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Surfactants and their mixtures under conditions of autoclave sulfuric acid leaching of zinc concentrate: Surfactant selection and laboratory tests

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Abstract: The influence of surfactants and their mixtures on the efficiency of the pressure leaching of zinc concentrates was studied by leaching tests and subsequent analysis, including granulometric and phase composition studies of the leaching products. Lignosulfonate (LS) and sodium dodecyl sulfate (SDS) were used as surfactants. Additional experiments were performed on artificial solutions to study the effect of surfactants on the solution surface activity by surface tension measurements. The obtained results indicated a synergistic effect of the combined LS and SDS addition, resulting in surface tension reduction. In a series of pressure leaching tests, the effects of the concentration of surfactants and their mixtures ($C_{\mathrm{LS/SDS}}$=0.2−0.8 g/L), temperature (T=120−140 °C), oxygen partial pressure ($p_{\mathrm{O_2}}$=0.5−0.7 MPa), and time (t=20−120 min) on the extraction of zinc, iron, copper and indium into solution were investigated. Based on the results, optimal parameters were determined to carry out the leaching of zinc concentrates: surfactant mixtures of the composition C_{LS}=0.6−0.8 g/L, C_{SDS}=0.2−0.6 g/L, $p_{\mathrm{O_2}}$=0.5 MPa, T=140 °C, and t=100−120 min. These optimal conditions result in extraction of 93%−94% zinc, 65%−66% indium, 64%−68% copper, and 48%−49% iron into solution.

Key words: autoclave leaching; zinc concentrate; sulfuric acid; surfactants; lignosulfonate; sodium dodecyl sulfate

1 Introduction

Among promising methods for the metallurgical processing of sulfide raw materials, autoclave methods based on the processes of direct hydrochemical oxidation using high-temperature regimes, sulfuric acid media, and gaseous oxidants (air or technical oxygen) meet the requirements of modern production in terms of ensuring resource-saving and environmental effects and technological flexibility [1−4]. In comparison with the traditional roasting–leaching scheme, this method has a number of technological advantages, namely,

(1) the possibility of rational cooperation with the standard scheme of zinc production at the stages of solution purification, electrolytic zinc precipitation and sulfuric acid regeneration;

(2) quantitative oxidation of sulfide sulfur in the composition of sphalerite into elemental sulfur, which remains in the leaching residues and completely eliminates any release of sulfur dioxide into the atmosphere:

$$2\mathrm{MeS}+2\mathrm{H_2SO_4}+\mathrm{O_2}\rightarrow 2\mathrm{MeSO_4}+2\mathrm{H_2O}+2\mathrm{S^0} \qquad (1)$$

(3) prospects for deep and intense dissolution of complex polymetallic products with fine mineral intergrowth due to the implementation of high-temperature sulfide oxidation conditions (above the melting point of elemental sulfur), as well as the use of the catalytic effect of polyvalent ions (copper, iron) concentrated in solutions during leaching.

However, the hydrochemical oxidation of sulfide minerals at temperatures above 112.8 °C

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also has a number of limitations. First of all, this is the formation of impermeable films of molten elemental sulfur on the surface of non-leached sulfides, which leads to a complete stop of oxidative dissolution processes [5,6].

The ability of some surfactants to eliminate the occluding effect of molten sulfur has opened up prospects for the implementation of high-temperature regimes and further intensification of autoclave processes [7,8]. There is information about the positive effect of aromatic amine derivatives, high relative molecular mass thioethers (sulfanes), a number of intermediate products of oil and gas processing (low-temperature rectification fractions, gas condensates, cyatim, extract of selective purification of oil fractions) in the literatures [9,10]. Recently, papers have appeared to use some classical anionic, cationic and nonionic surfactants [11,12], used in "soft" (in terms of pressure and temperature) leaching modes.

Despite such a wide surfactant range, since the first experiments on autoclave leaching [13] and up to now, the predominant distribution in the hydrometallurgical practice of processing zinc, lead–zinc and nickel–pyrrhotite concentrates has been received by wood processing products, namely, technical lignosulfonates (LS), quebracho extract and sulfite yeast mash concentrate [5,14,15].

The accumulated experience of the industrial development of autoclave technologies in the processing of zinc and nickel–pyrrhotite concentrates has revealed a number of features in the development of oxidative leaching processes in the presence of LS, which complicated the process control.

(1) The instability of the functional characteristics of technical LS was supplied by various pulp and paper mills. LS in the composition of liquors differ significantly in relative molecular mass, quantitative content of functional groups (sulfonate, methoxyl, phenyl, and other ones) and cationic composition [16].

(2) A decreased efficiency of LS as the duration of autoclave leaching increases. The influence of this factor was explained by the chemical LS destruction in the severe modes of thermal-oxidative treatment, as well as their priority adsorption on freshly formed (as the acid was neutralized) solid-phase hydrolysis products of iron(III) ions rather than on sulfides. This predetermined an increased LS consumption for leaching with a single introduction into the leaching pulp, or required a time-distributed portioned dosage [17].

(3) The optimal development of leaching processes was carried out in a narrow range of LS concentrations. With the deficiency (<0.05 g/L), sulfide underleaching was observed due to the formation of molten sulfur films on their surface, and at elevated concentrations (above 1 g/L), LS inhibited the process of mineral oxidation at the initial stage [18].

To solve the above issues, in addition to further in-depth study of structural features of LS, their behavior at the LS–sulfuric acid solution – S^0 ($Me^{n+}S$) interfaces at elevated temperatures and pressures, it is also possible to select other more effective surfactants, as well as LS–surfactant compositions.

According to preliminary estimates, the global production of surfactants is 10×10^6 t per year [19]. However, not all industrial surfactants meet the requirements necessary for their use in autoclave leaching. In general, the tasks aimed at choosing an effective surfactant or developing surfactant–surfactant compositions are, due to their diverse nature and phase behavior, very complex, but necessary to intensify autoclave leaching processes.

In this work, a scientifically substantiated selection of surfactants and LS−surfactant compositions (LS, sodium dodecyl sulfate [SDS], and LS−SDS) was carried out, and regularities of the autoclave sulfuric-acid leaching of zinc concentrate in their presence were studied in detail. The following tasks were set to carry out a scientifically based selection of surfactants: to study changes in the surface tension of surfactant solutions and their mixtures, to perform studies of the autoclave leaching processes of zinc concentrate, to establish the influence of the concentration of surfactants and LS−surfactant mixtures (0.2−0.8 g/L), temperature (120−140 °C), partial oxygen pressure (0.3−0.7 MPa), and operation time (20−120 min) on the extraction of zinc, iron and copper in solution, to assess the behavior of indium under the conditions under study, and to perform granulometric and phase analyses of the cake after leaching.

2 Experimental

2.1 Materials

We used zinc concentrate from the Uchalinsky deposit (Republic of Bashkortostan, Russian Federation). The chemical composition of the concentrate was analyzed by the complete decomposition of minerals in a 1:3 (volume ratio) mixture of hydrochloric and nitric acids followed by analysis of the solution on a novAA 300 atomic absorption spectrophotometer (Table 1).

Table 1 Chemical composition of zinc concentrate (wt.%)

Zn	Fe	Cu	S	In*
45.6	9.25	1.17	30.15	51.2

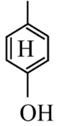
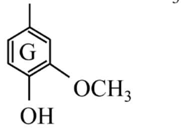
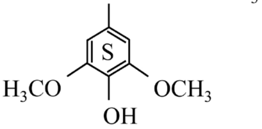
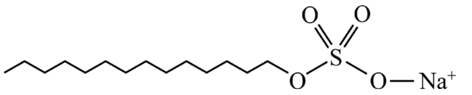
* g/t

The phase analysis of the concentrate was performed using an X-ray diffractometer (XRD). XRD results showed that the concentrate contained sphalerite (69.5%), pyrite (12.9%), and chalcopyrite (2.7%). Waste rock was represented by dolomite (4.2%), kieserite (7.7%), and silicon oxides (1.2%).

