i slično, od kojih je često ili efikasnija ili ekonomski opravdanija [2]. Slika 1 ilustruje razlike između pomenutih procesa, a slika 2 pokazuje tipove flotacijskih procesa.

Sl. 1. Ilustracija sličnosti flotacija, flotacija jona i molekula i flotacija minerala

- flotacijski aktivne mineralne čestice koncentrišu se na površini mehurića gasa, a flotacijski neaktivne ostaju u zapremini suspenzije;
- Površinski aktivne komponente rastvora koncentrišu se na površini mehurića, a površinski neaktivne ostaju u zapremini rastvora;
- Na površini mehurića koncentrišu se mineralne čestice pokrivene kolektorom;
- Na površini mehurića koncentriše se sublat (hemijski individualno jedinjenje), koji se sastoji iz koligenda (označava jon koji se izvlači) i kolektora;
- Joni Ba^{2+} vežu anjoni kolektora masne kiseline $RCOO^-$ sa površinom čestica kvarca;
- Joni CO_3^{2-} bivaju vezivno sredstvo među jonima UO_2^{2+} i četiri katjona alkilamonijum kolektora $R(R_2)_3N^+$

Sl. 2. Šema penaste separacije (a), jonske flotacije (b), flotoekstrakcije (c) i mehurastog frakcionisanja (d)

1. vazduh, 2. raspršivač vazduha, 3. vodeni rastvor, 4. isplivavajući mehurići, 5. sloj pene, 6. gornji proizvod, 6' i 6'' gornji proizvod, odnosno gornji proizvod koji se vraća na mokru penu i gornji proizvod koji se vraća pod penu, 7. početni rastvor, 7' i 7'' dodavani početni rastvor, odnosno početni rastvor dodavan ispod i iznad nivoa pene, 8. donji proizvod, 9. pena, 10. organska tečna faza

ADSORPCIJA NA POVRŠINI MEHURA GASA

Adsorpcija na površini mehura gasa predstavlja osnovu flotacije jona i molekula. [3]

Termodinamika adsorpcije: Osnovnu termodinamičku jednačinu međufazne granice tečno-gasovito dao je Gibbs:

$$d\sigma = -\eta_s dT - \sum_{i=1}^n \Gamma_i^0 d\mu_i \quad (1)$$

gde je:

σ - površinski napon

η_s - višak entropije u sistemu

T - apsolutna temperatura

Γ_i^0 - višak mase i -te komponente na jedinicu međufazne površine (adsorpcije)

μ_i - hemijski potencijal

n - broj komponentata u sistemu

Iz izraza datog u vidu jednačine 1 proističe jednačina adsorpcione izoterme.

$$d\sigma = - \sum_{i=1}^n \Gamma_i^0 d\mu_i \quad (2)$$

ili

$$\Gamma_i^0 = \frac{\partial \sigma}{\partial \mu_i} \quad (3)$$

Kada je

$$\mu_i = \mu_i^\ominus + RT \ln a_i^0 \quad (4)$$

gde je:

$\mu_i^\ominus$ - standardni hemijski potencijal

a_i^0 - aktivnost i -te komponente u zapremini rastvora

R - univerzalna gasna konstanta

$$d\sigma = -RT \sum_{i=1}^n \Gamma_i^0 d \ln a_i^0 \quad (5)$$

$$\Gamma_i^0 = - \frac{1}{RT} \frac{\partial \sigma}{\partial \ln a_i^0} \quad (6)$$

U jako razblaženim rastvorima gde je $a_i^0 \approx C_i^0/C_i^0$ - koncentracija i -te komponente u zapremini rastvora, pa umesto jednačine 6 imamo:

$$\Gamma_i^0 = - \frac{1}{RT} \frac{\partial \sigma}{\partial \ln C_i^0} \quad (7)$$

ili

$$\Gamma_i^0 = - \frac{C_i^0}{RT} \frac{\partial \sigma}{\partial C_i^0} \quad (8)$$

Sl. 3. Struktura adsorpcionih slojeva na međufaznoj granici tečno – gas za sisteme voda – rastvora na površinski aktivna supstanca

Iz jednačine 8 sledi da, ako komponente rastvora smanjuju površinski napon ($\frac{\partial \sigma}{\partial C_i^0} < 0$) adsorpcija na međufaznoj površini je ($\Gamma_i^0 > 0$) i obrnuto. Prvi slučaj nazivamo površinski aktivnim, a drugi površinski neaktivnim.

