

Article

Thermodynamics and Electrochemistry of the Interaction of Sphalerite with Iron (II)-Bearing Compounds in Relation to Flotation

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Abstract: The flotation recovery of sphalerite depends on the inorganic reagents concentrations in the liquid phase of suspension and pH. This paper presents the results of studies of the interactions of iron (II) containing ions with the sphalerite surface in water solutions at different pH levels. The thermodynamic and electrochemical studies were carried out to analyze possible interactions of sphalerite with iron (II) sulfate in a water environment and relate them to sphalerite flotation with potassium butyl xanthate and sodium dibutyl dithiophosphate. The results of the thermodynamic calculations revealed the possibility of interaction of the sphalerite surface with iron (II) hydrolysis products. The effect of the hydroxide ions concentration on precipitation of iron (II) hydroxides was examined. The findings showed that at pH = 8 there were no precipitates observed in water solutions of FeSO₄. Increasing pH of the solutions from 8 to 12 resulted in the formation of iron (II) hydroxides. The potentiometric studies revealed that in slightly alkaline solutions the Fe²⁺ and FeOH⁺ cations are potential-determining. In conclusion, the flotation tests with thiol collectors show the activation effect of iron (II) sulphate on sphalerite at low dosage and pH 12. This is evident by a higher flotation recovery of sphalerite at these conditions.

Keywords: flotation; sphalerite; iron sulfate; potassium butyl xanthate; sodium butyl dithiophosphate; thermodynamics; Gibbs thermodynamic potential; electrochemical potential; mineral electrode



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1. Introduction

The growth in the consumption of natural resources causes an intensification of the mineral deposits development [1], which leads to a decrease in the mineral resource base [2]. To provide resources for sustainable development, mining enterprises develop deposits with a low content of a useful component [3] with ores of complex material composition [4] located in difficult mining and geological conditions or near protected objects [5,6]. The depletion of reserves is associated with an increased pressure on the environment in regions with a high concentration of the mining industry [7,8].

The current situation requires the simultaneous solution of the following issues: reduction of industrial formations [9,10] and increasing the extraction of a valuable components [11], which will ensure the sustainable development of the mining industry. The transition to sustainable and intensive development of the economy is a priority task that can be achieved by reducing the loss of natural resources while minimizing the total environmental impact [12]. The issue of the resource provision of sustainable development is especially acute in the era of global shocks [13,14].

A promising vector for increasing the mineral resource base is the development of innovative technologies for deep processing of resources [15–17] and the improvement of

flotation technology. The industrial experience of flotation of sulfide copper-zinc, lead-zinc and polymetallic ores shows that the improvement of flotation technology is essential for increasing concentrate grade and metals recovery [18]. Typically, this is achieved by the optimisation of flotation circuits, the installation of modern equipment and optimization of the reagent schemes of flotation [19,20]. One of the directions in the development of reagent schemes of flotation is the study of the effect of collecting agent on the mineral surface under bulk or selective flotation conditions [21–25].

It is widely accepted that inorganic compounds are used as activators, depressors and pH-agents in flotation [18,20,26–30]. Although inorganic agents have been used in industrial flotation practice for decades to improve the selectivity of the flotation process, their interaction with sulfide minerals is still undiscovered or controversial. In the field there are a number of works in which the effect of copper and zinc sulfates on sphalerite flotation has been theoretically and experimentally studied [18,20,26,31–33]. Meanwhile, iron sulfate can be used as a modifying agent for sphalerite and pyrite [34,35]. However, there is a lack of research relating to iron sulfate action on sphalerite. Therefore, further studies are required to analyse the interaction of sphalerite with iron (II)-bearing compounds.

2. Materials and Methods

2.1. Procedure of Experimental Studies of Precipitates Formation in Alkaline Solutions

A chemical reactor with the volume of 0.07 l was used in the research. The reactor was filled with distilled water, and then the lime was added to adjust the pH. After that, either iron (II) sulfate or zinc sulfate were dosed in the solution. The amount of sulfates added was calculated based on their dosages during the flotation of sphalerite samples. Further studies involved mixing the solution, pH and oxidation-reduction potential (ORP) measuring, and monitoring whether precipitation was formed.