The concentrate was previously classified by sieving through a 74 μm sieve and then its particle size distribution was obtained using a laser diffraction particle size analyzer. The fraction containing at least 90% of particles with a size of ~60 μm was used in all experiments.

We used technical oxygen (from a cylinder), sulfuric acid H_2SO_4 (chemically pure), and few surfactants, namely, technical lignosulfonate from the Solikamsk Pulp and Paper Mill and sodium dodecyl sulfate (SDS), chemically pure grade. The main characteristics of these surfactants are given in Table 2.

Table 2 Main characteristics of surfactants

Surfactant	Structural formula	Characteristics
LS	Monomeric composition of LS  1 H: p-hydroxyphenyl unit  2 G: guaiacyl unit  3 S: syringyl unit	Elemental composition (wt.%) of LS: C 38.82, H 4.36, O 42.35, S 5.50, and Na 6.6; average relative molecular mass 9250
SDS		Chemical formula $CH_3(CH_2)_{11}OSO_3Na$; critical micelle concentration (CMC) 8.3 mmol/L; decomposition temperature 216 °C

2.1.1 Preparation of solutions

Sulfuric acid solutions of constant composition $C(H_2SO_4)$=120 g/L were prepared according to generally accepted methods.

The stock individual surfactant solution (LS/SDS) with C_{surf} 60 g/L was prepared by dissolving the surfactant powder in distilled water under stirring on a magnetic stirrer at (20±2) °C for 15 min. Working solutions with C_{surf}=0.2−0.8 g/L were obtained by introducing an aliquot of the stock surfactant solution into the leaching pulp. Binary solutions of surfactants (LS−SDS) were prepared similarly. In the LS−SDS solutions, the concentration of one component was varied at a constant concentration of the other.

2.1.2 Autoclave leaching of zinc concentrate

Experiments were carried out in a titanium autoclave unit with a volume of 1 L, equipped with stirring, temperature control, sampling, control and measuring facilities. The filling factor of the reactor was set at the level of 0.6. The liquid to solid ratio was 10:1 mL/g.

A weighed portion of the concentrate was placed into the autoclave, pulped with the sulfuric acid solution, and the solution of surfactants or their mixtures was added. The autoclave was sealed and heated to a predetermined temperature (120−140 °C), after which oxygen was supplied to the required pressure (oxygen partial pressure p_{O_2} was 0.3−0.7 MPa), and the temperature was automatically maintained with an accuracy of ±2 °C. The development of oxidation processes was controlled in time (20−120 min) by extracting (%) zinc, indium, copper and iron into the solution.

The pulp after leaching was filtered. The filtrate and wash water were analyzed for the content of zinc, iron, copper and indium ions.

The cake was repeatedly washed with distilled water, dried and weighed, and its granulometric and phase compositions and particle morphology were analyzed. The cake was conditionally divided into categories, namely, fine one (<150 μm), sands (150−400 μm), and granules (>400 μm).

2.2 Methods

Gravimetric measurements were carried out on an Ohaus Discovery analytical balance (USA) with weighing accuracy of ±0.0001 g.

The surface tension of surfactant solutions at the liquid–gas interface ($\sigma_{\text{l-g}}$) was estimated by the Rehbinder method. It is based on measuring the pressure at which an air bubble blown into a liquid through a capillary is separated. When a bubble is slowly pressed from the capillary into the liquid, an excess internal pressure (Δp) arises therein, which, according to the Laplace law (Eq. (2)), is determined by the surface tension ($\sigma_{\text{l-g}}$) and the curvature of the bubble surface (r):

$$\Delta p=\frac{2\sigma_{\text{l-g}}}{r} \tag{2}$$

Since it would be rather difficult to measure r experimentally, the difference in the heights of the manometric fluid in water ($\Delta h_{\text{H}_2\text{O}}$) and in the studied solution (Δh) was measured to determine $\sigma_{\text{l-g}}$ of the studied solutions. The surface tension $\sigma_{\text{l-g}}$ of the surfactant solutions studied was calculated using Eq. (3):

$$\sigma_{\text{l-g}}=\sigma_{\text{H}_2\text{O}}\frac{\Delta h}{\Delta h_{\text{H}_2\text{O}}} \tag{3}$$

A thermostatic cell was used to find the temperature dependence $\sigma_{\text{l-g}}=f(t)$. The solutions of surfactant reaction mixtures were additionally thermostated for 1 h before measurements.

Quantitative analysis of metal ions (Me^{n+}) was carried out on a novAA 300 atomic absorption spectrophotometer, Analytik (Jena, Germany). X-ray diffraction patterns of the concentrate and cake were obtained on an X-ray diffractometer XRD−7000 (Shimadzu, Japan) in Cu K_α radiation in the 2θ range of 0°−85°. The granulometric composition of the concentrate and cake was explored by sieve analysis and on a laser diffraction particle size analyzer HELOS&RODOS (Sympatec GmbH, Germany). The surface morphology of cake particles (grains, granules) was studied using a scanning electron microscope (VEGA3 SBU; TESCAN) equipped with an energy dispersive microanalyzer (Model X-act, AZTEC, Oxford Instruments, UK). A Micromed 3 microscope (Ningbo Sheng Heng Optic&Electronics Co., Ltd., China) was additionally used in a number of experiments.

3 Data processing

The extraction degree of metals (ε_{Zn}, ε_{Fe}, ε_{In} and ε_{Cu}, in %) was estimated taking into account the volume of samples according to Eq. (4):

$$\varepsilon^{i}_{\text{Me}}=\frac{C^{i}[V-v(i-1)]+\sum_{1}^{i-1}(C^{i}v)}{G_{\text{Me}}}\times 100\% \tag{4}$$

where $\varepsilon^{i}_{\text{Me}}$ is the metal extraction degree by the time of taking the ith sample; C^i is the metal concentration in the ith sample; v is the sample volume; V is the initial volume of the leaching solution; G_{Me} is the mass of metal in the concentrate sample (g).

The dissolution rate of minerals was estimated from the initial section of the dependences $\varepsilon_{\text{Zn}}=f(t)$.

4 Results and discussion

4.1 Surfactant selection for autoclave sulfuric acid leaching

It is well known that the conditions of autoclave sulfuric acid leaching are very severe. Temperature, the presence of oxidizers (sulfuric acid in the bulk and on the surface of minerals) hinder to make an a priori scientifically based choice of surfactants. Nevertheless, let us define some, in our opinion, fundamental criteria for the selection of surfactants for these conditions.

4.1.1 Surfactant class

According to the physicochemical mechanism of the effect of surfactants upon the interface and on the disperse system in general, KRUGLYAKOV [20] classifies surfactants into four groups: (1) The substances that are surfactants at the water–air interface. These include medium and higher homologues of aliphatic alcohols and acids. Surfactants of this group are moderately acting wetting agents, foaming agents and some of them (octyl and isoamyl alcohols) are defoamers; (2) The substances that are diverse in nature and are surfactants at various interfaces of condensed phases (solid–liquid and liquid–liquid). Such surfactants can be grouped by their action under the general name of dispersants. In addition, these surfactants also allow controlling selective wetting; (3) The surfactants that have the ability to form gel-like structures, i.e. being solid-phase, to a certain extent, in adsorption layers and in the bulk of phases. Most surfactants of this group are high relative molecular mass ones, natural or synthetic substances of complex structure with many polar groups (proteins, glucosides, polyvinyl alcohol, etc.). These surfactants are highly effective stabilizers of foams, emulsions, and suspensions; (4) The surfactants with detergent action. They combine the functions of the three previous groups of surfactants, and in addition, they are capable of the spontaneous formation of thermodynamically stable colloidal particles (micelles) in the bulk of the liquid phase and of the inclusion of washable contaminants into the core of micelles (solubilization). These include various anionic, cationic and non-ionic surfactants.