Ako posmatramo adsorpcioni sloj kao jedinstvenu površinsku fazu debljine δ , tada za i -tu komponentu rastvora možemo pisati.

$$\Gamma_i^0 = (C_i^a - C_i^0)\delta \quad (9)$$

Ako je Γ_i^0 veličina adsorpcije, ravnotežna za koncentraciju C_i^0 u zapremini rastvora, a C_i^a odgovarajuća koncentracija Γ_i^0 u adsorpcionom sloju.

Iz jednačine 8 i 9 sledi:

$$\frac{C_i^a}{C_i^0} = 1 - \frac{1}{\delta RT} \frac{\partial \sigma}{\partial C_i^0} \quad (10)$$

Predstavljena jednačina pokazuje za visoko površinski aktivne supstance odnos $\frac{C_i^a}{C_i^0}$ može dostići vrednost 10^4 do 10^6 i više. Sledeća ilustracija prikazuje konstrukciju adsorpcionog sloja.

- Nejonska površinski aktivna supstanca;
 - Jonska površinski aktivna supstanca (simetrični binarni neasociran elektrolit s površinski aktivnim katjonom);
- C^0 - koncentracija u zapremini rastvora;
 C^a - koncentracija u adsorpcionom sloju;
 C_+ i C_- - koncentracija katjona i anjona;
 1 - površinski aktivni molekuli
 2 - površinski aktivni joni
 3 - suprotno naelektrisani joni

Na osnovi razmatranja o strukturi adsorpcionog sloja očigledno je da kalkulacije zasnovane na jednačini 10 su samo ilustrativne prirode. Više veštački je pojam homogenosti debljine sloja adsorpcije u slučaju jonskih površinski aktivnih supstanci.

$$\frac{C_i^a}{C_i^0} = 1 - \frac{1}{\delta RT} \cdot \frac{\partial \sigma}{\partial C_i^0}$$

Pokretačke sile i teorijski aspekt floto-ekstrakcije jona i molekula

Osmotski pritisak Π iz Van't Hoff-e jednačine je

$$\Pi = cRT \quad (11)$$

U toj jednačini c je molarna koncentracija rastvorka, R je gasna konstanta a T je apsolutna temperatura na kojoj se nalaze rastvori. Hemijske potencijal vode mora biti u ravnoteži i istina obe strane semi-permeabilne membrane.

$$\mu_p^{tečno} = \mu_{p+\Pi}^{rastvor} \quad (12)$$

Za rastvor se može pisati

$$\mu_{p+\Pi}^{rastvor} = \mu_{p+\Pi}^{tečno} + RT \ln(x_w) \quad (13)$$

Promene hemijskog potencijala sa pritiskom mogu se uključiti na sledeći način

$$\mu_{p+\Pi}^{tečno} = \mu_p^{tečno} + \int_p^{p+\Pi} V_m dP \quad (14)$$

Kombinacijom jednačina 2, 3 i 4 uz pretpostavku da molska zapremina vode ($V_m, m^3 mol^{-1}$) = $1,80356E-05 m^3 mol^{-1}$ slabo varira u datom opsegu pritiska, važi:

