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A STUDY OF THE PARTIAL NEUTRALIZATION PROCESS OF SOLUTIONS OBTAINED DURING AUTOCLAVE DISSOLUTION OF PYRITE CONCENTRATE

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ABSTRACT

The process of the partial neutralization of solutions with high concentration of ferric ions and acidity (> 60g l^{-1} Fe^{3+} and H_2SO_4), obtained during autoclave dissolution of pyrite concentrate, has been studied. Two types of neutralizers have been used: limestone from deposit ore "Velikan" and a waste from cutting of marble plates - a fine and a coarse fraction.

It was found that for the neutralization process limestone and the fine fraction from marble's waste can be used successfully. Both reactants are with a high content of calcium carbonate (> 92 %). The use of the coarse fraction of marble was inappropriate, due to the high content of magnesium carbonate (33.51 %) and the low extraction of gypsum (~ 49 %).

The optimal parameters of neutralization process have been established: pH from 0.9 to 1.1, temperature 323K and time of neutralization 60 min. Gypsum, obtained under these conditions, has a high purity (< 0.05 % Fe, < 0.002 % Cu) and a high chemical activity. This makes it a suitable reactant for the conversion to ammonium sulfate, a commercial product that can be used as an artificial fertilizer.

Keywords: neutralization, limestone, waste's marble, Fe(III), sulfuric acid, gypsum, pyrite concentrate.

INTRODUCTION

It is well known that the high-pressure, high-temperature oxidative dissolution of pyrite concentrates or other sulfide minerals, results in solutions of high acidity and high concentration of ferric ions [1 - 4].

On an industrial scale, the process of neutralization of this type of solutions is usually accomplished with hydroxides or alkaline compounds. Depending of the nature of the neutralization agents used, they could be added as solids, solutions, suspensions or, as in the case of non-hydrate ammonia - as liquid or vapor.

According to Clifford, J. Lewis and Robert S. Boyton [5], the following bulk products are mostly used for neutralization: caustic soda (NaOH), soda ash (Na_2CO_3), high purity limestone ($CaCO_3$), dolomite limestone ($CaCO_3.MgCO_3$), quicklime (CaO), hydrated lime ($Ca(OH)_2$), dolomite (CaO.MgO) and ammonia (NH_3).

Limestone is the neutralizing agent most commonly used in practice due to its low cost. In addition to neutralization of the acid, it can be used for iron precipitation [6]:

$CaCO_3(s)+H_2SO_4(aq)\leftrightarrow CaSO_4(s)+H_2O+CO_2(g)$

$CaCO_3(s)+Fe_2(SO_4)_3(aq)+3H_2O\leftrightarrow 3CaSO_4(s)+$
$+2Fe(OH)_3(s)\ +3CO_2(g)$

According to the same authors the CO_2, released under the above reactions, acts a bufer and determines the upper pH limit (maximum pH of ~ 6.5), which reflects on the kinetics and the quantity of the used limestone. The pH of the solution should be constantly controlled in order to maintain optimal conditions for formation of Fe(III)-precipitate.

In practice, depending on the conditions of neutralization, calcium sulfate can precipitate as gypsum ($CaSO_4.2H_2O$), hemihydrate ($CaSO_4.H_2O$) or oranhydrite ($CaSO_4$) [4]. According to the same author, the temperature and the solubility of the above species have fundamental roles in calcium sulfate precipitation in the temperature range between 315 and 370K.

F. Bardand and E. Bilalhave held pilot plant tests

Table 1. Chemical composition of the synthetic solution.

Fe_{total}, g l^{-1}	Fe^{2+}, g l^{-1}	Fe^{3+}, g l^{-1}	Cu, g l^{-1}	H_2SO_4, g l^{-1}
59.56	1.06	58.50	1.25	58.7

with limestone from the Urgonien deposit (a limestone of very high purity) and with limestone from the Corbières deposit, characterised by high magnesium content [5]. They have investigated the physical and chemical aspects of gypsum precipitation with a limestone suspension, injected into waste streams with concentrations from 15 to 30 g l^{-1} H_2SO_4, at pH = 8 and temperature range from 298 to 363 K.The authors have found that the presence of magnesium leads to reduction of the crystal size and corresponding prolongation of the process of precipitation.

On the basis of the literature research above, we conclude that the high ferric ion concentration in the solution will adversely impact the quality of the gypsum product. The utilization of such gypsum is limited and in most cases it will have to be deposited in waste facilities, which could lead to environmental protection issues.