The mechanism of the functional action of surfactants (with LS as an example) under autoclave leaching conditions is implemented within the framework of a “washing scheme” through a series of successive stages, namely, surfactant adsorption on the ZnS/S^0 surface → wetting of ZnS/S^0 → dispersion of ZnS/S^0 → solubilization of S^0 [21]. Therefore, when choosing a surfactant, micelle-forming ones (Group IV) are preferred. Below, we will consider only this class of surfactants.

4.1.2 Surfactant concentration (C_{surf})

At low concentrations, surfactants are adsorbed at the interface and form true solutions. At high C_{surf}, surfactant molecules spontaneously associate to form aggregates (micelles) to minimize free energy. The surfactant concentration at which micelles begin to form is called the critical micelle concentration (CMC) [22]. The CMCs for most surfactants are given in reference books of physicochemical quantities [23]. At its CMC, a surfactant has the maximum surface-active effect. Therefore, for practical use, the surfactant concentration should be significantly higher than the CMC. Theoretically, under autoclave leaching conditions at higher C_{surf}, more elemental sulfur will be solubilized to form an intermediate phase or emulsion, resulting in higher metal recovery. However, it should be borne in mind that a high C_{surf} will affect the subsequent stages of processing, in particular, zinc electrodeposition from sulfate solutions.

4.1.3 Thermal stability

The thermal stability of surfactants depends on their structure, duration of thermal exposure, and temperature. High thermal stability is possessed by anionic surfactants, namely, alkylbenzene sulfonates (the ignition and auto-ignition temperatures of alkylbenzene sulfonate are 150 and 395 °C, respectively), alkyl sulfonates (the auto-ignition temperature for most of them is up to 270 °C), and primary alkyl sulfates (do not decompose when heated up to 190 °C). Cationic surfactants are less stable than anionic ones; their decomposition begins at temperatures above 150 °C. Amphoteric surfactants are mainly thermally unstable and are not used at high temperatures.

Thus, taking into account the average duration of autoclave leaching (~2 h), high acidity and the presence of oxidizing agents in the process under study, the surfactants from the class of alkylbenzene sulfonates and alkyl sulfonates could be more effective.

4.1.4 Surfactant stability in acidic media and in the presence of polyvalent ions

Let us note that there are no such data for a wide range of surfactants in the literature. The anionic surfactant–sodium dodecyl sulfate (SDS) is the most studied in this matter. The surface activity of SDS in acidic media depends on the nature of the acid used. A positive effect of hydrochloric acid on the change in surface activity was established and, consequently, the CMC in the SDS–water system [24]. In the presence of sulfuric [25] and nitric acid [26], SDS undergoes hydrolysis to form dodecanol. A number of works also note the surface activity of dodecanol [27,28].

In the presence of divalent and trivalent cations, the surface activity of most surfactants is lost due to a decrease in the surfactant solubility, and in some cases, their precipitation from solution.

The surfactants capable of forming ion-pair complexes with metal ions are more resistant to the presence of such metal ions [29]. This group includes anionic surfactants.

Thus, based on our analysis of literature data and the main criteria given for the conditions of autoclave leaching of sulfides, it is recommended to use surfactants from the group of anionic, micellar, thermally stable substances, capable of complexing with metals. These requirements are met by SDS, which will be used in our work.

4.2 Surface activity of solutions of individual surfactants and their mixtures

It is known that for the purposeful regulation of the physicochemical properties of dispersed systems that include the multicomponent heterogeneous “solution–concentrate” system, it is possible to use mixtures of polymers and surfactants [30]. Binary and multicomponent mixtures are characterized by greater or lesser efficiency than their individual components, i.e., they exhibit synergism or antagonism of their physicochemical action [31]. Since there are no data in the literature on the surface tension, and, consequently, the surface activity of LS−SDS mixtures, the surface tension of individual solutions of LS, SDS and their mixtures were measured beforehand. In binary LS−SDS solutions (C_{LS}=0.02−1.28 g/L, C_{SDS}=0.02−0.96 g/L), the concentration of one component was varied while the concentration of the other was constant. The surface tension of the mixtures was estimated in the temperature range of 20−70 °C.

As can be seen from the isotherms presented (Figs. 1(a) and (b)), the binary LS–SDS mixtures reduce surface tension more intensely than individual surfactants, i.e., show synergistic physicochemical action.

This effect is enhanced with increasing C_{surf} and reaches its maximum at the following composition of the binary mixture: C_{LS}=0.1−0.3 g/L, C_{SDS}=0.80−0.96 g/L. An increase in temperature (Fig. 1(c)) in the range of 20−70 °C further enhances the adsorption of LS and SDS at the “l–g” boundary, reducing σ by 3−5 mJ/m^2. Thus, we can assume the potential effectiveness of LS−SDS compositions for use in the conditions of autoclave leaching of polymetallic sulfide raw materials.

The following is our experimental data on autoclave sulfuric-acid leaching of zinc concentrate in the presence of LS, SDS, and their mixtures.

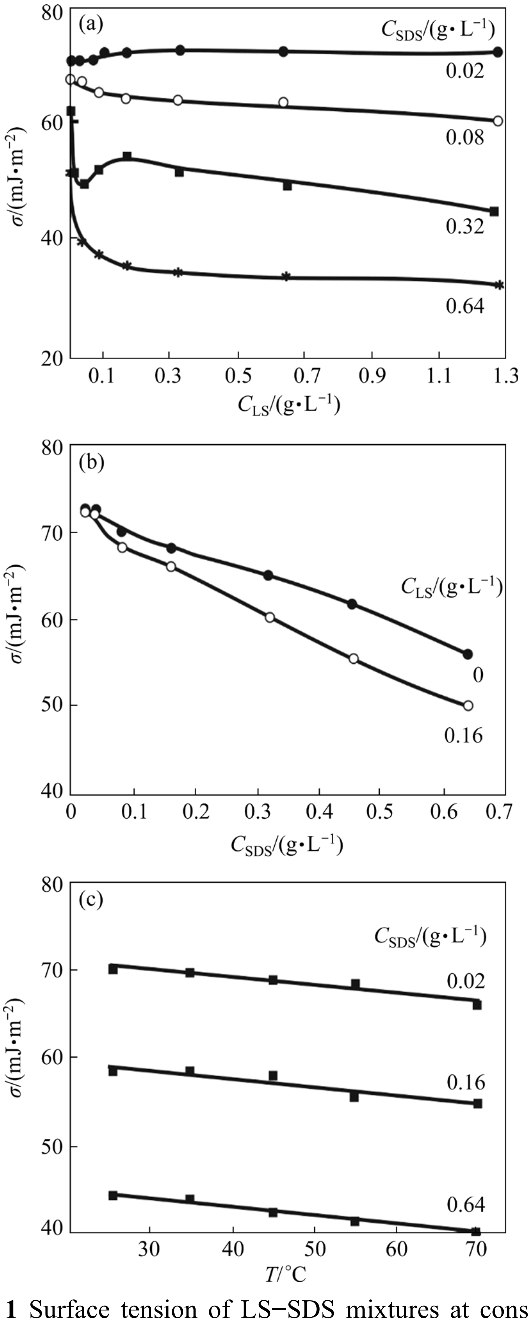


Fig. 1 Surface tension of LS−SDS mixtures at constant (a, b) and elevated (c) temperatures: (a, b) −20 °C; (c) C_{LS}=0.16 g/L