2.2. A Technique to Measure the Electrochemical Potential of Sphalerite Electrode

Mineral electrode was manufactured to study the interactions of sphalerite with working solutions of iron (II) sulfate. The electrode was made from a pure monolith sample of sphalerite. The sphalerite electrode coupled with a silver-chloride reference electrode was connected to a digital ionmeter and immersed into the working solutions, which were placed in an electrochemical cell. The measured electrochemical potentials were converted to hydrogen scale values. The lime was used to adjust the pH of 8, 10 and 12 of the working solutions.

2.3. Procedure of Sphalerite Flotation

A mechanical flotation cell with the volume of 0.1 L was used in the flotation experiments. Prior to flotation, the sphalerite sample (5 g) was crushed and sieved to the required fineness of $-74 + 44 \mu\text{m}$.

Potassium butyl xanthate (PBX) and sodium dibutyl dithiophosphate (SDTP) were used as collecting agents, and methyl isobutyl carbinol (MIBC) was used as frother. Iron (II) sulfate was used as the modifying agent, and calcium hydroxide was dosed as the pH-agent.

The ground quartz (25 g) was introduced into the flotation suspension before the frother was added to obtain the required solid content. The flotation time was 5 min, and then the products of flotation were dried and weighed. The initial pH of the working solution was 8, 10 and 12.

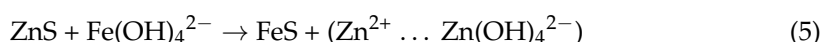
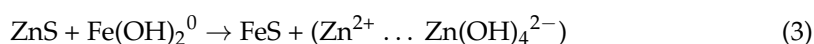
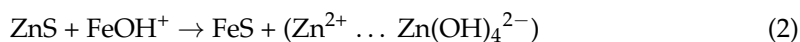
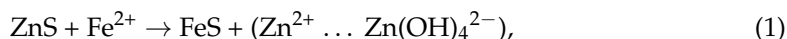
3. Results and Discussion

3.1. Thermodynamics of the Interaction of Sphalerite with Iron (II)-Bearing Ions

The study considered the possibility of the interaction of water-soluble compounds of iron (II) with the sphalerite surface in water under conditions that the layer of iron (II) sulfide is the main product formed on the surface of sphalerite particles. It follows

from previous research [8,19,21,22,36] in which the activation of sphalerite with copper (II) cations was studied.

The reactions of interaction of sphalerite with cations (Fe^{2+} , FeOH^+), molecules ($\text{Fe}(\text{OH})_2^0$), and high hydroxocomplexes ($\text{Fe}(\text{OH})_3^-$, $\text{Fe}(\text{OH})_4^{2-}$) are given below:



the products of Reactions (1)–(5), with exception of iron sulfide, are water-soluble zinc compounds that are in balance with the zinc hydroxide precipitates.

Table 1 presents the reactions, which are characterized by negative values of Gibbs thermodynamic potential, and hence, proceed.

Table 1. Reactions of interaction of water-soluble iron (II) compounds with the sphalerite surface.

Reactions		ΔG^0 , kcal	lgK _p	ΔG , (pH = 10) kcal
No	Equation			
A	$\text{ZnS} + \text{Fe}^{2+} + 2\text{OH}^- = \text{FeS} + \text{Zn}(\text{OH})_2^0$	−6.22	4.5581	+5.42
B	$\text{ZnS} + \text{Fe}(\text{OH})_3^- = \text{FeS} + \text{Zn}^{2+} + 3\text{OH}^-$	−0.47	0.3507	−17.44
C	$\text{ZnS} + \text{Fe}(\text{OH})_3^- = \text{FeS} + \text{ZnOH}^+ + 2\text{OH}^-$	−6.40	4.6884	−17.36
D	$\text{ZnS} + \text{Fe}(\text{OH})_3^- = \text{FeS} + \text{Zn}(\text{OH})_2^0 + \text{OH}^-$	−15.89	11.6475	−17.45
E	$\text{ZnS} + \text{Fe}(\text{OH})_4^{2-} = \text{FeS} + \text{Zn}^{2+} + 4\text{OH}^-$	−2.48	1.8181	−17.93
F	$\text{ZnS} + \text{Fe}(\text{OH})_4^{2-} = \text{FeS} + \text{ZnOH}^+ + 3\text{OH}^-$	−8.40	6.1590	−17.85
G	$\text{ZnS} + \text{Fe}(\text{OH})_4^{2-} = \text{FeS} + \text{Zn}(\text{OH})_2^0 + 2\text{OH}^-$	−17.89	13.1181	−17.93

The calculations show that only the reactions listed in the Table 1 are characterized with negative values of ΔG . Therefore Fe^{2+} , $\text{Fe}(\text{OH})_3^-$, $\text{Fe}(\text{OH})_4^{2-}$ present in solutions react with the sphalerite surface. Recent studies [8,21] confirmed that copper (II) sulfide is formed on the sphalerite surface due to its activation with copper sulfate. Similarly, it can be proposed that iron (II) sulfide is formed on the sphalerite surface when using iron sulfate solutions.