The aims of this research paper are: to precipitate gypsum with minimum content of iron and other impurities, and determine the optimal conditions for the process of partial neutralization of acidic solutions with high concentration of ferric ions.

EXPERIMENTAL

Feed solutions and research methodology

All experiments have been conducted either with a synthetic solution or with a pilot plant solution, obtained after high-pressure and high-temperature oxidation of pyrite concentrate in an autoclave.

The chemical composition of the synthetic solution is presented in Table 1. It has been prepared with pure laboratory reagents: ferric sulfate - $Fe_2(SO_4)_3.7H_2O$, ferrous sulfate- $FeSO_4.7H_2O$, copper sulfate - $CuSO_4.2H_2O$, concentrated sulfuric acid and demineralized water and has a composition very close to the pilot plant product.

The chemical composition of the solution obtained after autoclave dissolution of pyrite concentrate is presented in Table 2. A characteristic feature of the solution is the high concentration of ferric ions (58.54 g l^{-1}) and sulfuric acid (60.2 g l^{-1}).

The following materials have been used as neutralization reagents: pure analytical calcium carbonate, limestone from the Bulgarian Velikan deposit and two particle size fractions of a limestone waste from cutting of marble plates: a fine fraction (FF) and a coarse fraction (CF).

The chemical compositions of the reagents used are presented in Table 3. The mineralogical assays of representative samples of limestone and the two fractions of marble waste were analyzed in the Central Scientific Laboratory of the University of Chemical Technology and Metallurgy, Sofia.

It is evident that the Velikan limestone is with a high $CaCO_3$content (above 92 %), which is indicative of a very high grade. The grade of $CaCO_3$ in the fine fraction of marble waste is also very high (~ 94 %). Unlike the fine fraction, the coarse fraction contains ~ 67 % $CaCO_3$ and > 33 % $MgCO_3$.

Particle size analysis has been performed of both limestone samples and of the two fractions of marble waste. Mastersizer 2000, Malvern Instruments has been

Table 2. Solution composition after autoclave dissolution of pyrite concentrate.

$Fe_{\text{общо}}$ g l^{-1}	Cu g l^{-1}	Na mg l^{-1}	K mg l^{-1}	Mg mg l^{-1}	Mn mg l^{-1}	Mo mg l^{-1}	Ni mg l^{-1}	Pb mg l^{-1}
59.94	1.47	100	100	<10	16.16	25.4	76.64	40.22
Sb mg l^{-1}	Sn mg l^{-1}	P mg l^{-1}	Al mg l^{-1}	Ba mg l^{-1}	Be mg l^{-1}	Bi mg l^{-1}	Ca mg l^{-1}	Cd mg l^{-1}
<10	64.41	<10	900	<5	<0.5	18.88	200	<1
Co mg l^{-1}	Cr mg l^{-1}	As mg l^{-1}	La mg l^{-1}	Sc mg l^{-1}	H_2SO_4 g l^{-1}			
8.75	25.99	110.4	0.60	<0.5	60.2			

Table 3. Composition of the neutralization reagents used, % w/w.

Reagent	CaO ($CaCO_3$)	MgO ($MgCO_3$)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2
$CaCO_3$, pure analytical	56.08 (100.0)	-	-	-	-	-
Limestone “Velikan“	51.80 (92.56)	0.40	3.53	1.13	0.46	0.87
Marble waste, FF	52.75 (94.15)	1.70	0.81	0.06	0.01	1.08
Marble waste, CF	36.30 (67.79)	16.02 (33.51)	0.27	0.04	0.08	1.10

Table 4. Portion of particles in the separate factions of the three reagent types.

Reagent	Proportion in the fraction, %						
	<10 µm	-20+10 µm	-30+20 µm	-40+30 µm	-50+40 µm	-70+50 µm	-100+70 µm
Limestone (sample 1)	15.2	10.4	7.4	3.7	5.6	5.7	52
Limestone (sample 2)	17.3	11.5	8.0	4.0	5.8	5.3	48.1
Marble waste CF	3.2	3.7	3.7	2.3	4.0	4.9	78.2
Marble waste FF	49.6	37.6	11.0	1.6	0.2	-	-

used for the analysis. The particle size distribution of the reagents, calculated on the basis of the analysis performed is presented in Table 4.