4.3 Regularities of autoclave sulfuric acid leaching of zinc concentrate in the presence of surfactants

The hydrothermal treatment of zinc concentrate under autoclave conditions in the presence of surfactants and their mixtures is characterized by a variety of parallel reactions. The main processes, taking into account the elemental and phase composition of the concentrate, can be represented by the following reactions [32,33]:

$$ZnS+0.5O_2+H_2SO_4 \rightarrow ZnSO_4+S^0+H_2O \quad (5)$$

$$2FeS_2+0.5O_2+H_2SO_4 \rightarrow FeSO_4+S^0+H_2O \quad (6)$$

$$CuFeS_2+0.5O_2+2H_2SO_4 \rightarrow CuSO_4+FeSO_4+H_2O+2S^0 \quad (7)$$

These transformations in the initial period of leaching proceed in the kinetic region, and, as elemental sulfur is formed, they pass into the diffusion region. As for surface phenomena under the conditions under study, according to Ref. [34], the functional effect of surfactants is implemented within the adsorption-wedging and emulsifying mechanisms. In general, as will be shown below, the dissolution of minerals and the transition of valuable components into solution under autoclave conditions are significantly affected by the concentration of surfactants and their mixtures LS−SDS, temperature, partial oxygen pressure, and the duration of the operation.

4.3.1 Influence of concentration of surfactants and their mixtures on processes of autoclave sulfuric acid leaching

When assessing the effect of surfactants and their mixtures on the extraction of metals, $C_{LS/SDS}$ was varied, and p_{O_2}=0.5 MPa, T=140 °C, and t=120 min were constant.

In the absence of surfactant additives (Fig. 2), intense decomposition of the minerals occurs within the first 20 min of the experiment, after which the extraction of metals remains practically unchanged. The main cause of the process inhibition is the formation of elemental sulfur melts (S^0 melting point is ~112 °C). Molten S^0 blocks the surface of the concentrate particles, thereby contributing to the formation of sulfur-sulfide granules and stopping the process. In earlier studies, a similar dependence was observed [9], without surfactants, sphalerite decomposition and oxygen consumption were completed by 30 min of the process. The extraction of zinc and indium after 120 min of leaching is 58% and 53%, and that of copper and iron is 58% and 23%, respectively (Table 3).

The introduction of individual surfactant solutions into the leaching pulp in the entire range of concentrations used (with rare exceptions) not only intensifies the transition of valuable components into the solution, but also prolongs the

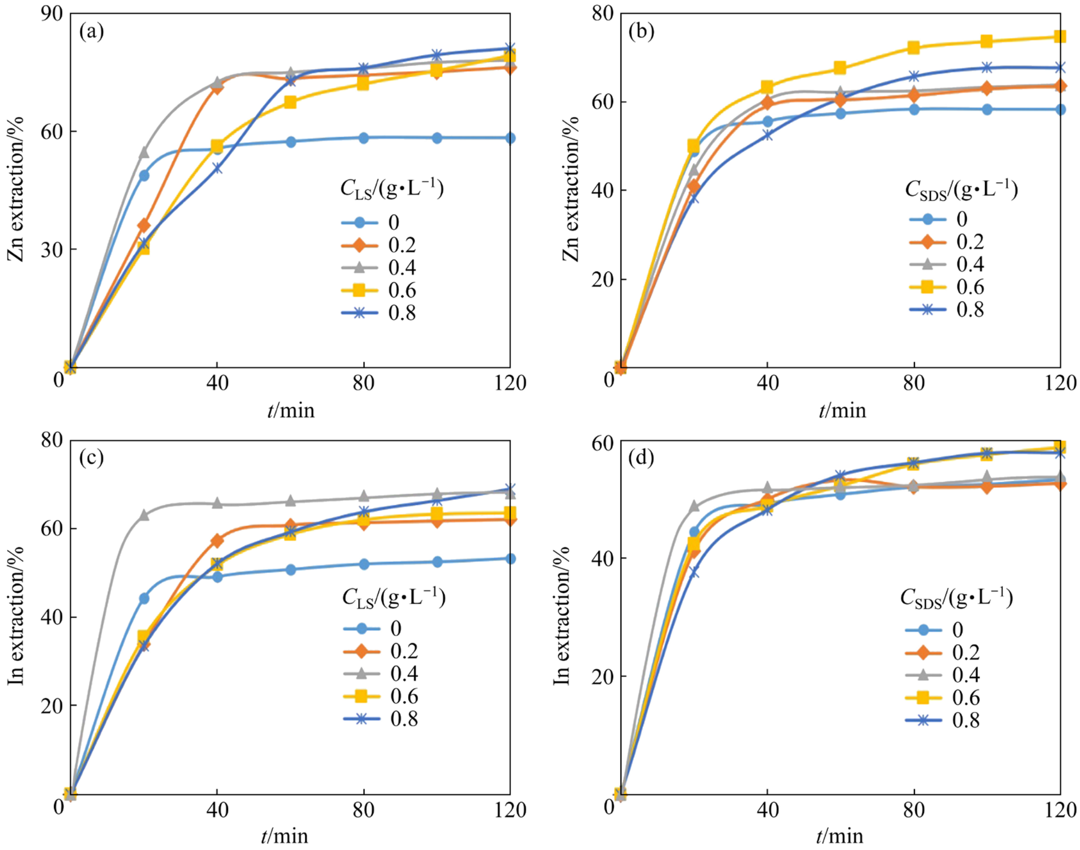


Fig. 2 Effect of surfactant concentration on extraction of zinc (a, b) and indium (c, d) into solution at 140 °C and under 0.5 MPa: (a, c) LS; (b, d) SDS

Table 3 Results of autoclave leaching of zinc concentrate in the presence of surfactants and their mixtures ($C_{\mathrm{H_2SO_4}}$=120 g/L, t=120 min)

$C_{\mathrm{surf}}/(\mathrm{g\cdot L^{-1}})$		T/°C	$p_{\mathrm{O_2}}$ /MPa	Metal extraction, ε/%				Granulation
LS	SDS			Zn	In	Fe	Cu	
−	−	120	0.5	52.8	48.3	14.9	42.7	Sands
−	−	130	0.5	56.5	51.1	20.6	45.4	Sands
−	−	140	0.5	58.4	53.4	22.9	58.2	Sands
−	−	140	0.3	50.9	50.8	17.7	34.0	Sands
−	−	140	0.7	61.1	59.1	30.9	59.6	Sands
0.2	−	140	0.5	76.3	62.1	25.6	50.7	Granules
0.4	−	140	0.5	78.2	68.1	37.2	66.4	Granules
0.6	−	140	0.5	79.3	63.6	51.2	68.6	Fine sediment
0.8	−	140	0.5	81.2	69.0	45.5	69.4	Fine sediment
0.8	−	120	0.5	78.1	85.0	23.7	44.6	Fine sediment
0.8	−	130	0.5	77.0	72.2	54.2	64.9	Fine sediment
0.8	−	140	0.3	69.3	63.8	11.5	32.7	Fine sediment
0.8	−	140	0.7	76.9	62.4	49.3	70.0	Fine sediment + granules
−	0.2	140	0.5	63.5	52.7	27.6	46.5	Sands
−	0.4	140	0.5	63.9	54.0	24.8	44.0	Sands
−	0.6	140	0.5	74.7	58.8	18.7	45.3	Granules
−	0.8	140	0.5	67.8	57.8	8.3	40.6	Sands
−	0.6	120	0.5	56.7	55.7	14.3	28.4	Sands
−	0.6	130	0.5	71.1	65.4	18.0	36.5	Granules
0.4	0.2	140	0.5	84.9	57.9	37.4	54.3	Fine sediment + granules
0.4	0.4	140	0.5	83.6	64.6	36.8	55.6	Fine sediment
0.4	0.6	140	0.5	79.0	66.3	36.3	51.0	Fine sediment
0.4	0.8	140	0.5	70.8	65.2	31.5	43.2	Fine sediment+ granules
0.4	0.6	120	0.5	74.4	65.1	19.5	34.6	Fine sediment
0.4	0.6	130	0.5	77.4	65.1	23.7	36.5	Fine sediment
0.4	0.6	140	0.3	32.2	38.8	13.7	36.5	Fine sediment
0.4	0.6	140	0.7	73.3	57.7	35.5	72.0	Fine sediment + granules
0.8	0.2	140	0.5	93.3	65.0	48.7	67.8	Fine sediment
0.8	0.4	140	0.5	94.1	66.1	49.1	63.7	Fine sediment
0.8	0.6	140	0.5	93.0	64.7	47.5	50.9	Fine sediment
0.8	0.8	140	0.5	63.8	62.4	47.5	50.9	Fine sediment
0.8	0.6	120	0.5	75.4	64.1	21.8	34.5	Fine sediment
0.8	0.6	130	0.5	93.7	59.6	44.7	50.0	Fine sediment
0.8	0.6	140	0.3	17.2	18.0	11.4	22.4	Fine sediment
0.8	0.6	140	0.7	75.7	70.2	35.2	58.7	Fine sediment + granules