It is widely accepted [23,24] that the concentration of $\text{Fe}^{3+}/\text{Fe}^{2+}$ depends on the pH and oxidation-reduction potential (ORP) of the liquid phase in which cations exist. Moreover, these factors affect the composition of surface compounds formed on the mineral. Furthermore, a significant concentration of Fe^{3+} is typically observed in strongly acid solutions with high oxidation potentials. These observations are consistent with the thermodynamic stability diagrams that were introduced by Garrels and Christ [26,37–39].

The studies revealed that $\text{Fe}(\text{OH})_2$ is formed under experimental conditions. This follows from the white-green colouring of precipitates which can be attributed to iron (II) hydroxide formation. That is why thermodynamic calculations were made for Fe^{2+} . In sulfide copper-zinc flotation circuits pH = 8–10 is typically observed. Further studies confirmed, with minor exception, that the introduction of iron sulfate into the solution at pH = 10 leads to the formation of precipitates of $\text{Fe}(\text{OH})_2$ sphalerite. That is why the analysis began with a pH = 10 case.

It is a common knowledge that thermodynamic equilibrium for a given chemical reaction is expressed as follows:

$$\Delta G = RT \ln K_{sp} - RT \ln K, \quad (6)$$

where ΔG is the change in the Gibbs free energy for the reaction; R is the universal gas constant; T is the absolute temperature; K_{sp} is the solubility product constant; and K is the equilibrium constant.

According to Equation (6), if $K_{sp} < K$ then the chemical reaction is irreversible and proceeds spontaneously ($\Delta G < 0$), otherwise it is irreversible and non-spontaneous. At $K_{sp} = K$ ($\Delta G = 0$) the reaction is characterized by an equilibrium state.

It follows from Table 1 that under standard conditions at pH = 10, Reaction (A) proceeds spontaneously as $\Delta G = -6.22$ kcal. The value of the equilibrium constant is $K_6 = 3.61 \cdot 10^4$. The values of $\text{Fe}(\text{OH})_2$ and Zn^{2+} concentrations in equilibrium with the hydroxide precipitates are $5.891 \cdot 10^{-6}$ and $1.7 \cdot 10^{-10}$ mol/L. However, substituting $R = 0.001987$ kcal, $T = 298.15^\circ$ and the above values into Equation (6) gives $\Delta G = +5.42$ kcal. A positive value of the change in the Gibbs energy shows that Reaction (A) could not proceed spontaneously. Apart this, further thermodynamic calculations showed that the Reactions (B)–(G) listed in Table 1 are irreversible and proceed spontaneously at pH = 10.

To sum up, thermodynamic analysis indicates that the dosing of iron sulfate into an alkaline suspension leads to an equilibrium in which iron (II) compounds dissolved in water exist in equilibrium with iron (II) hydroxides. In addition, there is a probability of Reactions (1)–(5) characterizing the interactions of sphalerite with Fe^{2+} , $\text{Fe}(\text{OH})_3^-$, and $\text{Fe}(\text{OH})_4^-$ (Table 1, (A)–(G)). According to thermodynamic calculations, if precipitation of iron and zinc hydroxides is formed in a sphalerite suspension at pH = 10, then the Reactions (B)–(G) proceed, giving the reasons for the interaction of $\text{Fe}(\text{OH})_3^-$ or $\text{Fe}(\text{OH})_4^-$ with sphalerite.

3.2. Experimental Study of Precipitates Formation during the Hydrolysis of Iron and Zinc Sulfates in Alkaline Solutions

The results of thermodynamics studies show that there is a high probability of interaction of $\text{Fe}(\text{OH})_3^-$ and $\text{Fe}(\text{OH})_4^{2-}$ with the sphalerite surface. The presence of $\text{Fe}(\text{OH})_3^-$ and $\text{Fe}(\text{OH})_4^{2-}$ in significant concentrations of alkaline solutions can lead to the formation of iron (II) hydroxide precipitates.

