AN ANALYTICAL STUDY OF THE NEUTRALIZATION PROCESS OF SOLUTIONS WITH HIGH CONCENTRATION OF Fe(III) IONS

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Received 28 September 2016
Accepted 01 December 2016

ABSTRACT

With the means of software HSC Chemistry ver.7.1 modules: Equations Reaction and Eh-pH diagrams a thermodynamic assessment of the neutralization process of sulfuric acid solutions with high concentration of ferric ions (> 60 g l^{-1}) with calcium carbonate and calcium hydroxide was carried out.

*Based on the calculated values of the energy of Gibbs and the equilibrium constants of the possible chemical interactions during the neutralization process with $Ca(OH)_2$ and $CaCO_3$ of a sulfuric acid solutions with a high concentration of ferric ions has been established that the neutralization process without participation of Fe^{3+} was thermodynamically more probable than in the presence of ferric ions. When $Ca(OH)_2$ (hydrated lime) was used as neutralizer, the probability to obtain a precipitate of $CaSO_4*2H_2O$ (gypsum) and FeO*OH (goethite) was the most thermodynamically probable, while using a neutralizer $CaCO_3$ (limestone), the most probable was a precipitate of gypsum and $Fe(OH)_3$. With increasing of the temperature from 25 to 60°C, the thermodynamic probability of goethite formation increases.*

*Based on Eh-pH diagrams of the system H_2SO_4-$CaCO_3$-$Fe_2(SO_4)_3$-$FeSO_4$-H_2O it was established that in the pH range from -2 to 6 and temperature 25°C the most stable compound is calcium sulphate dehydrate. With the increase of temperature up to 60°C the most stable compound is anhydrite. The diagrams were built for molar concentrations of the elements in the solution (expressed as mol/kg_{H2O}): 1,079 Fe_{total}, 0,622 S, 0,622 Ca and 0,622 C. The composition of the solution corresponds of the total iron and sulfuric acid concentrations and the quantity of $CaCO_3$ necessary for neutralization of 100 % H_2SO_4. At the oxidation potential (Eh > 0.8 V) and high acidity of the solution (pH from -2 to 0.5), the areas of stability of iron ionic complex $FeHSO_4^{2-}$ and Fe^{3+} ion were found. In practice this means that the process of neutralization have to be carried out at a high oxidation potential and pH < 0.5 in order to avoid co-precipitation of iron sludge: $Fe(OH)_3$ or FeO*OH.*

Keywords: thermodynamic analyses, neutralization process, sulfuric acid, calcium carbonate, calcium hydroxide Fe(III) and Fe(II) ions.

INTRODUCTION

Under the high temperature oxidation of the pyrite concentrate in an autoclave, solutions with high concentrations of ferric iron and sulfuric acid are formed as a result of the following reactions:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (2)$$

Or, in total

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (3)$$

According to Fleming [1] under high pressure and low acidity the ferric sulfate hydrolyzes to hematite (Fe_2O_3), whereas under high acidity it hydrolyzes to basic ferric sulfate - $Fe(OH)SO_4$:

$$2Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe_2O_3 + 3H_2SO_4 \quad (5)$$

$$2Fe_2(SO_4)_3 + 2H_2O \rightarrow 2Fe(OH)SO_4 + H_2SO_4 \quad (6)$$

As the process of neutralization of $Fe(OH)SO_4$ is very slow even in a highly alkaline environments (pH~10), he proposed hot treatment (90 - 140°C) of the solution with sulfuric acid, the so called „hot cure" process, under which the basic ferric sulfate decomposes to ferric sulfate:

$$Fe(OH)SO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2H_2O \quad (7)$$

Later the highly acidic ferric sulfate solutions are neutralized with limestone or lime. Depending on the quantity of the reagent and the temperature, the neutralization process proceeds under the following reactions:

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4^{*}2H_2O + CO_2 \quad (8)$$

$$Fe_2(SO_4)_3 + 3CaCO_3 + H_2O \rightarrow 2FeO.OH + 3CaSO_4 + 3CO_2 \quad (9)$$

$$Fe_2(SO_4)_3 + 3CaCO_3 + 3H_2O \rightarrow 2Fe(OH)_3 + 3CaSO_4 + 3CO_2 \quad (10)$$

