

## Analytical study of the process of sulphuric acid dissolution of Waelz-clinker with Eh - pH diagrams

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A thermodynamical analysis of the sulfuric acid dissolution process into oxidation and reducing conditions of the Waelz-clinker (a waste product of zinc production) was carried out. The analytical study was executed by the help of a professional program HSC Chemistry Ver. 5.11 as the module for the calculation and construction of Eh - pH diagrams. The Fe-Cu-S-H<sub>2</sub>O and Fe-Ag-S-H<sub>2</sub>O systems which describe the dissolution of iron, copper and silver compounds (oxides and sulfides) in a sulfuric acid medium were investigated. The influence of temperature (70 and 80°C) and oxidation potential on the substance composition of the solutions was determined based on the calculated and construction Eh - pH diagrams.

**Key words:** waelz clinker, dissolution, sulfuric acid, sodium sulfite, Eh pH- diagrams.

### INTRODUCTION

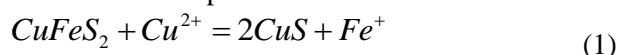
In the process of zinc production in waelz furnaces, a waste called waelz clinker is formed. It contains copper (1.92–2.0 %) and silver (128-146 g/t) in quantities comparable to those in ores which makes it a valuable raw material. The main reason of the lack of a method suitable for recovery of these metals is the high iron (36.87-37.35%) and carbon (13.55%) content in the clinker.

Besides, according to the waste product classifications, it falls within the „hazardous waste” category which requires search for a technology suitable for its treatment.

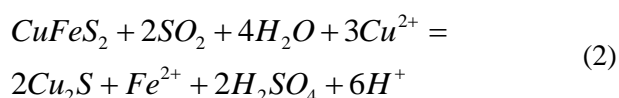
Currently, one of the main methods for clinker processing in Bulgaria is floatation which yields copper concentrate with high carbon content without, however, recovery of the silver.

In the world practice, there are a number of hydrometallurgical methods for recovery of copper and silver from lean raw materials, and quite a few research studies on the application of sulphuric-acid dissolution of copper bearing raw materials using SO<sub>2</sub> or Na<sub>2</sub>SO<sub>3</sub> as reducer were conducted over the recent years. According to a number of authors: C. Sequeira et al. [1], R. Bartlett et al. [2], E. Silvester et al. [3], W. Yuill et al. [4], G. Fuentes et al. [5] the purpose of sulphuric-acid dissolution of sulphide copper-bearing raw materials with sulphur dioxide as reducer is transformation of the more complex copper sulphides such as: chalcopyrite and bornite into the less complex sulphides chalcocite

(Cu<sub>2</sub>S), digenite (Cu<sub>1.8</sub>S) or covellite (CuS). The interaction takes place as follows:

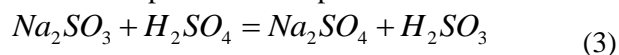


In the presence of reducer, such as sulphur dioxide, the reaction velocity is considerably increased [6]. The process can be described by the following reaction:



According to D. Collier et al. [6] SO<sub>2</sub> and Na<sub>2</sub>SO<sub>3</sub> (sodium sulphite) are the reducers most suitable for chalcopyrite and bornite. The authors explain the higher velocity of dissolution in the presence of SO<sub>2</sub> by dissolution of the hematite and clearing of the reacting surface of the sulphide-bearing minerals. According to Sohn and Wadsworth [7], the presence of SO<sub>2</sub> in the solution creates conditions for selective recovery of copper. At high concentration of Na<sub>2</sub>SO<sub>3</sub>, (for example, 150 g/l) the copper will precipitate in the form of double salt - Cu<sub>2</sub>SO<sub>3</sub>·CuSO<sub>3</sub>·2H<sub>2</sub>O [8].