$$-RT \ln(x_w) = \int_p^{p+\Pi} V_m dP = \Pi V_m \quad (15)$$

Dakle,

$$\Pi = -k_p T \ln(1 - x_s) \quad (16)$$

gde je k_p piezoscopic konstanta ($= \frac{R}{V_m}$),

Kada je x_s nizak, važi sledeća aproksimacija

$$\ln(x_w) = \ln(1 - x_s) = -x_s \quad (17)$$

pa je

$$\Pi V_m = x_s RT \quad (18)$$

Na malim vrednostima x_s

$$x_s = \frac{n_s}{n_w} \quad (19)$$

gde je n_s broj molova rastvorka n_w broj molova vode

$$\Pi = M_s RT \quad (20)$$

Gde je $M_s = \frac{n_s}{V}$, molarna koncentracija rastvora. Na niskom osmorskom pritisku do 0,5 MPa, idealna koligativna jednačina floto-ekstrakcije ima oblik:

$$\Pi = M_s RT \left(\frac{x_w V^2}{1 + x_s V} \right) \quad (21)$$

V je zapremina (u litrima) rastvora koji sadrži jedan litar vode. [4]

Opis uređaja i procesa

Uređaj floto-ekstrakcije sastoji se iz tri funkcionalno ukomponovane celine [5]:

- Pužne pumpe,
- Injektora ili prskalice,
- Kolona posude.

Sl. 4. Šematski prikaz uređaja floto-ekstrakcije

Funkcionalna povezanost uređaja prikazana je na slici 1. Mobilna pužna pumpa (Mozly) ima koš (1) za ulaznu pulpu, motor (2), pužno kolo (3) i tri izlazna otvora sa ventilima (4) (5) i (6). U košu pumpe vrši se kondicioniranje pulpe sa reagensom (obično je to flokulant) tako što se izlaz iz pumpe vraća u koš preko povratnog voda (5). U trenutku kada se pripremljena pulpa pušta u kolonu preko injektora (7) zatvoren je ventil za ispuštanje čiste vode (11) i ventil povratnog voda (5). Šaržno punjenje kolone (8) vrši se preko injektorskog elementa koji usisava vazduh (9) ili se vazduh ubacuje preko kompresora. U višem delu kolone iznad kondenzovane faze (10) nastaje dvofazni sistem karakterističan za izobarski i izotermiski makroskopski tok pulpe. Dvofazni sistem uvećava svoju zapreminu tako što injektor neprekidno puni kolonu, a meniskus kondenzovane faze koji je zapravo polupropustljiva membrana pomera se na više. Dinamička ravnoteža molekula vode kao rastvarača uspostavlja se na polupropustljivoj membrani odnosno meniskusu kondenzovane faze. Prenos mase supstance odnosno flokuliranog gela iz dela sa većim udelom kondenzovane faze u penastu ksero gel ostvaruje se na bazi osmotkog pritiska.

MATERIJAL I METODE

Jalovišta nastala u eksploataciji rude bakra imaju rastvorenu so bakra i to je takozvana plava voda. Da bi se inhibirala

precipitacija soli bakra potrebno je formiranje jedinjenja sa natrijum-stearatom iz sapuna. Natrijum-stearat je so natrijuma i stearinske kiseline. Ovo je jedna od osnovnih sirovina u proizvodnji sapuna. Proces njenog dobijanja je poznat još od davnina. [5] Dobija se reakcijom biljnih ulja sa natrijum-hidroksidom. Osim za proizvodnju sredstava za čišćenje koristi se i kao emulgator u raznim kremama, šamponima i prehranbenim namirnicama. Dobija se putem saponiranja tristearina sa sodom, te se tako dobija natrijum-stearat i glicerol. U reakciji natrijum-stearata sa plavom vodom pri flotoekstrakciji jednačina 1, dolazi do stvaranja gela bakar stearata koji u dvofaznom sistemu biva sakupljen na površini i mehanički uklonjen.