According to J.M. Casas at al [2] in acidic solutions the iron is present both in the species of free Fe^{2+} и Fe^{3+} ions and in the species of complex compounds: $FeSO_4^o$, $FeSO_4^+$ and $Fe(SO_4)_2^-$. The chemical reactions in the system can be described with the following equations:

$$Fe^{2+} + SO_4^{2-} \Leftrightarrow FeSO_4^o \quad (11)$$

$$Fe^{3+} + SO_4^{2-} \Leftrightarrow FeSO_4^+ \quad (12)$$

$$Fe^{3+} + 2SO_4^{2-} \Leftrightarrow Fe(SO_4)_2^- \quad (13)$$

$$H^+ + SO_4^{2-} \Leftrightarrow HSO_4^- \quad (14)$$

For determination of the type and quantity of ion species, J.M. Casas et al.[2] measured the density and conductivity in three systems: Fe(II)-H_2SO_4-H_2O, Fe(III)-H_2SO_4-H_2O and Fe(II)-Fe(III)-H_2SO_4-H_2O with high concentration of sulfuric acid H_2SO_4 (2.2 mol l^{-1}) and Fe_{total} (1.3 mol l^{-1}). The test work was performed under two temperatures: 25 and 50°C. The model calculations and experiments have shown dominant presence of HSO_4^-, H^+, Fe^{2+} and $Fe(SO_4)_2^-$ ions, whereas with increase of the temperature the concentrations of H^+ и Fe^{3+} fall and the concentrations of HSO_4^- and $Fe(SO_4)_2^-$ ions rise.

In the thermodynamic model by G. Yue at al. [3] other than the above relationships, the following are also taken into account:

$$Fe^{2+} + H^+ + SO_4^{2-} \Leftrightarrow FeHSO_4^+ \quad (15)$$

$$2Fe^{3+} + 3H_2O \Leftrightarrow Fe_2O_3 + 6H^+ \quad (16)$$

Based on the experiments and modelling, the authors above have determined that the allocation between the different ionic and non-ionic species depends on the initial concentration of total iron, the acidity of the solution, the Fe^{3+}/Fe^{2+} ratio and the temperature. Moreover, the larger portion of Fe(III) is allocated to precipitates or complex compounds and only a small portion remains in the form of Fe^{3+} ions.

P. Kobylin, T.Kaskiala and J.Salminen [4] use the method of minimizing Gibbs energy and a compiling method for calculating the model and creating phase diagrams of the systems H_2SO_4-$FeSO_4$-H_2O and H_2SO_4-$Fe_2(SO_4)_3$-H_2O for temperatures of 25°C, 45°C and 55°C and high concentration of sulfuric acid (5.2 mol/kg_{H2O}). At room temperature the system H_2SO_4-$FeSO_4$-H_2O contains: $FeSO_4.7H_2O$, $FeSO_4.H_2O$ and $FeSO_4$, while at higher temperatures only the species $FeSO_4.H_2O$ is stable.

The optimization of the phase diagram of the system $Fe_2(SO_4)_3$-H_2SO_4-H_2O has been done for standard temperature and by taking into account the activities of the ions and solubility of ferric sulfate in demineralized water. Upon constructing the diagram the presence of the complex ions: $FeSO_4^+$, $Fe(SO_4)_2^-$ and $FeHSO_4^{2+}$ which can form acidic solutions was not taken into account. According to the authors the primary compounds present in the system have been: $Fe_2(SO_4)_3.7H_2O$ and $Fe_2(SO_4)_3.H_2SO_4.8H_2O$.

Therefore, the neutralization process is expected to occur in the presence of iron in various species in the solution.

In metallurgical practice the process of neutralization of acidic solutions with high concentration of ferric sulfate can be conducted with various neutralizing agents.

The classification, proposed by C. Lewis et al. [5], for the most commonly used bulk commodities is presented in Table 1.

The neutralization reactions can be classified accord-

Table1. Bulk commodities for neutralizing sulfuric acid [5].

Neutralizer	Chemical formula	Name
Caustic soda	NaOH	Sodium hydroxide
Soda sh	Na_2CO_3	Sodium carbonate
Hi purity limestone	$CaCO_3$	Calcium carbonate
Dolomite limestone	$CaCO_3.MgCO_3$	Calcium-magnesium carbonate
Lime	CaO	Calcium oxide
Hydrated lime	$Ca(OH)_2$	Calcium hydroxide
Dolomite lime	CaO.MgO	Calcium-magnesium oxide

ing to their products into: i) reactions where all products are soluble; ii) reactions where only some of the products are soluble and iii) reactions with limestone with high content of magnesium carbonate or magnesium oxide.

The authors note that in the presence of high magnesium, it is necessary to conduct the process up to pH >10.2, in order to convert the soluble at pH = 7 $MgSO_4$, into insoluble $Mg(OH)_2$. The relevant reactions are:

$$Ca(OH)_2.Mg(OH)_2 + H_2SO_4 = CaSO_4 + 4H_2O + MgSO_4$$

soluble at pH=7.0 (17)

$$Ca(OH)_2.Mg(OH)_2 + MgSO_4 = CaSO_4 + 2Mg(OH)_2$$

insoluble at pH>10.2 (18)

According to M. Danovska at al. [6] ammonia is used for increasing of pH of the solutions. It is considered as an inexpensive neutralizer. Other alternative neutralizers are sodium hydroxide and limestone. Sodium hydroxide is highly active and the neutralization process can occur with or without formation of precipitate. The precipitates are compact and easy to filter. The limited use of NaOH is attributable to its high cost.