period of active dissolution of minerals (Figs. 2(a) and (b)). When C_{surf} ≤0.4 g/L, the transition of zinc and indium into the solution slows down after 40−60 min of leaching due to the formation of sulfur-sulfide granules (in the presence of LS) and sands (in the presence of SDS). With C_{LS} of 0.6−0.8 g/L and C_{SDS} of 0.6 g/L, the maximum extraction of zinc (78%−81% and 75%) and indium (64%−69% and 59%), respectively, is observed. In this case, only finely dispersed particles are found in the cake after leaching in the presence of LS, while sulfur-sulfide granules and sands are found in the presence of SDS.

The nature of the surfactant used influences the transition of copper and iron into solution. In the presence of LS, the total extraction of copper and iron increases by 11% and 28%, respectively. In the presence of SDS, an opposite effect is observed. The extraction of copper and iron reduces by 18% and 15%, respectively.

The introduction of mixtures (as well as individual surfactants) into the leaching pulp intensifies the total extraction of valuable components into the solution in comparison with the experiments in the absence of any surfactants (Fig. 3). However, when compared with the effect of LS, the leaching rates in the presence of surfactant mixtures depend on their composition. At C_{LS}=constant=0.4 g/L and varying C_{SDS}= 0.2−0.8 g/L, a decrease in the dissolution rate of sphalerite by a factor of 2.6 and a decrease in the total extraction of indium, copper and iron into solution are observed. In addition, the cake contains sulfur-sulfide granules.

With an increase in C_{LS} up to 0.8 g/L and C_{SDS} from 0.2 to 0.6 g/L, an increase in the dissolution rate of sphalerite by 1.6−1.8 times and the maximum extraction of zinc, indium and iron up to 94%, 66% and 49%, respectively, are observed. Copper extraction reduces by 19%. The bulk of the cake (96%−98%) is fine dispersion (~150 μm).

Higher concentrations of LS and SDS in their mixtures (0.8 g/L) inhibit the extraction of valuable components into solution.

Thus, the established surface-active effect of surfactant mixtures under the conditions of autoclave leaching of zinc concentrate is consistent with the previously established synergistic effect of the surfactants studied. Based on our experimental results, it is possible to find the optimal compositions of mixtures to allow achieving the maximum extraction of zinc, indium and iron under the conditions of autoclave leaching, namely, C_{LS}= 0.6−0.8 g/L, C_{SDS}=0.2−0.6 g/L.

4.3.2 Temperature influence on processes of autoclave sulfuric acid leaching in the presence of surfactants and their mixtures

The effect of temperature within 120−140 °C on the parameters of autoclave leaching of zinc concentrate was assessed at constant p_{O_2}=0.5 MPa, t=120 min, the concentrations of surfactants and their mixtures (C_{LS}=0.8 g/L, C_{SDS}=0.6 g/L, surfactant mixtures: C_{LS}=0.4 g/L, C_{SDS}=0.6 g/L (Mixture I), C_{LS}=0.8 g/L, C_{SDS}=0.6 g/L (Mixture II)).

With an increase in temperature of 120−140 °C in the absence of any surfactants, the extraction of valuable components increases by 5%−15% (Fig. 4(a), Table 3). The extraction rates

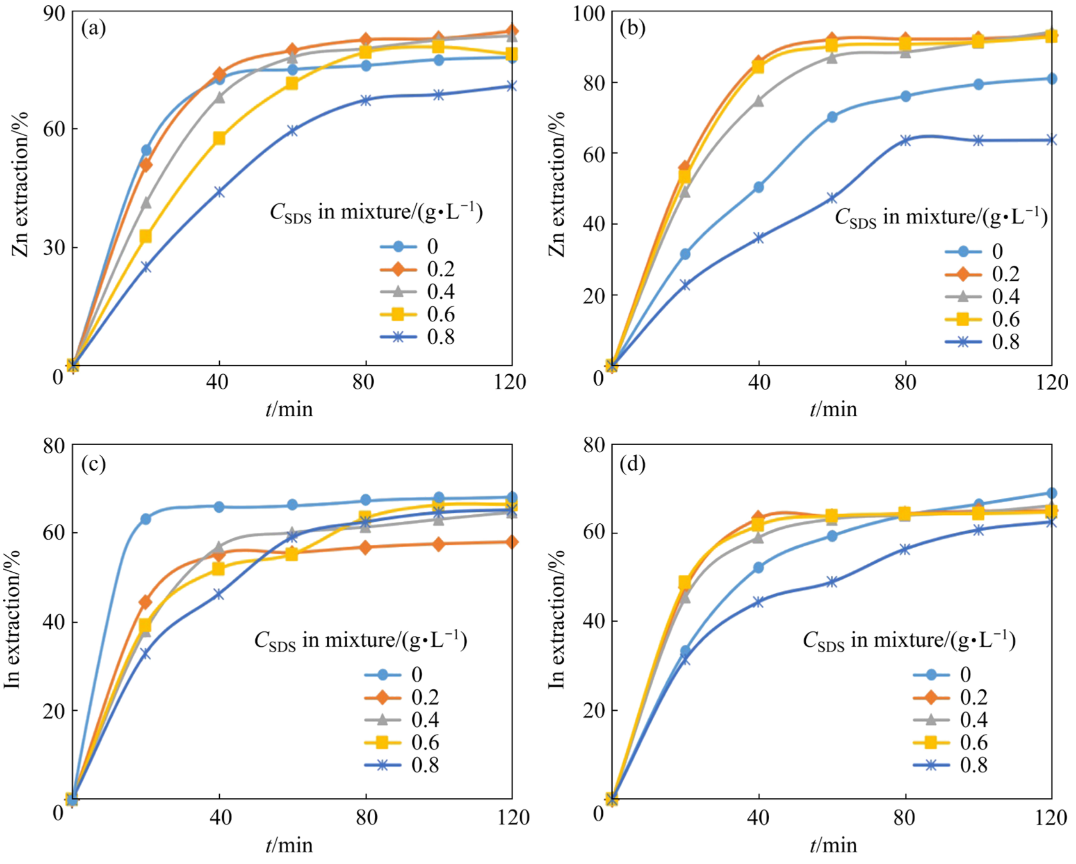


Fig. 3 Effect of composition and concentration of surfactant mixtures on extraction of zinc (a, b) and indium (c, d) into solution at 140 °C under p_{O_2}=0.5 MPa: (a, c) C_{LS}=0.4 g/L; (b, d) C_{LS}=0.8 g/L