Osoza je koligativno svojstvo i zavisi od broja čestica rastvorene supstance [6]. Ova osobina je upotrebljena da se izračuna potrebna masa sapuna kao reagensa za uspešnu floto ekstrakciju plave vode. Osmotski potencijal čiste vode se definiše kao nula kada je voda rastvarač. Osmotski potencijal rastvora ima negativne vrednosti u jedinicama pritiska. Na niskim koncentracijama se osmotski potencijal izražava Van't Hoff-ovom jednačinom.

$$\psi_{\Pi} = -M_sRT \quad (22)$$

Tabela 1. Vrednosti za izračunavanje osmotkog pritiska plave vode, i sapuna kao kolektora koji je dodavan u proces floto ekstrakcije

1	2	3	4	5	6	7	8
n, mol	R, Jmol ⁻¹ K ⁻¹	T, K	P, Pa	V, m ³	M, g/mol ⁻¹	m, g	h, m
Plava voda, rastvor bakar sulfata							
Količina soli u rastvoru	Molarna gasna konstanta	Temperatura	Osmotski pritisak	Zapremina u kojoj je rastvorena sol	Molarna masa soli CuSO ₄	Masa rastvorene soli	Visina pene
0,00414	8,314	293,0	10073,0	0,00100	159,610	0,660	1,027
Sapun							
Količina sapuna u rastvoru	Molarna gasna konstanta	Temperatura	Osmotski pritisak	Zapremina u kojoj je rastvoren sapun	Molarna masa sapuna	Masa rastvorenog sapuna	Visina pene
0,000424	8,314	293	10333,4	1E-04	306,46	0,13	1,053
9,79E-05	8,314	293	2384,65	1E-04	306,46	0,03	0,219
4,89E-05	8,314	293	1192,32	1E-04	306,46	0,015	0,118
1,63E-05	8,314	293	397,442	1E-04	306,46	0,005	0,040

Plava voda sa 0,662 $\frac{g}{l}$ $CuSO_4$ ima osmotski potencijal od oko 10000 Pa, tabela 1, što je dovoljno da drži stub vode od približno jednog metra. U eksperimentalnom postupku to je bilo očigledno kada je dodat penušač koji je smanjio površinski napon tečne faze i kada je došlo do stvaranja pene. Iznad površine vode tada se nadgrađuje dvofazni sistem tečno gasovito (pena) u kojem se može potencijalno izvršiti koncentracija soli bakar-sulfata. Naravno da je za stvaranje skrame bakar-stearata u obliku gela bilo potrebno dodati rastvor sapuna. Izračunavanje količine sapuna vrši se tako što se izjednače osmotski pritisci za plavu vodu i sapun kao kolektor što je prikazano u tabeli 1, kolona 4. Upotrebene su ukupno četiri različite doze sapuna u četiri odvojena opita, ali je najbolje rezultate dao onaj opit čiji se osmotski pritisak poklapao sa osmotskim pritiskom kojeg proizvodi rastvor plave vode. Obična laboratorijska flotacijska ćelija sa visinom od 30 cm ne bi zadovoljila postavljene uslove visine pene pa je ovaj račun dokaz da postoji najmanje jedan razlog što

se koristi kolona flotacija za floto ekstrakciju. Uređaj koji je korišćen za flotoekstrakciju plave vode ima značajnu karakteristiku visoke aeriranosti (u našem slučaju) rastvora što je jedino moguće postići pomoću povećanog ulaznog pritiska u ejektor. Preko pužne pumpe ostvaruje se dotok materijala i potrebni nadpritisak od 5 bara da bi se uspešno i efikasno izvršila potrebna flotoekstrakcija.

ANALIZA POSTIGNUTIH REZULTATA

Nakon tretmana plave vode sa natrijum-stearatom iz sapuna izvršena je hemijska analiza proizvoda prikazana u tabeli 1. FTIR analiza urađena je na uređaju **Thermo Fisher Scientific Nicolet IS-50**. Snimanje je rađeno ATR (Attenuated Total Reflectance – ometana totalna refleksija) tehnikom u opsegu od 4000 do 400 cm^{-1} i 32 skana pri rezoluciji 4. Po završenom merenju urađene su korekcije bazne linije, atmosferska (za eliminaciju signala gasova CO_2 i H_2O) korekcija[7].