Limestone is another very commonly used neutralizer. It is used under controlled conditions. Apart from neutralization of acid, limestone is also used for iron precipitation:

$$CaCO_{3(s)} + Fe_2(SO_4)_{3(aq)} + 3H_2O \leftarrow 3CaSO_{4(s)} + +2Fe(OH)_{2(s)} + 3CO_{2(g)} \quad (19)$$

The CO_2 released according to the reaction above acts as a buffer and determines the upper limit of pH (maximum pH ~ 6.5), which reflects upon the reaction rate and the quantity of reagent consumed. The resultant precipitates are very fine, slow settling and they are contaminated with iron.

Calcium sulfate can take the species of gypsum ($CaSO_4.2H_2O$), hemihydrate ($CaSO_4.H_2O$) or anhydrite ($CaSO_4$) [7]. According to Stumm [8], temperature is the primary parameter influencing the type of precipitate formed, particularly in the interval between 42 and 97^{o}C. In practice, the most common precipitate is gypsum but under certain conditions other species may form too.

Worldwide quantities of gypsum formed by the metallurgical and chemical industries significantly exceed its usage [9, 10]. One of the reasons for this is the low quality of gypsum due to co-precipitation of iron and other metallic ions.

According to some authors, it is necessary to conduct the process of neutralization with a controllable pH so that high purity gypsum can be formed so that it can find an alternative usage other than in construction works, e.g. for production of fertilizer [11, 12].

This article conducts thermodynamic analysis of the process of neutralization of ferric sulfate sulfuric acid solutions with two types of reagent: calcium carbonate and calcium hydroxide. The influence of temperature and pH of the solution has been examined over the stability ranges for the ionic and non-ionic species of the compounds present in solution according to the constructed Eh-pH diagram of the system $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-$CaCO_3$-H_2O.

EXPERIMENTAL

Chemical Composition of Solution

The chemical composition of the solution formed after the autoclave treatment of pyrite concentrate is provided in Table 2. The complexometric method was used for determination of concentration of Fe_{total} and Cu^{2+} ions in mother liquor. The concentration of Fe(II) was

Table 2. Chemical composition of the solution obtained after autoclave pressure oxidation of pyrite concentrate.

Fe_{total}, g l^{-1}	H_2SO_4, g l^{-1}	Cu, g l^{-1}	Na, mg l^{-1}	K, mg l^{-1}	Mg, mg l^{-1}	Mn, mg l^{-1}	Ni, mg l^{-1}	Pb, mg l^{-1}	Al, mg l^{-1}	Ca, mg l^{-1}	Cr, mg l^{-1}	As, mg l^{-1}
60.3	61.5	1.47	100	100	<10	16.16	76.64	40.22	900	200	25.99	110.4

determined by the bichromate method and the concentration of Fe(III) ions was determined by the difference in concentrations between Fe_{total} and Fe(II) ions. For evaluation of the impurities content the AAA and ICP analyzes were used. This involves the use of PERKIN-ELMER 5000 and Jeledyne Leeman Lab devices.

The concentration of Fe^{3+} and Fe^{2+} ions in the solution are 58,96 g l^{-1} and 1,34 g l^{-1}, respectively, and the concentration of sulfuric acid is 60.3 g l^{-1}. The low concentration of other elements present in the solution allows the process to be described through the system $Fe_2(SO_4)_3$-$Fe(SO_4)$-H_2SO_4-$CaCO_3$-H_2O.