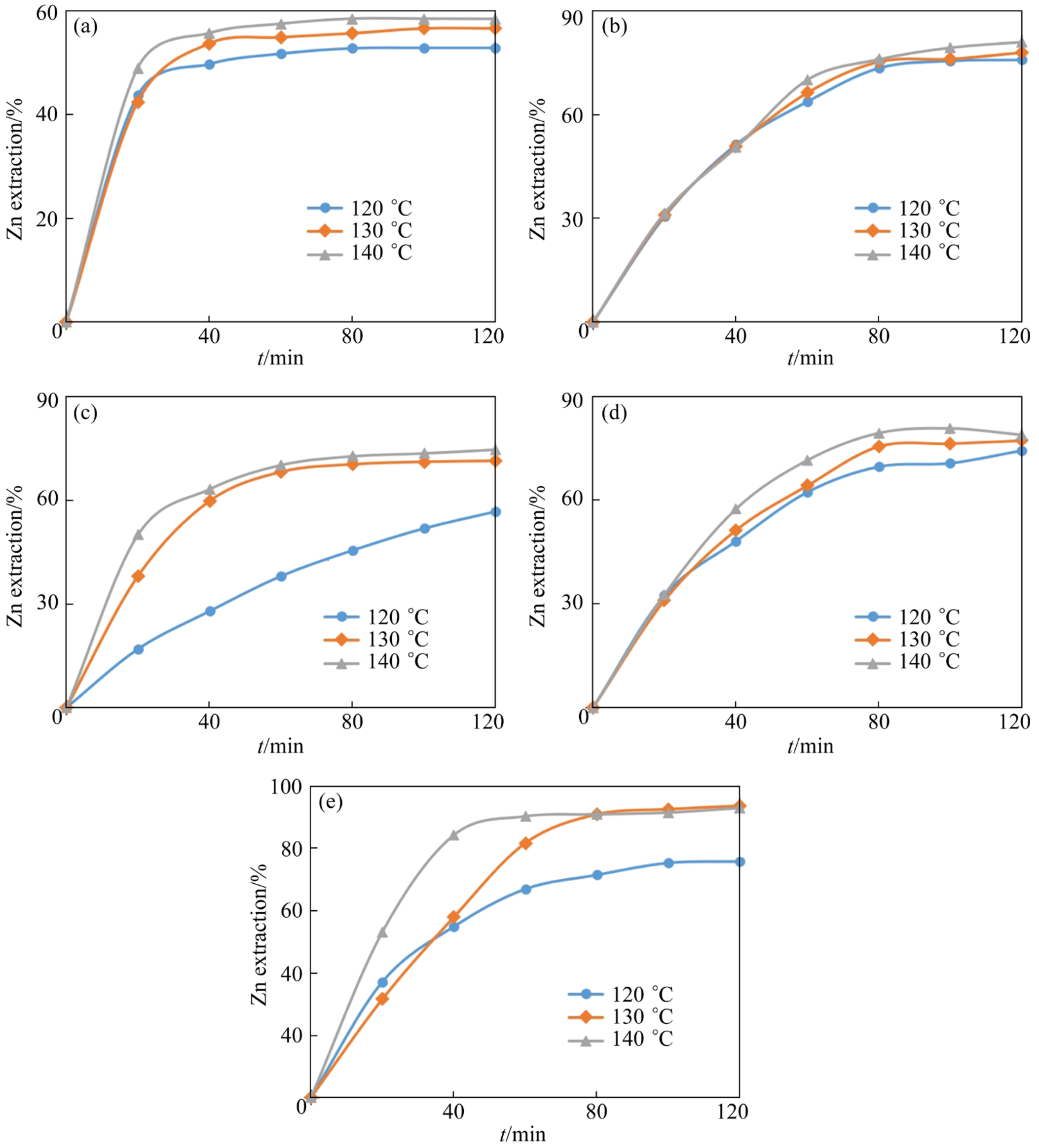


Fig. 4 Effect of temperature on extraction of zinc in the absence (a) and in the presence of surfactants (b, c) and their mixtures (d, e) under constant p_{O_2}=0.5 MPa: (b) C_{LS}=0.8 g/L; (c) C_{SDS}=0.6 g/L; (d) Mixture I; (e) Mixture II

after 120 min of leaching for zinc, indium, iron and copper are 58%, 53%, 23% and 58%, respectively. 80% of the cake consists of cake particles with sizes of 180−365 μm.

In the presence of LS, an intense increase in the extraction of zinc into solution is observed within the first 50 min of the process (Fig. 4(b)). For the entire leaching period (120 min) at 120−140 °C, 77%−78% of zinc passes into the solution. The maximum extraction 85% of indium is observed at 120 °C (Table 3). The extraction of copper and iron in the presence of LS increases by more than 20% with an increase in temperature from 120 °C up to 140 °C. The cake is represented by dispersed particles of ~150 μm in the entire temperature range.

At 120 °C, the extraction of zinc in the presence of SDS is comparable to that in the absence of surfactants (Fig. 4(c)). An increase in temperature makes it possible to raise the degree of zinc extraction up to 75%. The extraction of indium, copper and iron is also rising. However, increased temperatures lead to intensification of the formation of granules and sands: >93% of the cake is represented by particles larger than 120 μm.

An increase in temperature in the range of 120−140 °C when using surfactant mixtures leads to an increase in the total extraction of zinc, copper and iron (Fig. 4(d), Table 3). Mixture II is the most effective. In its presence, up to 93% zinc, 51% copper and 47% iron, respectively, pass into solution.

The total extraction of indium into solution in the presence of surfactant mixtures in the temperature range of 120−140 °C changes little and amounts to 60%−65% (Table 3).

Thus, an increase in the process temperature has an ambiguous effect on the leaching of zinc sulfide concentrate. In the presence of LS and Mixture II, it is recommended to carry out the leaching process at 120 and 140 °C, respectively.

4.3.3 Influence of oxygen partial pressure on processes of autoclave sulfuric acid leaching in the presence of surfactants and their mixtures

The partial pressure of oxygen (p_{O_2}), along with temperature, is a determining factor in the decomposition of sulfides [35−40]. In order to establish the effect of p_{O_2} (0.3−0.7 MPa) on zinc extraction, experiments were carried out at 140 °C in the presence of surfactants and their mixtures (Mixture I and Mixture II).

In the absence of surfactants, an increase of p_{O_2} from 0.3 up to 0.7 MPa naturally increases the extraction of zinc, indium, copper, and iron by 10%, 8%, 26%, and 13%, respectively (Fig. 5(a)). However, the role of pressure increase from 0.5 up to 0.7 MPa in sphalerite and chalcopyrite decomposition is insignificant, namely, the extraction of zinc and copper increases only by 3% and 1.5%, respectively (Table 3).

An increase in pressure in the presence of surfactants and their mixtures has an ambiguous effect on leaching rates (Figs. 5(b−d)). In the presence of LS, the rates and degrees of extraction of zinc, copper and iron increase with increasing pressure. However, the total extraction of indium increases more significantly with an increase of p_{O_2} up to 0.5 MPa.

In the presence of surfactant mixtures, an increase of p_{O_2} from 0.3 up to 0.5 MPa makes it possible to noticeably raise the extraction degree of all the metals studied. When Mixture I is used, ε_{Zn} and ε_{Fe} increase by 47% and 22%, respectively, and in the presence of Mixture II, the extraction of zinc and iron increases by 76% and 36%, respectively. The extraction of indium and copper is also growing (up to total of 66% and 51%, respectively) and almost does not depend on the composition of surfactant mixtures.

