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Analysis of the Autoclaval Leaching Opportunity of Pyrite Concentrates

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ABSTRACT: Physicochemical studies of the autoclave leaching process were carried out under various technological modes of opening pyrite concentrate in a hydrochemical medium. Assessed the completeness of their course according to the calculated values of the isobaric-isothermal potential at constant pressure, Gibbs energy (ΔGt0, kJ / mol) and the values of equilibrium constants (Kp). It has been shown that the final results of the process are influenced by various secondary reactions, one of the most important of which is the oxidation of elemental sulfur in a nitric acid medium to a sulfate form.

KEY WORDS: pyrite concentrate, autoclave, leaching, nitric acid, isobaric-isothermal potential, equilibrium constant.

I.INTRODUCTION

Copper production is one of the most important branches of non-ferrous metallurgy in Uzbekistan. The current problem of this industry is the completely inefficient processing of waste from this production, in particular, pyrite concentrate [1-7] emphasis only on sulfur as technogenic raw material. Meanwhile, industrial contents of noble metals, iron and some non-ferrous metals are known in its composition additionally to sulfur.

In this regard, there are known options for applied studies of hydrochemical methods for processing pyrite concentrates [8, 9] with complete extraction of iron and sulfur into a solution and concentration of noble metals in cake. Applied development [10] is also known for leaching this raw material with the extraction of elemental sulfur up to 44%. A comparative analysis of the results of these developments unequivocally indicates that leaching methods with the maximum conversion of sulfide sulfur to elemental form can be considered as optimal. Such transformation contributes to the disclosure of not only persistent forms of iron but also noble metals, it’s further extraction no longer presents technical difficulties. However, today there are no practical recommendations for the application of the method of such a transformation, which is due to the lack of relevant results of focused fundamental research. Therefore, the statement of problem in this study is to conduct physicochemical studies of the leaching process in various technological modes in order to obtain new information and knowledge of theoretical foundations. This knowledge has not only of scientific interest, but also of great practical importance, because it opens up the possibility of targeted control of a complex process, including chemical transformations, allowing to solvetheir optimization and intensification problems. We have not found such information regarding pyrite raw materials in the available literature.

II. OBJECTS AND METHODS OF RESEARCH

The pyrite concentrate is a product of the copper-molybdenum ores flotation at JSC «Almalyk MMC» of the Republic of Uzbekistan, the composition of the selected samples with the content of the main elements was: Fe 25.6%; S 26.7%; Au 4.55 g/t and Ag 12.3 g/t. The pyrite concentrates are classified as sulfide, acid and chemically resistant raw materials regarding the form of existence and gangue nature. According to the mineralogical composition, this raw material consists mainly of non-stoichiometric pyrite of the type: $(Fe_{0,98}\cdot Cu_{0,22}\cdot S_2)$, and $(Fe_{0,84}\cdot Ni_{0,13}\cdot Cu_{0,09}\cdot S_2)$, $(Fe_{0,09}\cdot Ni_{0,05}\cdot Cu_{0,02}\cdot S_{2,01})$, $[Fe_{0,09}\cdot (S,As)_{20}]$ and etc. [11].The noble metals have the composition of sulfides, including chalcopyrite impurities in the form of thin impregnations into this raw material.

III. RESULTS OF THE INVESTIGATIONS AND DISCUSSION

In this work, the economical expedient autoclave method is considered as suitable for implementing this leaching option among the many methods. It is known [12], the rate of leaching of mineral raw materials at ordinary temperatures and pressures is relatively small, and it increases significantly with increasing these factors. It is also known that aqueous solutions cannot be heated above 100^0C: boil, lose heat as a result of vaporization and, as a result, the mechanism of the chemical process is violated. For this reason, in order to solve the problem of the selected leaching option, the process is recommended to be carried out in thick-walled sealed metal vessels - autoclaves, which are also allow increasing the gases pressure, which increases the boiling point of water and aqueous solutions. The latter has a beneficial effect on the thermodynamic characteristics and chemical kinetics of the leaching process - the fundamental principles of the chemical process study, its laws, and the mechanism of occurrence depending on time and temperature. The nitric acid, the most common in the hydrochemistry of sulfide raw materials [13] was chosen as the leaching chemical reagent which leads to the following chemical reactions when interacting with metal sulfides (Table 1).