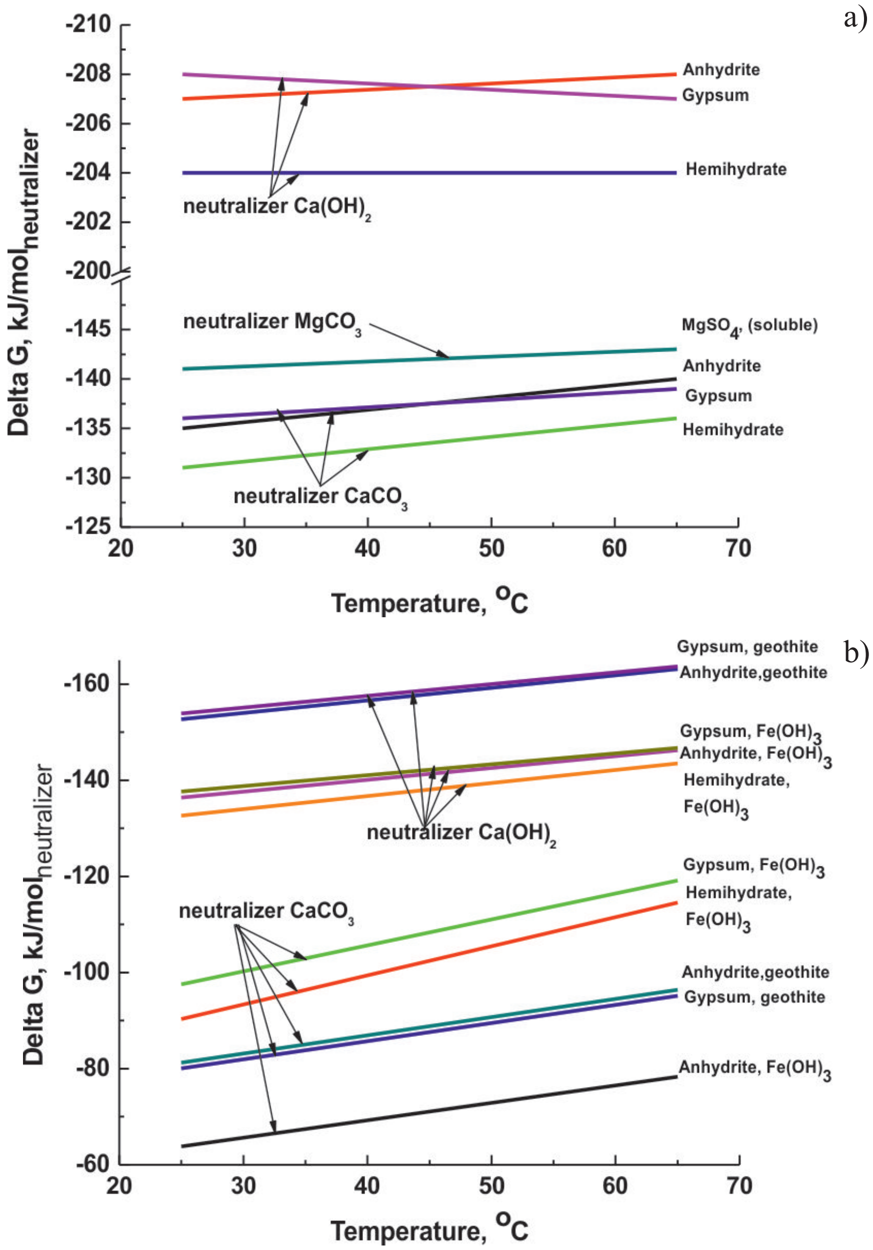

Fig. 1. Impact of temperature on the change of Gibbs function in the process of neutralization of sulfuric acid a) without and b) with the presence of Fe(III) ions in solution.

Table 3. Computed values of the Gibbs function and equilibrium constant of the possible chemical interaction during neutralization process.

Reaction	T = 25°C		T = 60°C	
	ΔG, kJ/mol	Log Kp	ΔG, kJ/mol	Log Kp
Reactions without participation of Fe^{3+} ions				
$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2(g)$	-135.13	23.676	-140.07	28.963
$CaCO_3 + H_2SO_4 + 0.5H_2O = CaSO_4*0.5H_2O + H_2O + CO_2(g)$	-131.59	23.043	-136.03	21.329
$CaCO_3 + H_2SO_4 + 2H_2O = CaSO_4*2H_2O + H_2O + CO_2(g)$	-136.342	23.888	-139.32	21.845
$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O$	-207.75	36.399	-208.02	32.618
$Ca(OH)_2 + H_2SO_4 + 0.5H_2O = CaSO_4*0.5H_2O + 2H_2O$	-204.14	35.767	-203.98	31.984
$Ca(OH)_2 + H_2SO_4 + 2H_2O = CaSO_4*2H_2O + 2H_2O$	-208.96	36.612	-207.27	32.500
$MgCO_3 + H_2SO_4 = MgSO_4(aq) + H_2O + CO_2(g)$	-141.63	24.815	-142.97	22.418
Reactions with participation of Fe^{3+} ions and neutralizer calcium carbonate				
$Fe(+3a) + 1.5SO_4(-2a) + 1.5CaCO_3 + 1.5H_2O = Fe(OH)_3 + 1.5CaSO_4 + 1.5CO_2(g)$	-63.80	16.592	-78.30	18
$Fe(+3a) + 1.5SO_4(-2a) + 1.5CaCO_3 + 2.25H_2O = Fe(OH)_3 + 1.5CaSO_4*0.5H_2O + 1.5CO_2(g)$	-90.28	15.819	-114.55	17.696
$Fe(+3a) + 1.5SO_4(-2a) + 1.5CaCO_3 + 4.5H_2O = Fe(OH)_3 + 1.5CaSO_4* 2.H_2O + 1.5CO_2(g)$	-97.52	17.087	-119.14	18.405
$2Fe(+3a) + 3SO_4(-2a) + 3CaCO_3 + H_2O = 2FeO*OH + 3CaSO_4 + 3CO_2(g)$	-80.05	41.602	-95.171	44.292
$Fe(+3a) + 1.5SO_4(-2a) + 1.5CaCO_3 + 3.5H_2O = FeO*OH + 1.5CaSO_4*2H_2O + 1.5CO_2(g)$	-81.27	21.358	-96.39	22.336
Reactions with participation of Fe^{3+} ions and neutralizer calcium hydroxide				
$Fe(+3a) + 1.5SO_4(-2a) + 1.5Ca(OH)_2 = Fe(OH)_3 + 1.5CaSO_4$	-136.43	35.678	-146.25	34.223
$1.3Fe(+3a) + 2SO_4(-2a) + 2Ca(OH)_2 + H_2O = 1.3Fe(OH)_3 + 2CaSO_4*0.5H_2O$	-132.66	46.488	-143.50	44.339
$Fe(+3a) + 1.5SO_4(-2a) + 1.5Ca(OH)_2 + 3H_2O = Fe(OH)_3 + 1.5CaSO_4*2H_2O$	-137.64	36.173	-146.72	33.998
$Fe(+3a) + 1.5SO_4(-2a) + 1.5Ca(OH)_2 = FeO*OH + 1.5CaSO_4 + H_2O$	-152.68	39.949	-163.12	38.190
$Fe(+3a) + 1.5SO_4(-2a) + 1.5Ca(OH)_2 + 2H_2O = FeO*OH + 1.5CaSO_4*2H_2O$	-153.89	40.444	-163.67	37.929