To testify the possibility of the precipitation of iron (II) and zinc hydroxides in the working solution, further experimental studies were carried out. Zinc and iron (II) sulfates were introduced into water solutions with varying pH. The alkalinity of solutions was adjusted with lime.

The findings showed that the precipitation of iron (II) hydroxide was not observed when the iron (II) sulfate solution was introduced into the lime solutions with pH = 8. However, increasing the alkalinity of lime solutions up to pH = 10 led to the formation of iron (II) hydroxides, which occurred at the concentration of iron (II) sulfate reached at its consumption of 100–800 g/t of sphalerite.

Moreover, there was a decrease of pH due to introducing iron (II) sulfate into the lime solutions. For initial pH = 8 (pH = 7.5 ± 0.23) a significant reduction of pH of the working solutions was observed at low concentration of FeSO_4 ($9.40 \cdot 10^{-6}$ mol/L). At initial pH = 10 (pH = 9.7 ± 0.08) a considerable decrease of pH to 8.43 was achieved at higher concentration of iron sulfate ($9.40 \cdot 10^{-5}$ mol/L), which was relevant to 200 g/t of FeSO_4 consumption. The maximum decrease of pH (from 9.70 to 6.13) was observed at 800 g/t.

The findings revealed the effect of the concentration of iron (II) sulfate on the reduction in pH at the initial pH = 8, although no precipitation was found. It follows from the studies that iron (II) cations interact with hydroxyl ions with the formation of FeOH^+ .

At initial pH = 10 the precipitates were formed indicating the reduction of the pH by 3.0–3.5 and the formation of $\text{Fe}(\text{OH})_2$ as a result of the interaction of Fe^{2+} and FeOH^+ with hydroxyl ions.

Furthermore, the effect of the iron (II) sulfate concentration on the oxidation-reduction potential (ORP) of solutions was observed. In general, increasing the concentration of iron sulfate led to a decrease in ORP. In particular, a decrease in the pH of working solutions from 9.7 to 7.5–6.13 as a result of an increase in iron sulfate dose resulted in the

decline of mean oxidation-reduction potential from 90 ± 27 mV (without FeSO_4) to 21 mV ($C(\text{FeSO}_4) = 3.76 \cdot 10^{-4}$ mol/L).

It is common knowledge that iron (II) compounds appear to have reducing properties, which is usually expressed as a change in the oxidation-reduction potential of the solution [22]. Hence, the platinum electrode can be used as an effective indicator of Fe^{2+} and FeOH^+ cations. Moreover, low values of the platinum electrode potential indicate high residual concentrations of iron (II) ions in the solution, even with the formation of iron (II) hydroxide.

The replacement of iron (II) sulfate with zinc sulfate showed a slight decrease in the pH after introducing ZnSO_4 into the working solutions with pH = 10. It follows from the studies that precipitates of $\text{Zn}(\text{OH})_2$ were formed. The maximum decline of pH ($\Delta\text{pH} = 1.8$) was observed at a zinc sulfate consumption rate of 800 g/t.

Apparently, the first stage in the interaction of iron (II) sulfate with water was the hydrolysis reactions. Moreover, the interactions of chemical compounds with hydroxyl ions take place in alkaline solutions. At comparable initial concentrations of both iron (II) sulfate and zinc sulfate, the differences in pH of the working solutions can be explained with a significant difference in $\text{Fe}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ solubility products, which are $1.0 \cdot 10^{-15}$ and $1.7 \cdot 10^{-18}$, respectively [22]. Hence, the formation of iron (II) hydroxide precipitates requires more hydroxyl ions compared to the formation of zinc hydroxides. This explains the significant decrease in pH when using iron (II) sulfates and a slight decline in pH associated with the dosages of zinc sulfate.

The findings (Table 2) showed that precipitation of iron (II) and zinc hydroxides occurred in working solutions with initial pH = 10. Therefore, thermodynamic calculations of Gibbs free energy for the Reactions (1)–(5) were carried out at pH = 10 using equilibrium concentrations of ions appearing in the reactions. This made it possible to estimate a thermodynamic probability of whether these reactions proceed both under standard conditions and at pH = 10.

Meanwhile, the increase of solution alkalinity up to pH = 12 revealed differences in the influence of iron (II) and zinc sulfate on the formation of precipitates. The precipitates of iron (II) hydroxide were formed at the same initial concentrations of FeSO_4 as at pH = 10. However, zinc hydroxides were formed only at high consumption of ZnSO_4 . The observations also revealed a slight reduction (0.3–0.4) in pH in strong alkaline solutions.