A simultaneous increase of p_{O_2} up to 0.7 MPa

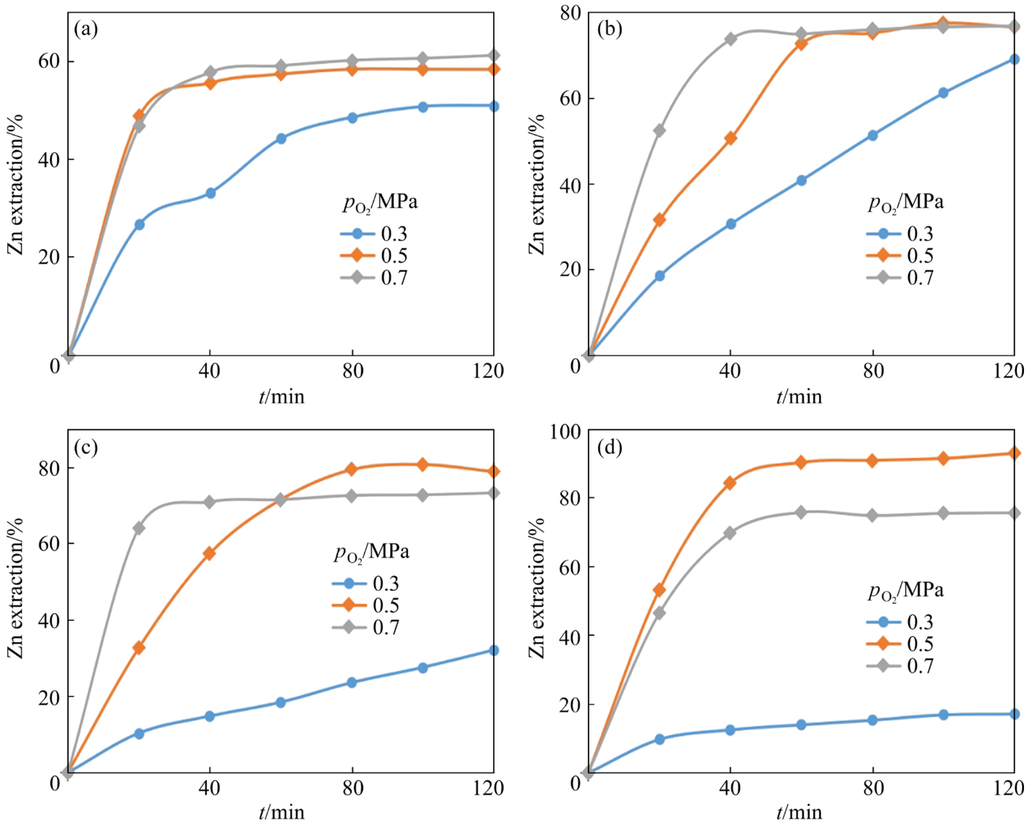


Fig. 5 Oxygen partial pressure effect on zinc extraction in the absence (a) and in the presence of surfactants (b) and their mixtures (c, d) at 140 °C: (b) C_{LS}=0.8 g/L; (c) Mixture I; (d) Mixture II

and C_{LS} from 0.4 up to 0.8 g/L in the surfactant mixture promotes the formation of sulfur-sulfide granules in the cake.

A general analysis of the leaching parameters and the granulometric cake composition shows that any further increase of $p_{\mathrm{O_2}}$ to 0.7 MPa is inexpedient. The leaching indicators remain close to those at 0.5 MPa. The cake contains sulfur-sulfide granules, reaching a size of 30 mm in some cases.

Thus, it is recommended to carry out the leaching process at $p_{\mathrm{O_2}}$=0.5 MPa in the presence of Mixture II (C_{LS}=0.8 g/L and C_{SDS}=0.6 g/L).

4.4 Cake analysis

The used sulfide zinc concentrate from the Uchalinsky deposit contains 90% of particles with sizes around 60 μm. After leaching in the absence of surfactants, the cake (Figs. 6(a, b)) is 95% represented by conglomerates of particles with sizes within 150−400 μm (sands) due to the formation and occluding action of elemental sulfur. The phase analysis of these conglomerates shows that the cake particles include sphalerite (57.1%), chalcopyrite (2.5%), pyrite (18.2%), lead compounds, elemental sulfur (19.6%), and gangue components (Fig. 7).

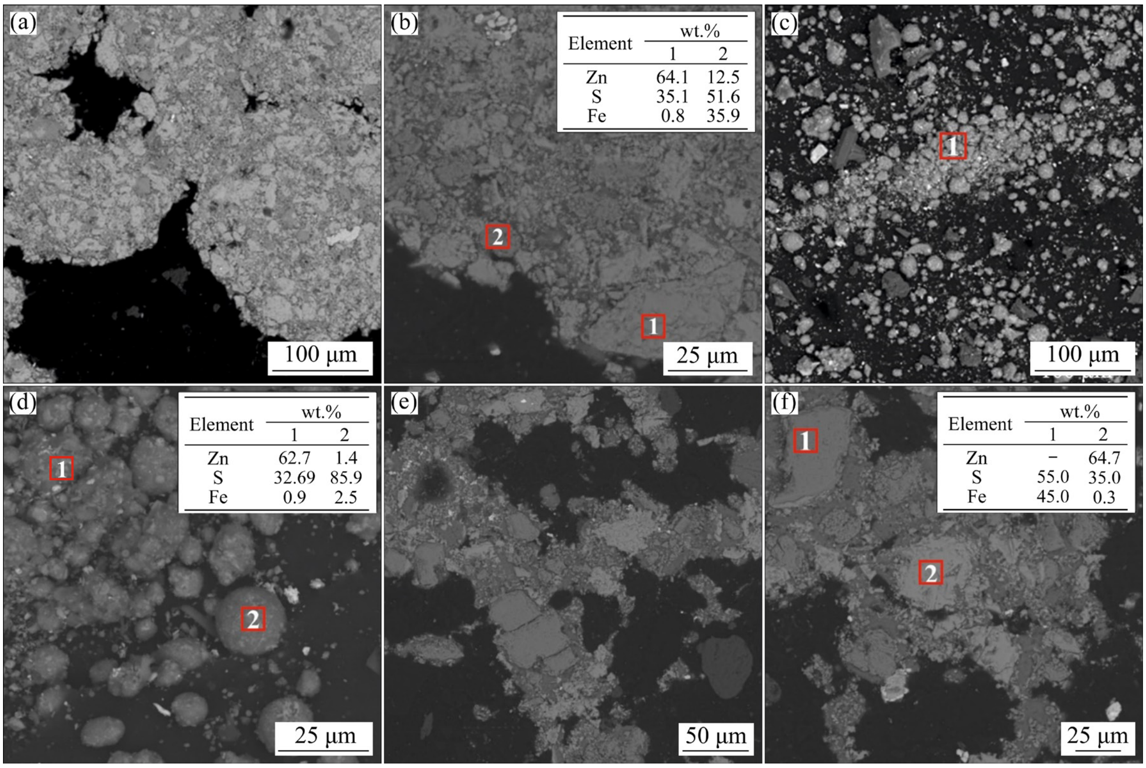
(1) Leaching conditions: C_{LS}=0.4−0.8 g/L, 140 °C, 0.5 MPa

The mineralogical and granulometric composition of the cakes after leaching in the presence of LS depend on its content in the pulp. When C_{LS}≤0.4 g/L, several types of particles are found in the cake, namely, (1) fine particles consisting of crystalline formations represented by waste rock, as well as spherical particles 15−25 μm in size, consisting of elemental sulfur with adhered sulfide particles (Figs. 6(c, d), Fig. 7(c)); (2) sulfur-sulfide granules with diameters of more than 500 μm, including particles of zinc and iron sulfide, and elemental sulfur (Fig. 7 (b)).

With C_{LS}>0.4 g/L, the cake was 85% represented by dispersed particles with sizes around 150 μm containing zinc sulfides (22%−24%), iron sulfides (20%−22%), and elemental sulfur (47%−49%) (Fig. 7(d)).