In the samples of limestone more than 50 % of the particles are with a size of -100+70 µm and ~ 25 - 28 % are with a size of less than 20 µm. In the coarse faction of marble waste, more than 78% of the particles are with a size -100+70 µm, whereas marble waste, fine faction is characterized with a substantial share (~ 87.2 %) of fine particles with a size below 20 µm. Taking into account the high content of $CaCO_3$ in this waste product (> 94 %), it can be expected that it will be very suitable as a reagent in the process of neutralization.

The tests were conducted with 100 ml solutions in glassware, with a magnetic agitator and a heating plate. The test solutions are characterized with high concentration of ferric ions, in order to avoid co-precipitation of Fe(III). The tests have been performed with a shortfall of the reagent, respectively 70, 80 and 90 % of the stoichiometric quantity. The necessary quantity of reagent was calculated as per the reaction:

$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4.2H_2O + CO_2$

The reagent was added as a 20 % suspension in water, gradually and with intensive agitation.

The extent of neutralization α is determined as a ratio of the mass of sulfate sulfur in the precipitate to the theoretically, calculated per the neutralization reaction.

$$\alpha = \frac{m_{.sludge}(S_{SO_4})_{sludge}}{m_{theor.}.(S_{SO_4})_{teor.}}.100,\%$$

where: m_{sludge} and $m_{theor.}$ are, respectively, the mass of the precipitate after the test and the mass of the theoretically calculated quantity of gypsum, according to the predetermined extent of neutralization;

The quantity of sulfate sulfur in the precipitate was determined by the mass method with a 20 % solution of $BaCl_2$. Buchner funnel and a vacuum pump were used to separate the precipitate product from the solution. The precipitate was washed with a solution of and sulfuric acid in water with a ratio of 1:10, then it was dried and weighed on an analytical balance.

The complexometric method was used for determination of the concentration of Fe_{total} and Cu^{2+} ions in

Table 5. Conditions and results of neutralization with pure $CaCO_3$.

No	Conditions			Products					
	T, K	Neutralized acid, %	Reagent g	Sludge (Gypsum)			Filtrate		
				Mass, g	Fe %	Cu %	V ml	Fe^{3+} g l^{-1}	Fe^{2+} g l^{-1}
1	293	80	4.82	8.36	0.09	0.028	102	55.73	0.65
2		90	5.42	8.97	0.81	0.032	100	54.72	0.56
3	323	70	4.30	7.54	0.03	0.019	95	55.32	0.69
4		80	4.82	8.53	0.09	0.027	96	56.13	0.54
5	343	80	4.82	8.82	0.10	0.031	92	57.62	0.60
7		90	5.42	9.27	1.01	0.038	88	57.11	0.57

the filtrate. The concentration of Fe(II) was determined by the bichromate method and the concentration of Fe(III) ions was determined by the difference in the concentrations of $Fe_{total}$and Fe(II) ions. For evaluation of the impurity content, AAA and ICP analyzes were performed with PERKIN-ELMER 5000 and Jeledyne Leeman Lab devices. The concentration of free sulfuric acid was determined by titration with 0.1N NaOH, solution, in the presence of an indicator methyl orange, with the pH-Meter HI223 of Hanna Instruments.

RESULTS AND DISCUSSION

Partial neutralization with pure calcium carbonate

Initially, in order to determine the extent of neutralization of the acid and the purity of the precipitates, the tests were conducted with a solution, obtained after autoclave dissolution of pyrite concentrate, and pure calcium carbonate as the neutralizer. The tests were done at 3 temperatures: 293, 323 and 343 K, with 70, 80 и 90 % shortfall of the reagent versus the stoichiometric quantity. The time for neutralization was 30 minutes. In all tests the precipitate was washed twice on the filter with a water – sulfuric acid solution 1:1. The conditions of the tests and the obtained results are presented in Table 5 and Fig.1.

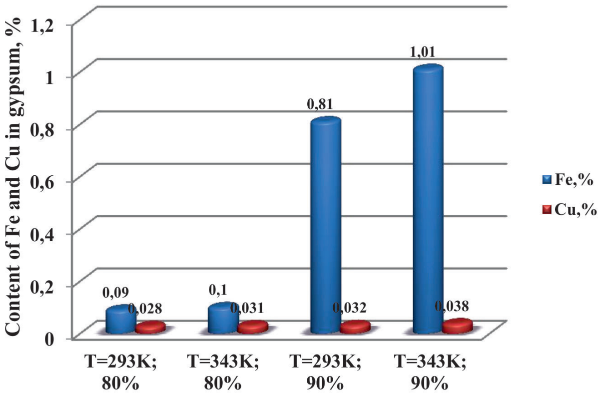

Fig. 1. Effect of the extent of neutralization on the content of impurities in the resulting gypsum.