Table 1. Chemical reactions of nitric acid with metal sulfides

$2\ FeS_2 + 8HNO_3 = Fe_2(SO_4)_3 + NO_2\uparrow + 6NO\uparrow + S^0\downarrow + 4\ H_2O$	(1)
$2\ FeS_2 + 4HNO_3 + 3\ O_2 = Fe_2(SO_4)_3 + 2NO_2\uparrow + S^0\downarrow + 2\ H_2O$	(2)
$FeS_2 + 6HNO_3 = Fe(NO_3)_3 + 3NO_2\uparrow + 2S^0\downarrow + 3\ H_2O$	(3)
$FeS_2 + 3HNO_3 + 0{,}75\ O_2 = Fe(NO_3)_3 + 2\ S^0\downarrow + 1{,}5\ H_2O$	(4)
$2\ FeS_2 + 2\ HNO_3 = Fe_2O_3 + 4\ S^0\downarrow + 2\ NO\uparrow + H_2O$	(5)
$2\ FeS_2 + HNO_3 + 1{,}25\ O_2 = Fe_2O_3 + 4\ S^0\downarrow + NO_2\uparrow + 0{,}5\ H_2O$	(6)
$6FeS_2 + HNO_3 + 9H_2O + 10\ O_2 = 3Fe_2O_3\cdot 4SO_3\cdot 9H_2O\downarrow + HNO_2$	(7)
$2Fe_{0,98}\cdot Cu_{0,22}\cdot S_{2,0} + 8\ HNO_3 + 0{,}76\ O_2 = Fe_{1,96}(SO_4)_{2,94} + Cu_{0,44}(SO_4)_{0,44} + 0{,}62S^0 + 8NO + 4H_2O$	(8)
$2Fe_{0,84}\cdot Ni_{0,13}\cdot Cu_{0,09}\cdot S_{2,0} + 8HNO_3 + 0{,}16O_2 = Fe_{1,68}(SO_4)_{2,52} + Cu_{0,18}(SO_4)_{0,18} + Ni_{0,26}(SO_4)_{0,26} + 1{,}04S^0 + 8NO\uparrow + 4H_2O$	(9)
$2Fe_{0,09}\cdot Ni_{0,05}\cdot Cu_{0,02}\cdot S_{2,01} + HNO_3 + 0{,}14O_2 = Fe_{0,18}(SO_4)_{0,27} + Cu_{0,04}(SO_4)_{0,04} + Ni_{0,10}(SO_4)_{0,10} + 3{,}61S^0 + NO\uparrow + 0{,}5\ H_2O$	(10)
$6CuFeS_2 + 22HNO_3 = 6Cu(NO_3)_2 + 3Fe_2O_3 + 12S^0\downarrow + 10NO\uparrow + 11H_2O$	(11)
$2CuFeS_2 + 6HNO_3 + 2O_2 = 2Cu(NO_3)_2 + Fe_2O_3 + 4S^0\downarrow + 2NO_2\uparrow + 3H_2O$	(12)
$6CuFeS_2 + 18HNO_3 + 16{,}5O_2 = 6Cu(NO_3)_2 + 3Fe_2O_3\cdot 4SO_3\cdot 9H_2O\downarrow + 8S^0\downarrow + 6NO_2\uparrow +$	(13)
$S^0 + 2HNO_3 = H_2SO_4 + 2NO\uparrow$	(14)
$2FeS_2 + 4HNO_3 + H_2SO_4 + 0{,}5\ O_2 = Fe_2(SO_4)_3 + 4NO\uparrow + 2S^0\downarrow + 3H_2O$	(15)
$FeS_2 + H_2SO_4 + 0{,}5\ O_2 = FeSO_4 + 2S^0\downarrow + H_2O$	(16)
$2FeSO_4 + 2HNO_3 + H_2SO_4 = Fe_2(SO_4)_3 + 2NO_2\uparrow + 2H_2O$	(17)
$6Fe^{3+} + 4SO_4^{2-} + 14H_2O = 3Fe_2O_3\cdot 4SO_3\cdot 9H_2O\downarrow + 10H^+$	(18)
$Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2SO_4$	(19)
$Fe_2(SO_4)_3 + 6H_2O = 2\ Fe(OH)_3 + 3H_2SO_4$	(20)
$CuSO_4 + S^0 + H_2O = CuS\downarrow + H_2SO_4 + 0{,}5\ O_2\uparrow$	(21)
$CuS + 4HNO_3 = Cu(NO_3)_2 + S^0\downarrow + 2NO_2\uparrow + 2H_2O$	(22)
$6CuFeS_2 + 18HNO_3 + 16{,}5O_2 = 6Cu(NO_3)_2 + 3Fe_2O_3\cdot 4SO_3\cdot 9H_2O\downarrow + 8S^0\downarrow + 6NO_2\uparrow + 9H_2O$	(23)
$2NO + O_2 = 2NO_2\uparrow$	(24)
$4NO + O_2 + 2H_2O = 4HNO_2$	(25)
$2NO + 0{,}5\ O_2 + H_2O = 2HNO_2$	(26)
$2NO_2 + H_2O = HNO_2 + HNO_3$	(27)
$3HNO_2 = HNO_3 + 2NO\uparrow + H_2O$	(28)
$2NO + 4H^+ = N_2\uparrow + 2H_2O$	(29)

It can be seen, the studied chemistry of the process is not simple: the final results of the process (reactions 1-13) are affected by various secondary reactions (reactions 14-23), one of the most important is the oxidation of elemental sulfur in a nitric acid medium to a sulfate form. These forms cause a chain of secondary processes with the formation of both water-soluble sulfates of non-ferrous metals (copper, nickel, etc.) and iron, as well as, deposits of copper sulfide, ferrous jarosite, oxides and hydroxides, etc.