The fundamental difference appeared in working solutions with the coexistence of precipitates. At pH = 10 an increase in the concentration of iron (II) sulfate ($C(\text{FeSO}_4) > 9.4 \cdot 10^{-5}$ mol/L) led to a decline in the oxidation-reduction potential. This indicates that if water-soluble iron (II) compounds exist in the liquid phase during flotation of sphalerite then the liquid phase of the suspension exhibits reduction properties. On the contrary, increasing the initial concentration of zinc sulfate resulted in the growth of the oxidation-reduction potential, which indicates an increase in the oxidation properties of zinc sulfate solutions. The maximum observed growth was of 60 mV.

Apart from pH = 10, in strong alkaline solutions (pH = 12) the oxidation-reduction potential was relatively stable and no effect of concentration on its values was observed.

The evidence from the studies of the formation of iron (II) and zinc hydroxides precipitation under conditions typical for sphalerite froth flotation showed that flotation can proceed with and without precipitation, which are determined with reagents consumption and pH.

Table 2. The results of the precipitation of iron (II) and zinc hydroxides.

pH of the Working Solutions	Consumption of Iron (II) Sulfate or Zinc Sulfate, g/t	Initial Concentration of FeSO ₄ /ZnSO ₄ , mol/L	pH of Working Solution after Mixing		Oxidation-Reduction Potential (ORP) of Working Solution, mV		The Presence of Precipitates Fe(OH) ₂ /Zn(OH) ₂ (+), (−) *
			CaO/FeSO ₄	CaO/ZnSO ₄	CaO/FeSO ₄	CaO/ZnSO ₄	
8	0	0	7.76	7.30	264	244	
	20	9.40·10 ^{−6} /8.87·10 ^{−6}	7.76/7.1	7.30/7.25	264/61.2	244/243	(−)/(+)
	100	4.70·10 ^{−5} /4.44·10 ^{−5}	7.70/6.43	7.35/7.18	264/68.3	224.1/246.5	(−)/(+)
	200	9.40·10 ^{−5} /8.87·10 ^{−5}	7.65/6.42	7.4/7.22	206/60.3	256.7/240.3	(−)/(+)
	400	1.88·10 ^{−4} /1.77·10 ^{−4}	7.32/6.36	7.57/7.2	178/48.8	245.1/152.4	(−)/(+)
	800	3.76·10 ^{−4} /3.55·10 ^{−4}	7.16/6.31	7.54/7.23	114/52.1	193.4/232.1	(−)/(+)
10	0	0	9.86	9.65	79	100	
	20	9.40·10 ^{−6} /8.87·10 ^{−6}	9.61/9.61	9.68/9.32	81/84	108/116	(−)/(+)
	100	4.70·10 ^{−5} /4.44·10 ^{−5}	9.88/9.98	9.82/9.37	84/94	104/119	(+)/(+)
	200	9.40·10 ^{−5} /8.87·10 ^{−5}	9.67/7.53	9.78/8.43	66/49	108/146	(+)/(+)
	400	1.88·10 ^{−4} /1.77·10 ^{−4}	9.64/6.19	9.81/8.14	151/57	105/157	(+)/(+)
	800	3.76·10 ^{−4} /3.55·10 ^{−4}	9.70/6.13	9.83/8.01	72/21	105/161	(+)/(+)
12	0	0	11.65	11.85	15	3	
	20	9.40·10 ^{−6} /8.87·10 ^{−6}	11.77/11.77	11.86/11.84	−3/−4	3/3	(−)/(−)
	100	4.70·10 ^{−5} /4.44·10 ^{−5}	11.83/11.57	11.87/11.83	−6/6	3/4	(+)/(−)
	200	9.40·10 ^{−5} /8.87·10 ^{−5}	11.79/11.67	11.88/11.81	−2/1	3/5	(+)/(−)
	400	1.88·10 ^{−4} /1.77·10 ^{−4}	11.86/11.69	11.87/11.75	−5/−1	3/7	(+)/(+)
	800	3.76·10 ^{−4} /3.55·10 ^{−4}	11.85/11.48	11.86/11.60	−6/−11	4/13	(+)/(+)

* (−)—precipitation; (+)—no precipitation.