Analytical examination of the sulfuric acid neutralization process

The analytical examination of the neutralization process has been performed with the help of the software product HSC Chemistry ver.7.1, modules: Reaction Equations и Eh-pH diagrams.

RESULTS AND DISCUSSION

Computation of Gibbs function

Initially, on the basis of the literature survey the possible chemical reactions during the process of neutralization with calcium carbonate, calcium hydroxide and magnesium carbonate were determined with or without presence of ferric ions. The calculations have been performed at two temperatures - 25 and 60°C at atmospheric pressure. The temperature of 60°C corresponds to the temperature of product solutions after their release from the autoclave. The calculated values of the Gibbs function for one mole of neutralizing agent ($\Delta G, kJmol_{neutralizer}$) and the equilibrium constants ($LogKp$) are presented in Table 3.

The influence of temperature on the change of the Gibbs function during neutralization with and without

Table 4. Types of ionic and nonionic forms in the system $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-$CaCO_3$-H_2O and Gibbs energy of formation at T = 25 and T = 60°C.

Species	ΔG, kJ/mol		Species	ΔG, kJ/mol	
	T=25°C	T=60°C		T=25°C	T=60°C
Calcium			Iron		
Ca	0.000	0.000	Fe	0.000	0.000
CaO	-603.299	-599.588	$Fe(OH)_3$	-703.280	-688.714
$Ca(OH)_2$	-898.238	-887.958	$Fe(OH)_2$	-486.972	-477.593
Ca(+2a)	-552.807	-553.895	FeO*OH	-490.754	-482.243
CaOH(+a)	-716.824	-712.698	$FeSO_4$	-824.888	-482.432
$CaCO_3$(a)	-1321.625	-1308.412	$Fe_2(SO_4)_3$	-2265.455	-2227.726
$CaHCO_3$(+a)	-1797.120	-1770.635	$FeSO_4.7H_2O$	-2510.934	-2451.635
$CaSO_4$	-1436.585	-1420.112	$FeSO_4.H_2O$	-1079.787	-10606.821
$CaSO_4.2H_2O$	-1797.120	-1770.635	Fe(+3a)	-17.191	-13.286
$CaSO_4.0.5H_2O$	-1436.585	-1420.112	Fe(+2a)	-91.568	-91.352
Sulfur			$FeSO_4$(+a)	-772.970	-754.559
S	0.000	0.000	*$FeHSO_4$(+a)	-841.990	-841.988
H_2S(a)	-27.644	-26.589	*$FeHSO_4$(+2a)	-775.479	-763.814
HS(-a)	12.445	16.062	*$Fe(SO_4)_2$(-a)	-1524.599	-1506.667
H_2SO_4	-689.916	-675.411			
HSO_4(-a)	-755.673	-740.047			
SO_4(-2a)	-744.718	-724.630			