(2) Leaching conditions: mixtures with C_{LS}= 0.4−0.8 g/L, C_{SDS}=0.2−0.8 g/L, 140 °C, 0.5 MPa

The addition of a mixture of 0.4 g/L LS and 0.2−0.8 g/L SDS promotes an increase in the proportion of particles with sizes of ~50 μm, and an increase in the concentration of SDS enhances this effect.



(b)

Element	wt.% 1	wt.% 2
Zn	64.1	12.5
S	35.1	51.6
Fe	0.8	35.9

(d)

Element	wt.% 1	wt.% 2
Zn	62.7	1.4
S	32.69	85.9
Fe	0.9	2.5

(f)

Element	wt.% 1	wt.% 2
Zn	−	64.7
S	55.0	35.0
Fe	45.0	0.3

Fig. 6 SEM images and elemental analysis of cake obtained by leaching in the absence (a, b) and in the presence of surfactants (c, d) and their mixtures (e, f) at 140 °C and $p_{\mathrm{O_2}}$=0.5 MPa; (c, d) C_{LS}=0.4 g/L; (e, f) Mixture I

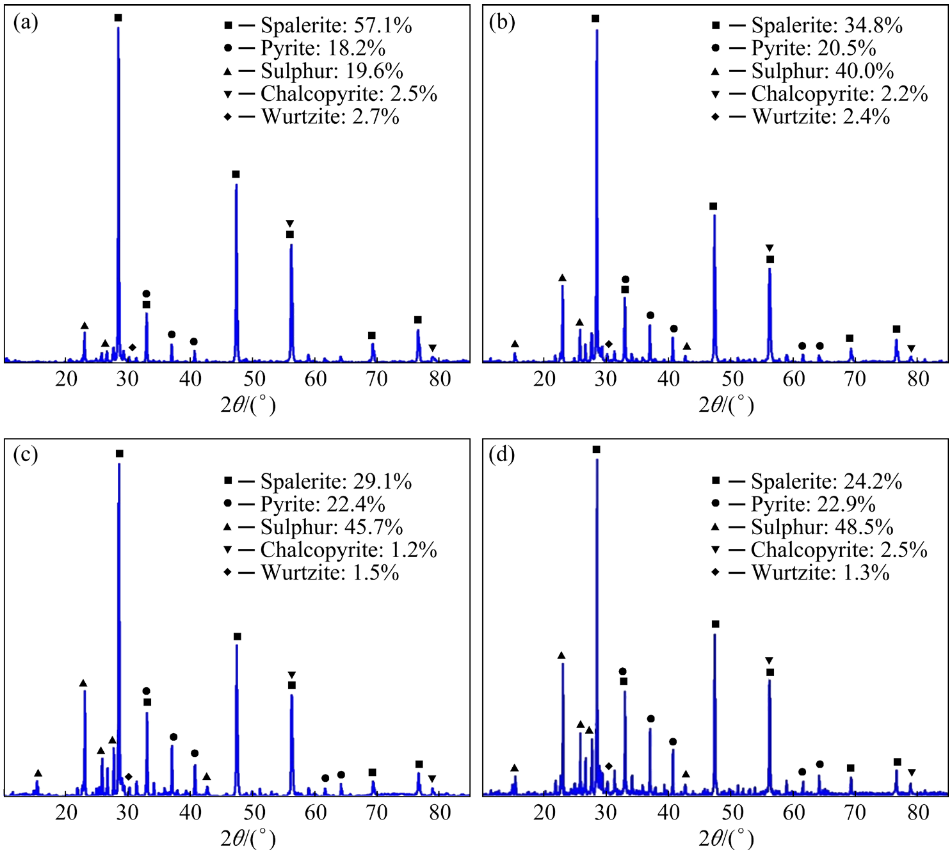


Fig. 7 XRD patterns of cake obtained by leaching in the absence (a) and in the presence of surfactants (b, c, d) at 140 °C and p_{O_2}=of 0.5 MPa: (b) C_{LS}=0.4 g/L, granules; (c) C_{LS}=0.4 g/L, dispersed sediment; (d) C_{LS}=0.8 g/L

The addition of a mixture of 0.8 g/L LS and 0.2 g/L SDS has the highest effect in suppressing the formation of granules; when using it, the proportion of particles with sizes of ~50 μm is 90.8%. However, a further increase in C_{SDS} in the mixture up to 0.6 g/L causes an increase in the proportion of particles with sizes of 150−400 μm (50%), and at 0.8 g/L, despite the 83% content of particles with sizes of ~50 μm, the extraction degree of metals decreases.

Thus, our granulometric and chemical analyses of the cake are consistent with the previously obtained data on the autoclave leaching of zinc concentrates and indicate the effectiveness of the use of such surfactant mixtures. The mixtures of the composition C_{LS}=0.6−0.8 g/L and C_{SDS}=0.2−0.6 g/L have the highest surface effect and can be recommended for autoclave leaching of zinc concentrates at 140 °C and p_{O_2}=0.5 MPa.

5 Conclusions

(1) During oxidative leaching of the concentrate in sulfuric acid solutions in the absence of surfactants, the extraction of zinc into solution does not exceed 50%−63% due to the blocking of the sphalerite surface by molten elemental sulfur films. The insoluble residues contain spheroidal sulfur-sulfide aggregates larger than 150 μm, consisting of particles of non-leached sphalerite and insufficiently crystallized films of elemental sulfur;

(2) Introduction of individual solutions of the surfactants and their mixtures into the leaching pulp makes it possible to intensify the process of transition of valuable components into solution. The surfactants and compositions used, according to their ability to eliminate the shielding effect of elemental sulfur, are arranged in the following row: SDS < mixture I (C_{LS} 0.4 g/L, C_{SDS} 0.6 g/L) < LS < mixture II (C_{LS} 0.8 g/L, C_{SDS} = 0.6 g/L);

(3) Quantitative extraction of zinc (93%−94%), indium (65%−66%), iron (48%−49%) and copper (64%−68%) into solution is ensured by using the surfactant mixture with the composition C_{LS}= 0.6−0.8 g/L and C_{SDS}=0.2−0.6 g/L under the following conditions: p_{O_2}=0.5 MPa, T=140 °C, t=100−

120 min. Under these optimal conditions, a stable development of oxidative processes is achieved with no formation of sulfur sulfide granules.

Acknowledgments

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锌精矿高压釜硫酸浸出条件下的表面活性剂及其混合物：表面活性剂选择和实验室测试

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摘　要：通过浸出实验和对浸出产物的粒度、相成分等的后续分析研究表面活性剂及其混合物对锌精矿加压浸出效果的影响。所用表面活性剂为木质素磺酸盐(Lignosulfonate, LS)和十二烷基硫酸钠 (sodium dodecyl sulfate, SDS)。通过测量表面张力研究表面活性剂对人工模拟溶液表面活性的影响。 结果表明，同时添加 LS 和 SDS 具有协同效应，导致表面张力降级。在一系列加压浸出实验中，研究表面活性剂及其混合物浓度($C_{LS/SDS}$=0.2~0.8 g/L)、温度(T=120~140 ℃)、氧分压(p_{O_2}=0.5~0.7 MPa)和时间(t=20~120 min)等参数对溶液中锌、铁、铜和铟浸出效果的影响。根据研究结果确定的锌精矿浸出的最优参数为：C_{LS}=0.6~0.8 g/L、C_{SDS}=0.2~0.6 g/L、p_{O_2}=0.5 MPa、T=140 ℃和 t=100~120 min。在最优条件下溶液中的锌、铟、铜和铁的浸出率分别为 93%~94%、65%~66%、64%~68%和48%~49%。

关键词：高压釜浸出；锌精矿；硫酸；表面活性剂；木质素磺酸盐；十二烷基硫酸钠

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