3.3. Electrochemistry of the Sphalerite Electrode in Iron (II) Sulfate Solutions at Different pH Values

Figure 1 shows the effect of pH on the potential of a sphalerite electrode immersed in an iron (II) sulfate solution and ORP. The X-axis indicates the equilibrium pH values that were established after mixing. The observations found that although the initial pH values of solutions were 8, 10 and 12, a slight decrease in pH values was observed after the introduction of iron (II) sulfate into lime solution.

Moreover, pH affected the potential of a sphalerite electrode and ORP. At initial pH = 8 a linear dependency was observed between the potential of a sphalerite electrode and ORP on the one hand, and pH on the other hand. In general, increasing pH resulted in the growth of potentials. However, the increase in equilibrium pH values can be due to the steady increase in concentration of potential-determining ions (Fe²⁺, FeOH⁺) in iron (II) sulfate solutions, since the initial pH values were constant. Similar trends were also observed in solutions with pH = 10 and 12.

Despite the hydration of iron (II) cations at pH = 8, precipitation was not observed (Table 2). Therefore, the total equilibrium concentration of iron (II) was equal to the initial concentration of the iron (II) sulfate solution. This made it possible to calculate the concentrations of all the variations of iron (II) compounds (ions, molecules) and to estimate the effect of those on ORP and the sphalerite electrode potential. The calculations

of the equilibrium concentrations of Fe^{2+} , $FeOH^+$, $Fe(OH)_3^-$, $Fe(OH)_4^-$ were based on “ $FeSO_4-H_2O$ ” system analysis, which is given in details in [23].

Figure 2 demonstrates experimental data for sphalerite electrode potentials and ORP of iron (II) sulfate solutions in which the electrodes were immersed at pH = 8 as a function of the negative common logarithm of concentrations of either Fe^{2+} or $FeOH^+$ (pFe^{2+} or $pFeOH^+$).

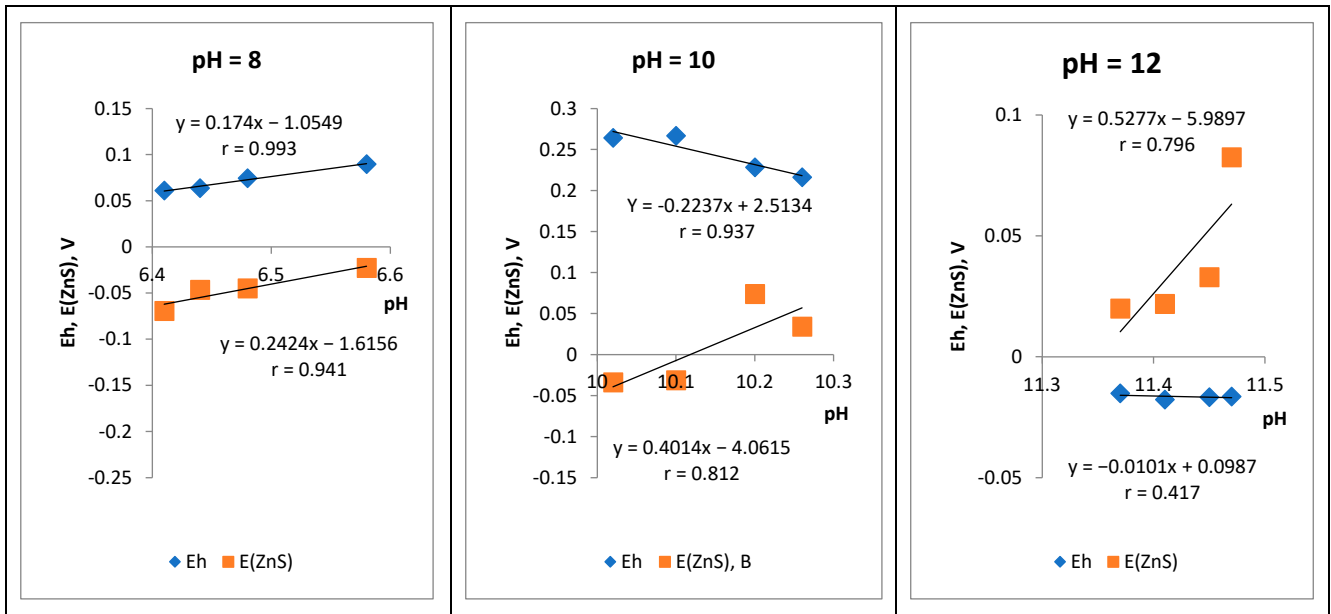


Figure 1. Effects of pH on the potential of a sphalerite electrode immersed in an iron (II) sulfate solution and ORP.