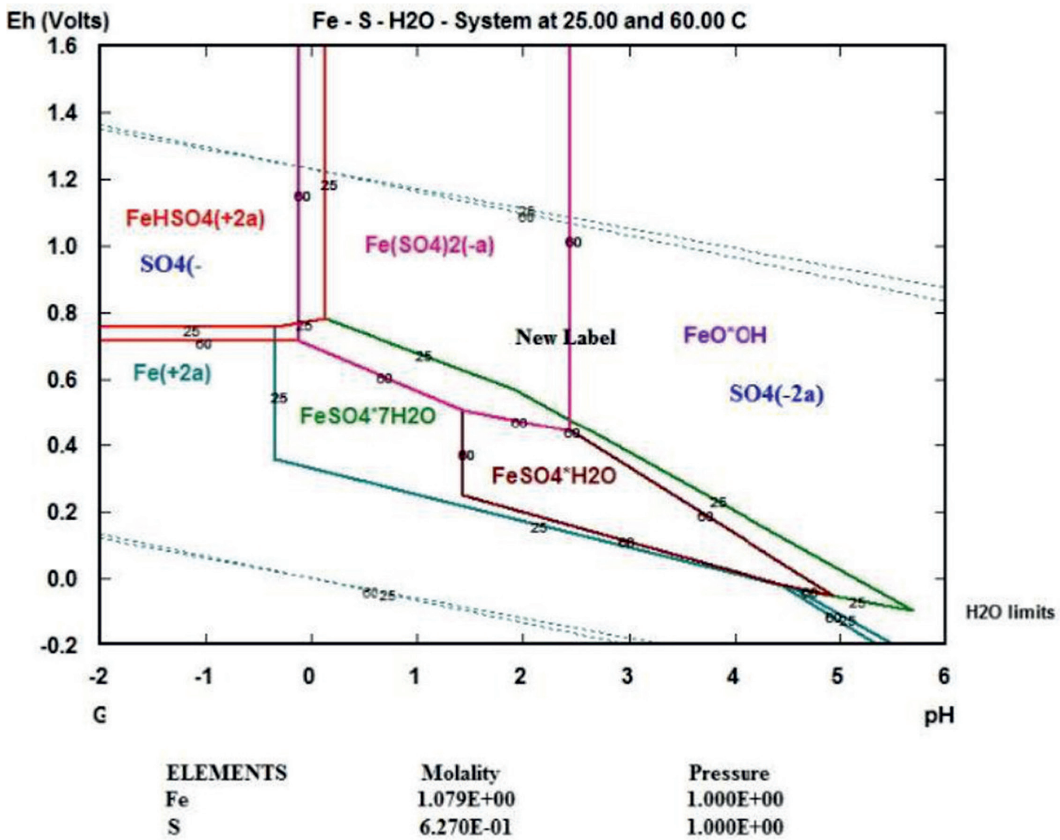

Fig. 2. Impact of temperature on the stability ranges of ionic and non-ionic forms of Fe(III) and Fe(II) in the system $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-H_2O.

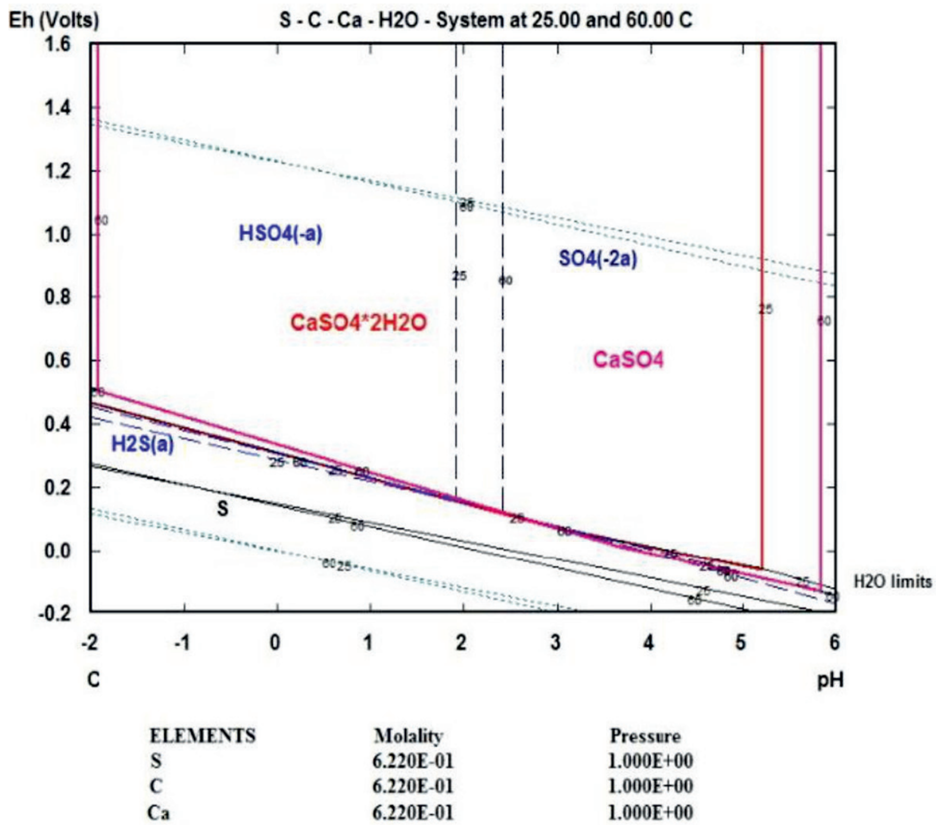

Fig. 3. Impact of temperature on the stability regions of ionic and non-ionic species of the substances in the system H_2SO_4-$CaCO_3$-H_2O.

the presence of ferric ions in solution is shown on Figs. 1a and 1b.

The analysis of the obtained results shows that, among the two reagents, it is more favored the neutralization to take place with hydrated lime. The thermodynamic likelihood for the process of neutralization when using $MgCO_3$ is a little higher than that of $CaCO_3$. The main difference between the two reagents is that neutralization by magnesium carbonate yields a soluble product $MgSO_4$ (at pH ~ 7).