In the opinion of S. I. Sobol [9], the chemical interactions taking place during dissolution of different metal sulphides with the participation of sulphur dioxide or sodium sulphite are accompanied by separation of elementary sulphur. When sodium sulphite is used, initially the reaction runs with separation of sulphurous acid:

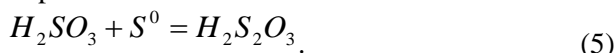


Which, upon heating, can decompose with emission of sulphur dioxide

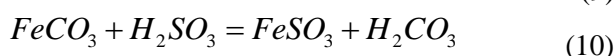
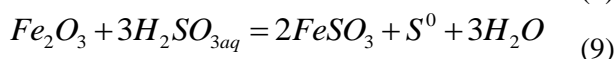
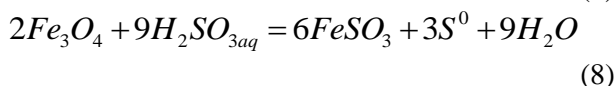
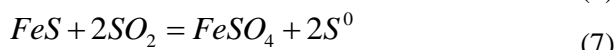
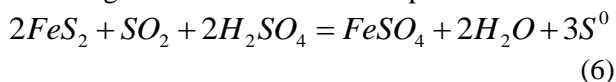
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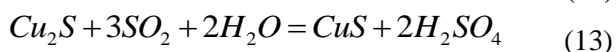
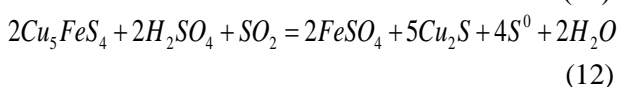
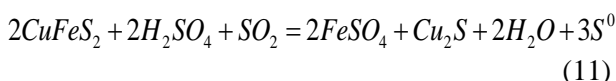
or form thiosulphate upon reaction with free sulphur



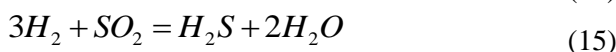
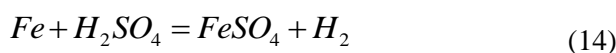
During dissolution of the iron-bearing minerals in the presence of SO<sub>2</sub> (or sulphurous acid) the following chemical reactions take place:



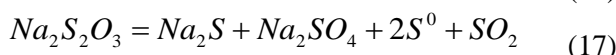
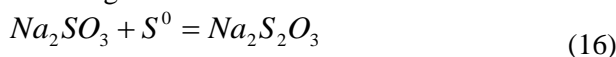
Dissolution of the copper-bearing sulphide phases according to [6] takes place through the reactions:



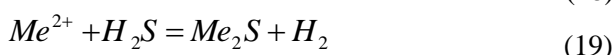
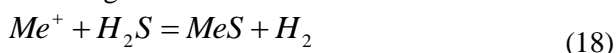
In principle, the reactions of metal sulphide dissolution in the presence of SO<sub>2</sub> do not result in formation of hydrogen sulphide. However, in the presence of a metal phase in the raw material, for example iron, in gaseous hydrogen sulphide is released in the system as a result of the following interactions:



Upon introduction of Na<sub>2</sub>SO<sub>3</sub> in the solution formation of Na<sub>2</sub>S is also possible as a result of the following reactions:



The reaction products (H<sub>2</sub>S and Na<sub>2</sub>S) sulphidize metal ions present in the solution by one of the following reactions:



Where Me<sup>2+</sup> and Me<sup>+</sup> are: Cu<sup>+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>2+</sup>, etc.

Herein, a thermodynamic analysis of the process of sulphuric-acid dissolution in the reducing medium of waelz clinker is carried out and Eh-pH

diagrams have been built in order to assess the thermodynamic probability of execution of the reactions and stability of the elements in the Fe-Cu-S-H<sub>2</sub>O and Fe-Ag-S-H<sub>2</sub>O systems.

#### Chemical and Mineralogical Composition of Clinker

The chemical composition of waelz clinker is presented in Table 1. It is determined by means of atomic adsorption analysis.

**Table 1.** Chemical composition of the waelz-clinker

Fe, %	Cu, %	Ag g/t	S, %	C, %	Others
36.87	1.92	128	4.33	13.55	~43.23

Beside the elements indicated in the table in the column „others”, the total content of Pb, Zn, Mn, As below 1%, NaO, K<sub>2</sub>O, CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> etc., is indicated.