Tabela 2. Raspodela i hemijska analiza proizvoda flotoekstrakcije plave vode

	M %	Cu %	Fe %	S %	M*Cu	M*Fe	M*S	R Cu	R Fe	R S
Konc.	0,74	2,65	0,13	8,23	1,961	0,096	6,1	94,5	33,8	9,9
Otok	99,26	0,00115	0,0019	0,56	0,114	0,188	55,6	5,5	66,2	90,1
Ulaz	100,00	0,0208	0,0028	0,62	2,075	0,284	61,7	100	100	100

IR (infra-crvena) spektroskopija se koristi pretežno kao doprinos utvrđivanju strukture organskih molekula (ali i neorganskih aniona), na način da se na osnovu položaja apsorpcionih traka mogu utvrditi funkcionalne grupe koje figurišu u molekulu. **IR** spektri su vibracioni spektri, tj. apsorpcija **IR** zračenja potiče od vibracionih prelaza u molekulu, odnosno, prilikom apsorpcije zračenja dolazi do promene frekvencije oscilacije određene veze između dva atoma. Na osnovu energije zračenja koja je potrebna za određeni vibracioni prelaz, (**IR** spektar je uređeni niz takvih energija) tj.

za promenu frekvencije vibracije hemijske veze, zaključuje se između koja dva atoma povezana hemijskom vezom se dogodio vibracioni prelaz.

U slučaju gela koji tokom jonske flotacije plavih voda ispliva na površinu i za koji se pretpostavlja da je nerastvorna so bakra i organskih kiselina sapuna (to je uglavnom stearinska, mada su uvek prisutne u nekoj meri palmitinska, oleinska i dr. budući da je reč o komercijalnom sapunu), pored standardne AAS analize za utvrđivanje procenta bakra u uzorku („čvrstoj“ fazi koja je isplivala), radi se i **IR**

analiza da bi se nedvosmisleno pokazalo da je gel ustvari nerastvorna so Cu(II) kationa, i anjona organske prirode (koji potiču od u vodi rastvornih natrijumovih i kalijumovih soli viših masnih kiselina koje čine sapun). Stoga, ako se pogleda *IR* spektar osušenog gela, pri čemu obavezno treba imati u vidu da sušenjem na vazduhu sva zarobljena voda ne može u potpunosti da ispari, može se zaključiti sledeće:

Intenzivna traka (~ 1100) potiče najvećevratnije od $S=O$ veze (valentna vibracija – promena dužine $S=O$ veze), sulfatnog aniona koji je koprecipitirao pri formiranju „čvrste faze“.

Traka (~ 1450) potiče od $C-H$ veze (CH_2 – deformaciona vibracija, tj. promena ugla hemijske veze; ova traka je po prirodi srednjeg intenziteta, ali budući da je broj

CH_2 grupa u molekulu veliki ovde je jasno uočljiva).

Slabo uočljiva traka (~ 1650) je COO^- -valentna simetrična vibracija rezonantne strukture karboksilnog aniona).

Traka koja bi trebala da bude najvećeg intenziteta (~ 1720), a to je valentna $C=O$ vibracija, izostaje zato što izdvojeni gel ne sadrži masne kiseline već soli masnih kiselina.

Traka (3000 – 3500) potiče od $O-H$ veze (valentna vibracija; proširena zbog vodoničnih veza između molekula vode, na 3600 vidi se mali pik $O-H$ veze koja nije vodonično spregnuta). Dakle *IR* spektar nedvosmisleno pokazuje da uzorak sadrži molekule sa ugljovodoničnim lancem ($C-H$ veza), karboksilnom grupom (COO^-), i molekule vode, slika 5.