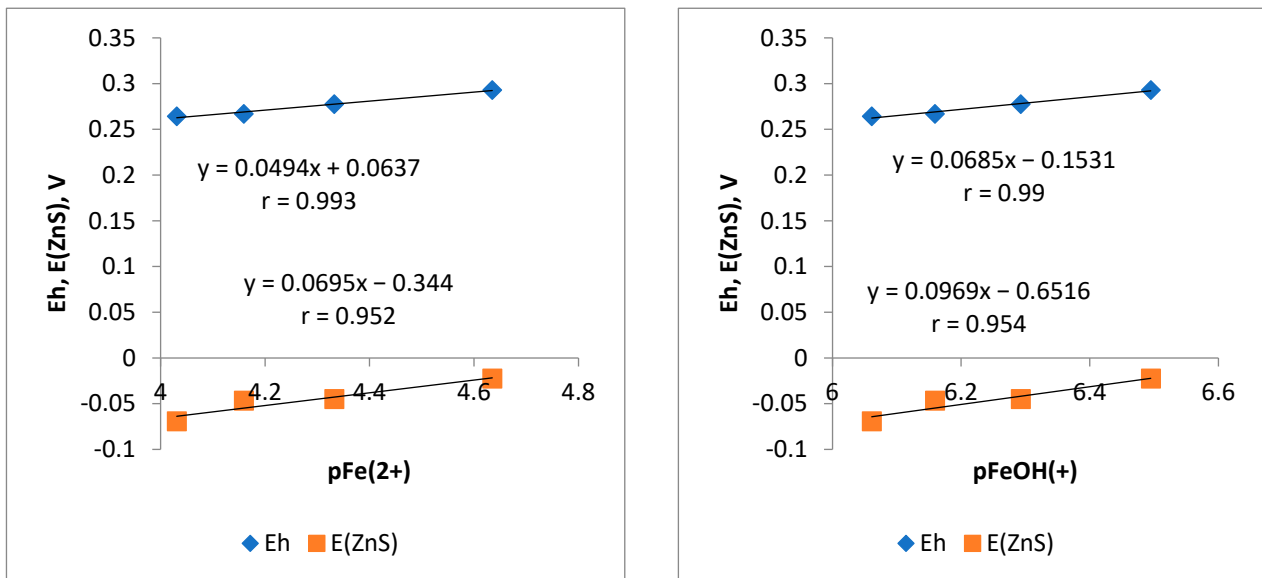


Figure 2. Sphalerite electrode potentials and ORP of iron (II) sulfate solutions in which the electrode was immersed (pH = 8) as a function of the negative common logarithm of concentrations of either Fe^{2+} or $FeOH^+$ (pFe^{2+} or $pFeOH^+$).

The findings showed the linearity of the experimental data, which can be approximated as follows:

$$Eh = 0.0637 + 0.0494pFe^{2+}, r = 0.993, \tag{7}$$

$$E_h = -0.1531 + 0.0685p\text{FeOH}^+, r = 0.99 \quad (8)$$

$$E(\text{ZnS}) = -0.344 + 0.0695p\text{Fe}^{2+}, r = 0.952 \quad (9)$$

$$E(\text{ZnS}) = -0.6516 + 0.0969p\text{FeOH}^+, r = 0.954 \quad (10)$$

This proves that Fe^{2+} and FeOH^+ are potential-determining cations, the concentration of which affects the ORP and the potential of the sphalerite electrode. In this case, expressions (7) and (8) show the reducing properties of considered solutions, and approximations (9) and (10) indicate a possible replacement reaction of Zn^{2+} in the sphalerite surface layer for Fe^{2+} or FeOH^+ into solution, leading to the formation of FeS. Further flotation tests of sphalerite samples using thiol collectors confirmed the previous conclusions.

3.4. Flotation of Sphalerite Treated with Iron Sulphate Solutions by Thiol Collectors

The flotation tests of sphalerite, the effects of copper, zinc and iron ions on flotation recovery, preparation of sphalerite samples and related procedures are given in details in [29,30]. In the present paper, specific attention is paid to flotation of sphalerite in the absence or in the presence of iron (II) hydroxides precipitates, which can be associated with pH 8 or 12, respectively. Figure 3 shows the results of sphalerite flotation with potassium buthyl xanthate and sodium dibuthyl dithiophosphate. The sphalerite suspension was conditioned with iron (II) sulfate solutions of a particular concentration before dosing the collector.