The mineralogical studies of the clinker carried out show that the main minerals in the clinker are magnetite, hematite, jarosite, siderite, metal iron, pyrite, bornite, chalcocite, arsenic pyrite, pyrrhotite, galenite, sphalerite (10-15 %), oxides; calcium, iron, lead, zinc and copper sulphates and carbonates (5 %), aluminum silicates of potassium, sodium, magnesium, iron, lead and copper (20-25 %) and carbon (15-20 %).

The phase analyses of iron and copper in the clinker show that ~28 % of the iron is in metal phase, ~ 58 % as FeO and the rest is in the form of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. The copper is found mainly in a sulphide phase (~ 80 %). The rest of the copper is distributed between the oxide (~ 15 %) and metal (~ 5 %) phases. Silver in the clinker is found mainly in the form of sulphide.

Therefore, the process of dissolution of iron, copper and silver compounds (oxides and sulphides) in a sulphur-acidic medium with the participation of sulphur dioxide or sodium sulphite as reducer can be described by the systems Fe-Cu-S-H<sub>2</sub>O and Fe-Ag-S-H<sub>2</sub>O.

#### Analytical Investigation of the Process of Waelz Clinker Dissolution

The analytical investigation is carried out by means of a professional code HSC Chemistry Ver. 5.11. Two modules are used: Reaction Equation and Eh-pH diagrams.

#### Computation of Gibbs function

On the basis of the literature study carried out as above, the possible reactions in both investigated systems were divided in two main groups: reactions with participation of reducer and reactions with formation of copper and silver sulphides. The

**Table 2.** Computed values of the Gibbs function and equilibrium constant of the possible chemical interactions during reducing dissolution of the clinker

Reactions	T=25°C		T=80°C	
	ΔG, kJ	LogK	ΔG, kJ	LogK
<b>A. Reactions with participation of reducer</b>				
$\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_3(\text{a})$	-111,33	19.51	-115,05	17,02
$\text{Fe} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2(\text{g})$	-135.01	23.65	-138,57	20,49
$\text{SO}_2(\text{g}) + 3\text{H}_2(\text{g}) = \text{H}_2\text{S}(\text{g}) + 2\text{H}_2\text{O}$	-207.52	36.37	-191,58	28,34
$2\text{FeS}_2 + \text{SO}_2(\text{g}) + 2\text{H}_2\text{SO}_4 = 2\text{FeSO}_4 + 2\text{H}_2\text{O} + 5\text{S}^0$	-124,07	21.74	-117,27	17,3
$\text{FeS} + 2\text{SO}_2(\text{g}) = \text{FeSO}_4 + 2\text{S}$	-122.74	21.52	-102,36	15,14
$2\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 + \text{SO}_2(\text{g}) = 2\text{FeSO}_4 + \text{Cu}_2\text{S} + 2\text{H}_2\text{O} + 4\text{S}^0$	-149.69	26,24	-139,52	26,84
$2\text{Cu}_5\text{FeS}_4 + 2\text{H}_2\text{SO}_4 + \text{SO}_2(\text{g}) = 2\text{FeSO}_4 + 5\text{Cu}_2\text{S} + 4\text{S}^0 + 2\text{H}_2\text{O}$	-91,45	16,03	-80,79	11,95
$\text{Cu}_2\text{S} + 3\text{SO}_2(\text{g}) + 2\text{H}_2\text{O} = 2\text{CuS} + 2\text{H}_2\text{SO}_4$	-25.65	4.51	-4,69	-0,69
$\text{Na}_2\text{SO}_3 + \text{S}^0 = \text{Na}_2\text{S}_2\text{O}_3$	-3.61	2.64	-3.306	2.046
$\text{Na}_2\text{S}_2\text{O}_3 = 3/4\text{Na}_2\text{S} + 1/4\text{Na}_2\text{SO}_4 + \text{SO}_2(\text{g})$	138.12	-24.20	126.99	-18.78
<b>B. Reactions of sulfide formation</b>				
$\text{CuFeS}_2 + \text{Cu}^{+2} = 2\text{CuS} + \text{Fe}^{+2}$	-73,53	12.89	-73,36	10,85
$2\text{Cu}^{2+} + \text{H}_2\text{S}(\text{a}) + 4\text{e}^- = \text{Cu}_2\text{S} + \text{H}_2(\text{g})$	-189,72	33.065	-191,44	28.32
$2\text{Ag}^+ + \text{H}_2\text{S}(\text{a}) + 2\text{e}^- = \text{Ag}_2\text{S} + \text{H}_2(\text{g})$	-166,10	29.08	-158,12	23.39