In reactions with and without oxygen, the fact of a significant decrease in the consumption of acid in the presence of oxygen (reactions 1-6) draws attention. In addition, in the presence of oxygen, lower nitrogen oxides are oxidized to higher oxidation states, followed by acid regeneration (reactions 24-29). The facts of the ease of oxidation of nitric oxide to dioxide (reaction 24) in an oxygen medium and the subsequent disproportionation reaction (27) accompanied by the formation of the unstable in aqueous solutions nitrous acid(reaction 28), which are confirmed by the corresponding thermodynamic calculations (Table 1).)

The study of the theoretical foundations of the hydrochemical opening of pyrite concentrate was carried out by studying the physicochemical laws of the chemical process, both in time and depending on the temperature regime of the process. As it is known from the theory of metallurgical processes, the thermodynamic studies are carried out to determine the equilibrium conditions of chemical reactions in the studied system depending on temperature, and kinetic ones are performed depending on time due to study of the calculated chemical reactions rates, and the mechanism of the leaching process is clarified.

In order to thermodynamic evaluation of the pyrite concentrate opening process in a hydrochemical medium via above-mentioned chemical reactions direction and it's completeness, the calculations were performed:
1) the values of the isobaric-isothermal potential - free energy at constant pressure, Gibbs energy (ΔG_s^0, kJ / mol), and
2) the values of the equilibrium constants (Kp) at condition when the rates of the direct and reverse reactions are equal.

The calculations were carried out for several temperatures: 298, 383 and 433K (25.110 and 160^{0}C), the temperature choice was due to technological considerations and the specific features of elemental sulfur, which melts at 385-388K (112-115^{0}C) with abnormally low viscosity at 428-433K (155-160^{0}C) [14.15, p. 320]. The calculations used reference data on the thermodynamic quantities ΔG^0_{298} and entropy (ΔS^0_{298}, J / mol · K) [16-18]. The calculation results are given in table 2. The calculations were carried out according formulas:
1) $\Delta G_s^0 = \Delta G^0_{298} - \Delta T \cdot \Delta S^0_{298} + \Delta T \cdot \Delta C_p^0]_{298}^{T} - T \cdot \Delta C_p^0]_{298}^{T} \cdot \ln(T/298)$ [20], the formula was used with the assumption $C_p^0 = 0$;
2) for reactions with evolution of the gas phase, the formula [21] was used: $\log Kp = -52.236 \cdot \Delta G_s^0 / T - 0.99431 \cdot \Delta n$;
3) for reactions without gas phase evolution $\lg Kp = -\Delta G_s^0/(2,3RT)$ (32) [17], where $R = 8.31$ J / mol · K; $\Delta T = 298 - T$; Kp is the equilibrium constant; Δn– increment of the number of moles of gaseous products.

Table 2. The calculated values of the isobaric-isothermal potential and the values of the equilibrium constants (K_p) at various temperatures.

No reaction	Δn	298K		383K		433K	
		$-\Delta G^0_{298}$	$\lg K_p$	$-\Delta G^0_{298}$	$\lg K_p$	$-\Delta G^0_{298}$	$\lg K_p$
1	6	319.83	54.0	315.75	41.0	313.43	35.75
2	2	62.2	10.25	55.63	7.0	51.73	5.73
3	3	347.1	59.0	337.5	44.0	331.6	38.0
4	0	-113.46	-19.92	-96.63	-13.2	-86.73	-10.48
5	2	59.5	10.0	56.2	7.25	54.13	6.03
6	1	93.98	15.50	88.28	11.17	84.88	9.33
7	0	-275.36	-49.26	-273.95	-38.36	-273.12	-33.94
8	8	181.1	30.0	163.7	18.5	144.6	13.5
9	8	-147.65	-27.75	-160.23	-19.75	-167.65	-18.25
10	1	113.98	25.50	99.28	9.17	94.88	6.33
11	10	96.92	16.08	91.71	11.75	90.21	10.0
12	2	92.2	14.25	75.63	9.0	61.73	6.73
13	6	311.53	53.4	309.77	40.5	311.43	33.75
14	2	344.1	56.0	331.5	41.0	327.6	33.07
15	4	111.53	33.4	109.77	30.5	110.43	29.75