Sl. 5. *IR* spektar prosušenog gela

Drugi *IR* spektar je spektar taloga koji se iskristalisao nakon uparavanja rastvora. Na osnovu samog izgleda taloga predpostavlja se da je talog u najvećoj meri plavi kamen ($CuSO_4 \cdot 5H_2O$). *IR* spektar to potvrđuje. Sigurno je da u rastvoru „plave vode“ postoje i druge soli koje su se tokom uparavanja zajedno taložile sa očigledno najviše zastupljenim (bakar(II)-sulfatom), ali

one u *IR* spektru nisu vidljive; tj. *IR* spektar indicira sulfat (sulfit), vodu, i moguće nitrat (nitrit).

Na osnovu *IR* spektra uzorka dobijenog uparavanjem rastvora slika 6 može se zaključiti sledeće:

Intenzivna traka (~ 1100) potiče od $S=O$ veze (valentna vibracija) sulfatnog aniona SO_4^{2-} .

Sl. 6. IR spektar uzorka uparenog rastvora

Široka traka ($\sim 3600\text{--}2700$) je od $\text{O} - \text{H}$ veze. Sve što je prethodno rečeno u vezi prisustva vode u uzorku isto važi i za upareni talog.

Traka srednjeg intenziteta (~ 1680) potiče najverovatnije od nitrata ($\text{N} = \text{O}$) valentna vibracija. Dakle IR spektar nedvosmisleno pokazuje da uzorak sadrži molekule sa ugljovodoničnim lancem ($\text{C} - \text{H}$), karboksilnom grupom ($\text{C} - \text{O}$ traka, i $\text{C} = \text{O}$ traka), i molekule vode

ZAKLJUČAK

Svaki fizički sistem poseduje energiju u izvesnoj količini. Količina energije sistema nije apsolutna vrednost već relativna u odnosu na referentno stanje ili referentni nivo. Početkom XX veka, W. Nernst je izvršio klasifikaciju različitih oblasti hemije na osnovu tipa energije unete u sistem: termohemija, elektrohemija, fotohemija itd. Naziv mehanohemija se odnosio na deo reakcija pokrenut mehaničkom energijom odnosno na reakcije koje su inicirane procesom frikcije, lomljenja, tokom mehaničkog tretiranja čvrstih komponenti. Aktivacijska

energija mehanohemijskog tretmana potrebna je sistemu radi omogućavanja spoljašnjoj sili da poveća površinu materijala, da bi došlo do delovanja reagenasa u procesu pneumatske flotacije raznih suspenzija. Procesi obogaćivanja mineralnih sirovina u flotacijskim sistemima zasnovani su na elektrohemiji, adsorpciji i katalitičkom delovanju reagenasa na jedinice koje treba razdvojiti kao komponente sistema. Da bi u flotoekstrakciji došlo do transporta rastvorene supstance u vidu gela ka površini, energija aktivacijemora imati uticaj na sistem da energetska barijera koja se opire tom transportu treba biti savladana spoljašnjom silom. Veličina adsorpcije odnosi se na tečno gasovito, a kod čvrste materije dolazi do promene međumolekulskih i intramolekulskih sila. Intramolekulske sile su sile koja drže zajedno atome i time formiraju molekul ili jedinjenje. Intramolekularne sile obuhvataju sve tipove hemijskih veza. One su jače od intermolekulskih sila, koje se javljaju između atoma ili molekula koji nisu vezani. Energija aktivacije reagujućeg sistema u nekom uređaju (reaktoru) ima veoma važnu ulogu na fizičke karakteristike

sistema u smislu selektivnog razdvajanja komponenata sistema. U radu je pokazano da se može izračunati intenzitet intramolekularnih sila kao sila osmotskog pritiska, i to se može koristiti za izračunavanje potrebne količine reagensa za uspešnu flotoekstrakciju.

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