thermodynamic probability for the possible chemical interactions to take place is assessed in a temperature range from 25 to 80 °C at atmospheric pressure. The computed values of the Gibbs function and equilibrium constants are given in Table 2.

The analysis of results obtained shows that the process of clinker dissolution in a sulphuric acid medium in the presence of reducer ( $\text{SO}_2$  or  $\text{Na}_2\text{SO}_3$ ) will take place with formation of elementary sulphur and sulphides.

The reaction of hydrogen sulphide generation from  $\text{SO}_2$  and  $\text{H}_2$  present in the system has the highest value of the Gibbs function ( $\Delta G = -208.99$  kJ). The latter will form upon dissolution of the metal iron. The reactions of sulphidization of the copper ions ( $\Delta G = -189,72$  kJ) and silver ions ( $\Delta G = -166,10$  kJ) present in the solution are also thermodynamically probable.

The low value of the Gibbs function of the reaction with formation of sodium thiosulphate and its decomposition to  $\text{Na}_2\text{S}$  is thermodynamically impossible in the conditions of the investigation. In all interactions with the participation of  $\text{SO}_2$  accompanied by temperature rise the values of  $\Delta G$  and  $\text{LogK}$  negligibly decrease.

#### Computation and building of Eh-pH diagrams

A module of the code HSC Chemistry – Eh-pH Diagrams is used to determine the stability ranges of ionic and nonionic forms of the substances Fe-Cu-S- $\text{H}_2\text{O}$  and Fe-Ag-S- $\text{H}_2\text{O}$  present in the studied systems. In the process of building the diagrams, the molar composition of the solution was taken into consideration. The computations were carried

out for molar concentrations of the elements present expressed as mol/kg $\text{H}_2\text{O}$ : 0.175 Na, 1.727 S, 0.66 Fe, 0.030 Cu and 0.000186 Ag. They correspond to the molar composition obtained upon dissolution of 20 g clinker (Table 1) in 100 ml solution with concentration 150 g/L  $\text{H}_2\text{SO}_4$  and 75 g/L  $\text{Na}_2\text{SO}_3$ . The analysis is carried out with serial multiplication of the diagrams: Na-S- $\text{H}_2\text{O}$ ; Na-S-Fe- $\text{H}_2\text{O}$ , Na-S-Cu- $\text{H}_2\text{O}$ , Na-S-Ag- $\text{H}_2\text{O}$ , Na-S-Fe-Cu- $\text{H}_2\text{O}$  and Na-S-Fe-S- $\text{H}_2\text{O}$ .

The species of ionic and nonionic forms of the substances present in the solution and the Gibbs function used in building of the respective diagrams are presented in Table 3.

Figure 1 presents a diagram of Na-S- $\text{H}_2\text{O}$  at temperature 25 and 80°C.

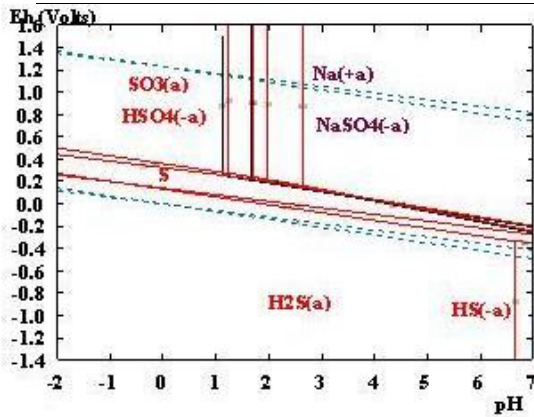
It can be seen that with rising of the temperature to 80°C the stability range of sulphur and of the  $\text{HSO}_4^-$  and  $\text{NaSO}_4^-$  ions negligibly expands in the direction of a higher potential and lower acidity.