It is evident also that the calculated values of ΔG and LogKp with neutralization reactions in the presence of ferric ions are approximately two times lower. When using $Ca(OH)_2$ it is most likely to form a precipitate of gypsum and goethite (or anhydrite and goethite) and it is least likely to form hemihydrate and $Fe(OH)_3$. When using calcium carbonate the biggest probability is to form gypsum and $Fe(OH)_3$ and the least probability is for precipitation of anhydrite and $Fe(OH)_3$. From here it can be concluded that in practice the two processes: neutralization and precipitation of ferric ions will take place simultaneously. With the increase of temperature the probability of co-precipitation of calcium sulfate and ferric precipitates is increasing.

Computation and building of Eh-pH diagrams

A module of the code HSC Chemistry – Eh-pH Diagrams was used to determine the stability ranges of ionic and nonionic forms of the substances in $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-$CaCO_3$-H_2O system. In the process of building of this diagram the molar composition of the productive solution was taken into consideration. The computations were carried out for molar concentrations of the basic elements present in the solution expressed as mol/kg_{H2O}: 1,079 Fe_{total}, 0.622 S, 0,622 Ca and 0,662 C. They correspond to the molar composition of solution obtained during oxidation of pyrite concentrate in autoclave (Table 1) and the quantity of $CaCO_3$ necessary for neutralization 100% of the sulfuric acid.

The analysis is carried out in temperature interval from 25 to 60°C and pH from -2 to 6 through progressively compilation of the simpler into more sophisticated

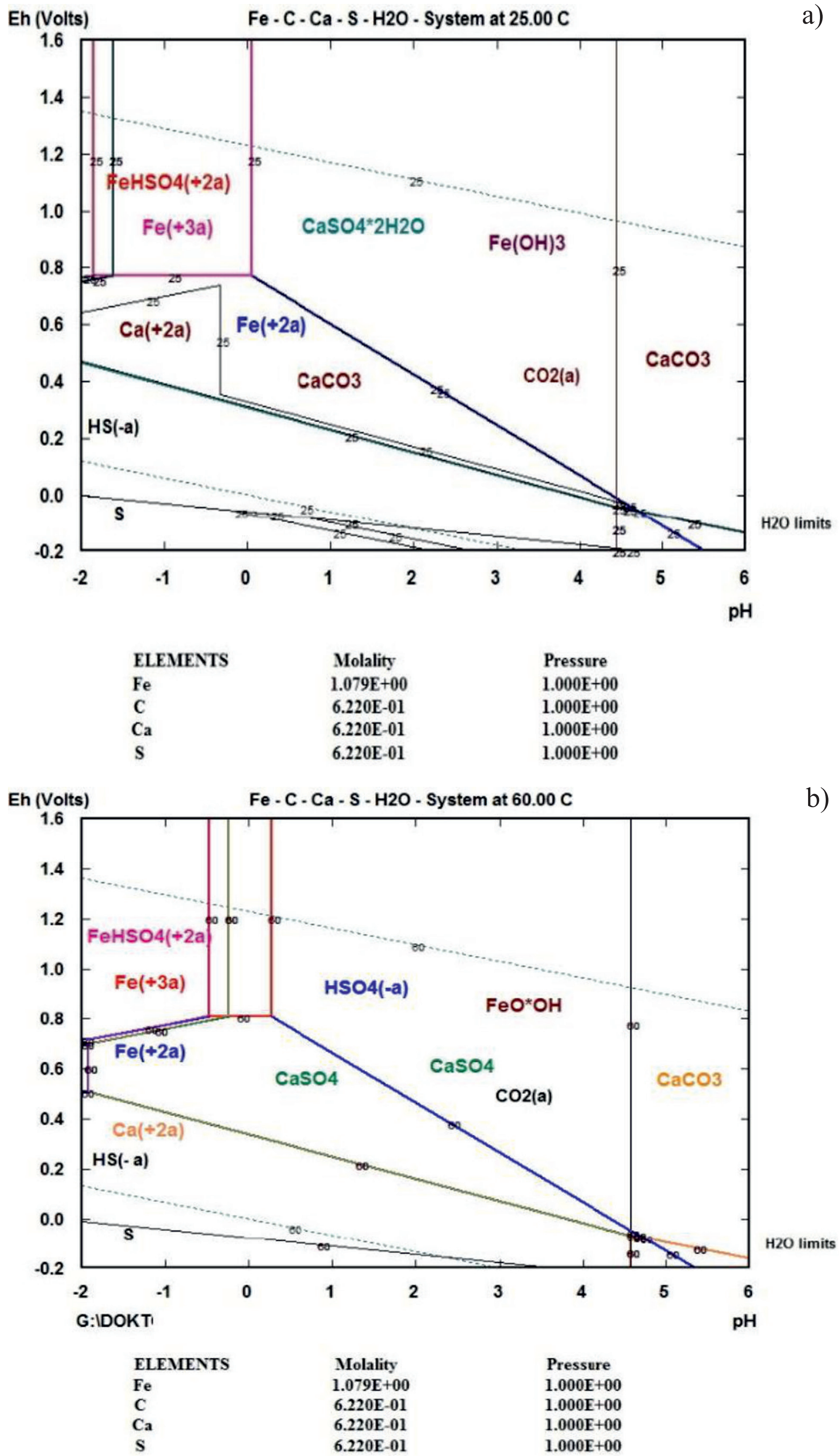

Fig. 4. Combined Eh-pH diagram of the system $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-$CaCO_3$-H_2O at temperatures of a) 25°C and b) 60°C.

diagrams: $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-H_2O, H_2SO_4-$CaCO_3$-H_2O, and $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-$CaCO_3$- H_2O.