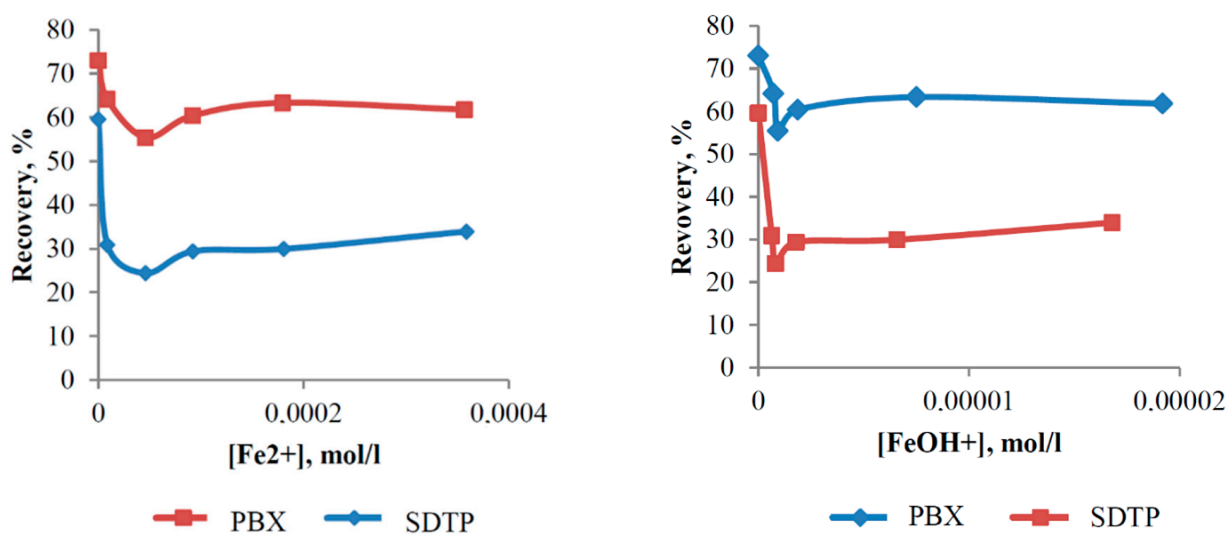


Figure 3. The flotation recovery of sphalerite ($-74 + 44 \mu\text{m}$) with potassium buthyl xanthate and sodium dibuthyl dithiophosphate (dosage 100 g/t, pH = 8) as a function of Fe^{2+} and FeOH^+ concentration.

The findings revealed the effect of iron (II) sulfate on the flotation recovery of sphalerite by PBX and SDTP in alkaline suspensions. At pH = 8 the dosage of iron (II) sulfate resulted in the depression of sphalerite flotation for both collectors. However, increasing the pH up to 12 resulted in an activation of the sphalerite and in the growth of flotation recovery of sphalerite in the froth product. A significant increase in sphalerite recovery was observed at low dosages of iron (II) sulfate.

In summary, the study revealed different effects of iron (II) sulfate on the flotation recovery of sphalerite under weak and strong alkaline conditions. Apparently, the reasons for that are the different mechanisms of interactions of sphalerite particles with iron (II)-bearing compounds which are dissolved in the liquid phase, and hence the differences in surface composition affecting flotation recovery.

4. Conclusions

1. The results of thermodynamic calculations revealed the possibility of interaction of the sphalerite surface with the products of iron (II) hydrolysis. The iron (II) sulfide was considered as the most probable product which was formed on the sphalerite surface.
2. The effect of the concentration of hydroxide ions on the precipitation of iron (II) hydroxides was experimentally studied. At the initial pH = 8 and at all the studied concentrations of iron (II) sulfate in the working solutions, the precipitation process was not observed. However, an increase in the pH of the solutions up to 8 and 12 led to the formation of iron (II) hydroxides.
3. The potentiometric studies established that the Fe^{2+} and FeOH^+ cations are potential-determining in weak alkaline solutions.
4. In conclusion, the flotation tests demonstrated the effect of the dose of iron (II) sulfate and pH on the flotation recovery of sphalerite with thiol collectors. Interestingly, an activation effect of iron sulfate on sphalerite flotation was observed at pH = 12. This resulted in an increase in the flotation recovery of sphalerite at low dosages of iron sulfate in suspension.

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