Figures 2, 3 and 4 present the triple diagrams Na-S-Fe- $\text{H}_2\text{O}$ , Na-S-Cu- $\text{H}_2\text{O}$  and Na-S-Ag- $\text{H}_2\text{O}$  built for 80°C.

The analysis of the Eh-pH diagrams shows that in a highly acidic medium and low reduction potential, the stable phases are  $\text{FeS}_2$ ,  $\text{CuS}$ ,  $\text{Cu}_2\text{S}$  and  $\text{Ag}_2\text{S}$ . Upon reduction of the solution's acidity the stability of these phases shifts towards lower potentials which, in practice, means establishment of a highly reducing medium. Therefore, upon dissolution of the clinker at low reduction potential, one can expect, besides the  $\text{Fe}^{2+}$  ions, the presence of insoluble  $\text{FeS}_2$  as well.

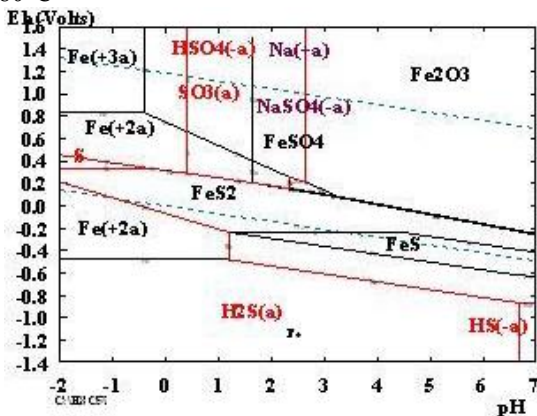
**Table 3.** Types of ionic and nonionic forms in the systems Na-Cu-Fe-S-H<sub>2</sub>O and Na-Ag-Fe-S-H<sub>2</sub>O and free energy of their formation

Species	$\Delta G^0_{298}$ (kJ/mol)	Species	$\Delta G^0_{298}$ (kJ/mol)	Species	$\Delta G^0_{298}$ (kJ/mol)
<b>Cooper</b>		<b>Iron</b>		<b>Silver</b>	
Cu	0.000	Fe	0.000	Ag	0.000
Cu <sup>2+</sup>	65.52	Fe <sup>3+</sup>	-10.96	Ag <sup>2+</sup>	268.63
Cu <sup>+</sup>	45.76	Fe <sup>2+</sup>	-91.82	Ag <sup>+</sup>	71.7
CuFeS <sub>2</sub>	-190.53	FeO	-241.79	Ag <sub>2</sub> O	-7.50
Cu <sub>5</sub> FeS <sub>4</sub>	-394.85	Fe <sub>2</sub> O <sub>3</sub>	-725.99	Ag <sub>2</sub> S	-41.79
CuO	-123.00	FeS	-102.04	Ag <sub>2</sub> SO <sub>3</sub>	-396.19
Cu <sub>2</sub> O	-143.65	FeS <sub>2</sub>	-156.66	Ag <sub>2</sub> SO <sub>4</sub>	-600.29
CuS	-56.73	FeSO <sub>4</sub>	-805.69	AgSO <sub>4</sub> <sup>-</sup>	-648.92
Cu <sub>2</sub> S	-87.48				
CuSO <sub>4</sub>	-640.61				
Cu <sub>2</sub> SO <sub>4</sub>	-636.51				
<b>Sulfur</b>		<b>Sodium</b>		<b>Sulfuric acid</b>	
S	0.000	Na	0.000	H <sub>2</sub> SO <sub>4</sub>	
HS <sup>-</sup>	17.93	Na <sup>+</sup>	266.03	H <sub>2</sub> SO <sub>3</sub> (a)	-667.18
H <sub>2</sub> S(a)	-27.09	Na <sub>2</sub> S	-352.53	H <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (a)	-524.29
SO <sub>2</sub> (a)	-297.74	Na <sub>2</sub> SO <sub>3</sub>	-990.26	H <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (a)	-518.24
SO <sub>3</sub> (a)	-505.03	Na <sub>2</sub> SO <sub>4</sub>	-1248.22		-595.17
SO <sub>3</sub> <sup>2-</sup>	-457.41	NaSO <sub>4</sub> <sup>-</sup>	-982.96		
SO <sub>4</sub> <sup>2-</sup>	-712.25				