The species of ionic and nonionic forms of the substances present in the solution and the Gibbs functions used in building of the respective diagrams for both studied temperatures are presented in Table 4.

Fig. 2 presents Eh-pH diagram of the $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-H_2O system at temperature 25°C and 60°C.

An analysis of the Eh-pH diagram of the system $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-H_2O shows that with high oxidation potential (Eh > 0.8 V) and high acidity (pH from -2 to 0.2) there is a complex ferric ion $FeHSO_4$(+2a) in the solution. The presence of this ion has been commented in [3]. With increase of temperature the stability region of this ion expands.

With the reduction of the redox potential and the acidity of the solution to pH ~ 2.5, $Fe(SO_4)_2$(-a) becomes a stable species in solution. In the range of pH from 2.5 to 6 and low temperature $Fe(OH)_3$ is present in the system whereas at temperature of 60°C the main species is goethite (FeO*OH).

With decrease of the redox potential and pH of the solution, the ions of Fe^{2+} and $FeSO_4*7H_2O$ under low temperature and $FeSO_4*H_2O$ under high temperature becomes stable.

The impact of temperature on the stability regions of the ionic and non-ionic species of the compounds in the system H_2SO_4-$CaCO_3$-H_2O (without the ions of iron) is shown on Fig. 3.

It is evident that at normal temperature in the pH range of -2 to ~ 5.3 $CaSO_4*2H_2O$ (gypsum) becomes the stable phase, while at higher temperature - 60°C, $CaSO_4$ (anhydrite) is the stable phase.

Combined Eh-pH diagrams of the system $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-$CaCO_3$-H_2O characterizing the process of neutralization of sulfuric acid with $CaCO_3$ in the presence of ferric and ferrous ions at temperatures of 25°C and 60°C are shown on Figs. 4a and 4b.

The analysis of the ionic and non-ionic species of the substances present in the solution shows that at temperature of 25°C and pH > 0.5 $CaSO_4*2H_2O$ (gypsum) and $Fe(OH)_3$ will precipitate whereas at 60°C $CaSO_4$ (anhydrite) and goethite (FeO*OH) will precipitate predominantly. In both systems at redox potential Eh > 0.8 V and pH in the range of -2 to 0.5 there are stability regions of Fe^{3+} ions and of the ferric complex $FeHSO_4$(+2a).

Contrary to ferric ions, ferrous ions are stable in the whole examined range of pH (from -2 to 6), and with the reduction of acidity (pH > 0.5) there is an abrupt narrowing of its stability region.

According to the analytical investigation it can be concluded that, in order to obtain gypsum or anhydrite of high purity out of solutions with high ferric iron concentrations, it is necessary the neutralization process to be conducted at pH ~ 0.5 in order to avoid the co-precipitation of iron compounds.

CONCLUSIONS

On the basis of the calculated values of the Gibbs function and the equilibrium constants a thermodynamic evaluation of the possible chemical reactions has been performed for the process of neutralization of sulfuric acid solutions with high concentration of ferric ions with $Ca(OH)_2$ and $CaCO_3$. It was determined that when using $Ca(OH)_2$ (hydrated lime) the highest probability is to obtain an precipitate of gypsum and goethite and the lowest probability is for the precipitation of hemihydrate and $Fe(OH)_3$. When calcium carbonate is used, the highest probability is for the formation of gypsum and $Fe(OH)_3$ and the lowest probability is for the precipitation of anhydrite and $Fe(OH)_3$. With increase of temperature from 25 to 60°C, the thermodynamic probability for formation of those precipitates increases.

The analysis of the regions of stability of ionic and non-ionic species in Eh-pH diagram for the system: $Fe_2(SO_4)_3$-$FeSO_4$-H_2SO_4-$CaCO_3$-H_2O, which describes the neutralization process of sulfuric acid solution with high concentration of ferrous and ferric ions and their complexes showed that at Eh > 0.8 V and high acidity of the solution, there is a region of stability of the ionic ferric complex $FeHSO_4^{2-}$ and of Fe^{3+} ions. Therefore, in order to produce gypsum with high purity, it is necessary the neutralization process of solutions with high concentration of ferric ions (~60 g l^{-1}) to be performed up to pH < 0.5 in order to avoid co-precipitation of iron precipitates: $Fe(OH)_3$ or FeO*OH.

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