16	0	99.97	17.08	93.71	13.75	91.21	9.0
17	2	98.2	16.25	77.63	11.0	64.73	8.73
18	0	-24.6	-4.3	-39.9	-5.4	-48.9	-5.9
19	0	8.23	1.44	-32.27	-4.3	-54.67	-6.6
20	0	10.23	3.64	-22.27	-6.3	-24.67	-8.6
21	1	103.90	22.50	92.28	8.17	91.88	5.33
22	2	64.2	11.25	56.63	8.0	50.73	6.73
27	0	31.7	5.56	-	-	-	-
28	2	75.9*	15.4	-	-	-	-

The values of ΔG_s^0 and logKp are assigned to a sulfur atom in the mineral *[19]. The results show that pyrite is fully opened at 298K. The hydrolysis of iron salts is not excluded (reactions 19, 20) at elevated temperatures in presence of a sufficiently high content of sulfate ion in the solution, and iron can precipitate in the form of jarosite, which is a source of sulfur loss, but it allows easy filtering of precipitation. It can also be seen from Table 2 that the dissolution of iron oxides in an acidic medium at room t = 298 K is practically impossible (reaction (19) Kp = 10-1.44).

This process really becomes possible (Kp = 10-4.3-6.6). With increasing temperature to 383-433K.Moreover, iron hydroxide (reaction 20) is able to dissolve in an acidic medium (Cr = 10-3.64) even at 298K. Thus, calculations of Gibbs energy and chemical equilibrium constants of possible chemical reactions between nitric acid and sulfides of iron, copper, etc., show a rather high probability of their occurrence with the formation of elemental sulfur, hematite and water-soluble compounds of non-ferrous metals (copper, nickel, etc.).

The important role of chemical reactions reflecting the behavior of nitrogen oxides by reactions (24-29), especially with their conversion to nitric acid, is obvious in the studied process mechanism. This mechanism in assessing the applied value of the process has particular importance from both an economic and environmental point of view. The dependence of the components behavior in the gas phase is known mainly on pressure and temperature. In this regard, the partial pressures (p_i) and molar composition (C_i) of nitrous gases were calculated at autoclave pressures of 2, 3 and 4 MPa and temperatures of 380 and 433K (107 and 160^0C). The choice of such temperatures is specific, as shown above, due to the features of elemental sulfur. The calculations were carried out according to the known method [22]. The calculation results are given in table. 3, showing the proportion of nitric oxide in the mixture decreases, while the polymerized forms increase with increase in the total pressure of the vapor-gas mixture under isothermal conditions. This indicates the fact that when the hydrometallurgical process is carried out under optimal technological conditions, increased pressures contribute to a greater degree of oxidation of lower nitrogen oxides to higher ones, which creates favorable conditions for acid regeneration during autoclave leaching.

Table 3. Partial pressures (p_i) and molar composition (C_i) of nitrous gases depending on temperature (T, K) and pressure (P, MPa) in the presence of oxygen and HNO_3 concentration of 25 wt.%.

P, MPa	T, K	p_i				C_i			
		NO	NO_2	N_2O_4	N_2O_3	NO	NO_2	N_2O_4	N_2O_3
2,0	380	17,23	177,11	2,11	8,44	0,73	8,66	0,10	0,31
	433	18,67	179,11	2,01	8,07	0,81	8,67	0,08	0,37
3,0	380	19,14	288,12	3,23	15,63	0,48	8,74	0,10	0,45
	433	20,25	289,22	3,12	14,55	0,54	8,75	0,09	0,39
4,0	380	22,10	376,63	6,11	31,22	0,04	8,61	0,16	0,74
	433	21,07	377,40	4,81	22,11	0,43	8,62	0,10	0,41

From Table 3, it is also seen that an increase in the temperature of the hydrochemical system in the autoclave under isobaric conditions (at constant gas pressure) is unfavorable: the degree of polymerization of lower nitrogen oxides to higher ones decreases. This confirms the positive effect of lower temperatures on the oxidation state of NO in NO_2, and creates favorable conditions for acid regeneration along with increased pressures. Thus, the process should be carried out with oxygen supply at the lowest possible operating temperatures and high pressures to ensure the regeneration of nitric acid during the leaching of pyrite concentrate in order to reduce its consumption.

IV. CONCLUSION

The research results make it possible to correctly select the optimal conditions for the leaching of pyrite concentrates, to reveal its capabilities and, on the basis of the obtained data, to recommend an effective processing option with the requirements for high recovery of the elemental sulfur and the hematite form of iron.

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