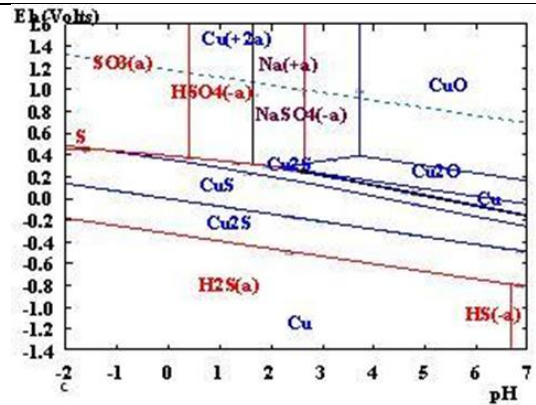
Elements	Molality	Pressure
Na	1.750E-1	1.000E+00
S	1.727E+00	1.000E+00

**Fig. 1.** Eh-pH diagram of the system Na-S-H<sub>2</sub>O at 25 and 80°C



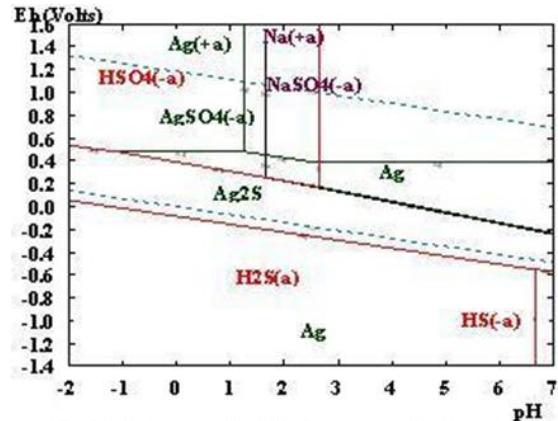
Elements	Molality	Pressure
Na	1.750E-01	1.000E+00
Fe	6.600E-01	1.000E+00
S	1.727E+00	1.000E+00

**Fig. 2.** Eh-pH diagram of the system Na-Fe-S-H<sub>2</sub>O at 80°C



Elements	Molality	Pressure
Na	1.750E-01	1.000E+00
Cu	3.020E-02	1.000E+00
S	1.727E+00	1.000E+00

**Fig. 3.** Eh-pH diagram of the system Na-Cu-S-H<sub>2</sub>O at 80°C



Elements	Molality	Pressure
Na	1.750E-01	1.000E+00
Ag	1.860E-04	1.000E+00
S	1.727E+00	1.000E+00

**Fig. 4.** Eh-pH diagram of the system Na-Ag-S-H<sub>2</sub>O at 80°C

Figures 5 and 6 present Eh-pH summary diagrams of the systems Na-Cu-Fe-S-H<sub>2</sub>O and Na-Ag-Fe-S-H<sub>2</sub>O at a temperature of 80°C.

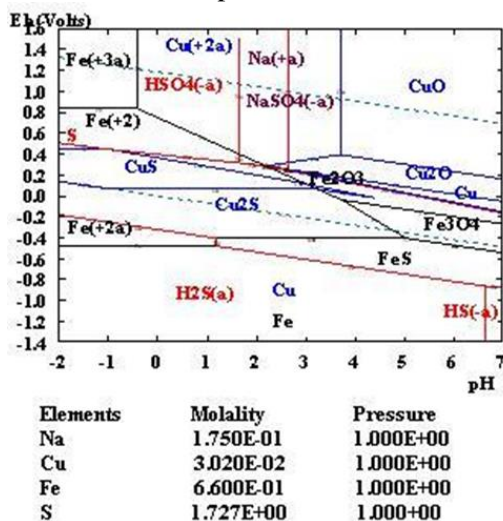


Fig. 5. Eh-pH diagram of the system Na-Cu-Fe-S-H<sub>2</sub>O at 80°C

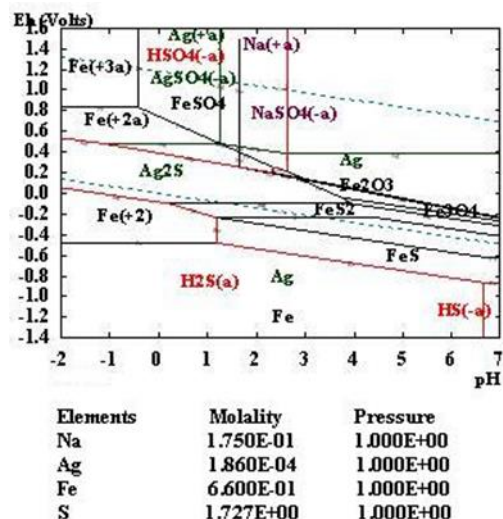


Fig. 6. Eh-pH diagram of the system Na-Ag-Fe-S-H<sub>2</sub>O at 80°C

The diagrams indicate that at initial concentration of H<sub>2</sub>SO<sub>4</sub> – 150 g/l, i.e. high acidity (pH ~ -1.5), the simple sulphides of copper and silver are stable phases in both systems. The electrochemical potentials of the stability range of copper sulphides vary as follows: of CuS from 0.1V to 0.43V, and of Cu<sub>2</sub>S from 0.2V to 0.12V. The stability range of Ag<sub>2</sub>S is at a potential from -0,1V to 0.55V. At the same pH of the solution the stable phase of iron are the ions of Fe<sup>2+</sup> (-0,52÷0.82V).

## CONCLUSION

On the basis of computed values of the Gibbs function, a thermodynamic assessment of the possible chemical interactions taking place during dissolution of the waelz clinker in sulphuric acid in the presence of reducer (Na<sub>2</sub>SO<sub>3</sub>) is made. It is determined the raise of temperature (from 25 to 80°C) has a negligible effect on the investigated reactions.

The analysis of the stability ranges of ionic and nonionic forms in the systems Na-Cu-Fe-S-H<sub>2</sub>O and Na-Ag-Fe-S-H<sub>2</sub>O shows that the process of waelz clinker dissolution in a highly acidic medium (pH ~ -1.5) in the presence of sodium sulphite reducer (0.3 mol/L) will take place with formation of copper and silver sulphides.

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## **АНАЛИТИЧНО ИЗЛЕДВАНЕ НА ПРОЦЕСА НА РАЗТВАРЯНЕ НА ВЕЛЦ-КЛИНКЕР В СЯРНА КИСЕЛИНА С ПОМОЩТА НА Eh – pH ДИАГРАМИ**

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(Резюме)

Проведен е термодинамичен анализ на процеса на разтваряне на велц-клинкер (отпадъчен продукт от производството на цинк) в сярна киселина. Аналитичното изследване е реализирано с помощта на професионална програма HSC Chemistry вер. 5.11, като модул за изчисляване и построяване на Eh - pH диаграми. Изследвани са системите Fe-Cu-S-H<sub>2</sub>O и Fe-Ag-S-H<sub>2</sub>O, които описват разтварянето на железни, медни и сребърни съединения (оксиди и сулфиди) в сярно-кисела среда. Влиянието на температурата (70 и 80 °C) и окислителния потенциал върху състава на разтворите е определен на основа на изчислените и построени Eh - pH диаграми.