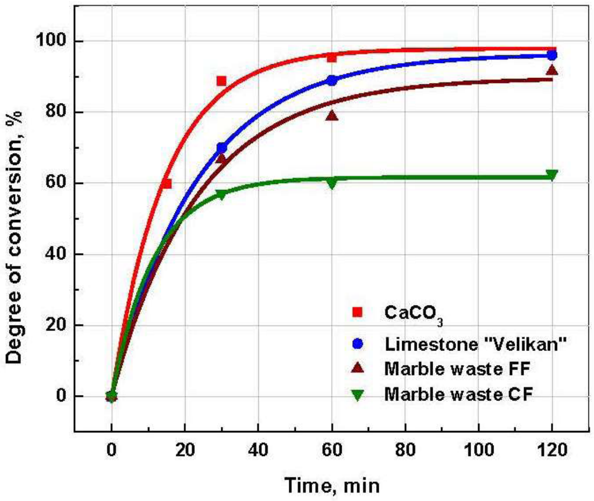

Fig. 2. Influence of the time of neutralization on the extent of conversion of calcium carbonate into gypsum upon using different types of reagents.

It can be seen that the increase in the extent of neutralization above 80 % leads to the higher contamination with iron precipitates of approximately one order of magnitude. The impact of temperature on the content of impurities is negligible. On the other hand, temperature impacts the type of the product. According to W. Stumm [7], at temperatures of ~315 K or a slightly higher, the most stable species is gypsum. At lower temperatures

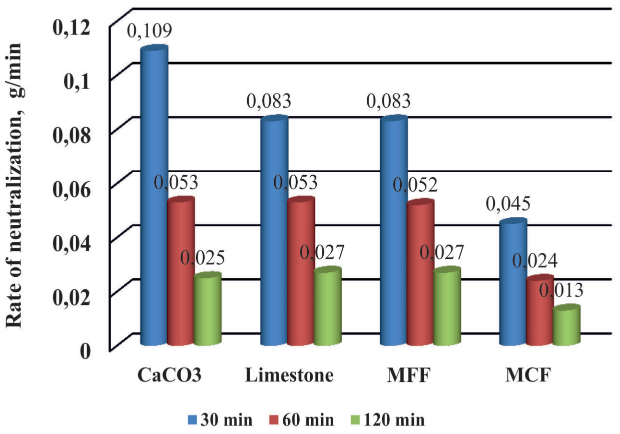

Fig. 3. Rate of neutralization with the use of various reagents.

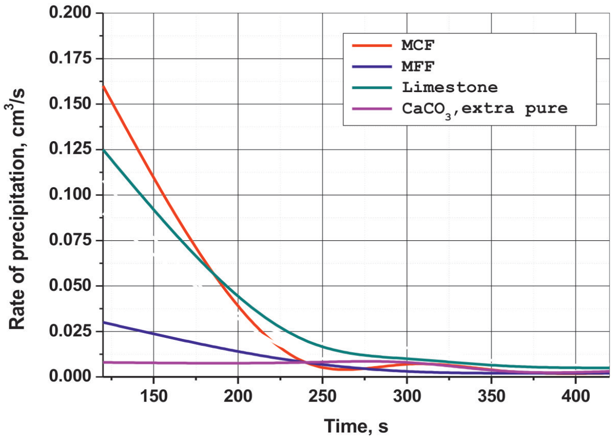

Fig. 4. Influence of the reagent used on the rate of precipitation.

hemihydrate is formed, while at higher temperatures, anhydrite is obtained. Therefore, all further investigations have been performed with an extent of neutralization of 70 % and a temperature of 323 K.

Partial neutralization with limestone and waste from marble cutting

The influence of the type of reagent and the duration of neutralization on the conversion of calcium carbonate into gypsum, has been studied with a 70 % extent of neutralization and temperature of 323 K. The conditions of the neutralization and the obtained results with the 3 reagent types and pure $CaCO_3$ are presented in Table 6 and on Fig. 2.

The analysis of the relationships shows that significant differences in the behavior of limestone and marble cutting waste are observed during the first 30 minutes. The highest conversion rate is achieved with pure calcium carbonate and the lowest conversion rate – by the marble waste, coarse fraction.

The rates of sulfuric acid neutralization using various reagents are presented in a graphical form on Fig. 3. They are expressed as quantity of neutralized acid per unit of time. The neutralization rates using limestone and marble waste, fine fraction (MFF) are almost identical. Contrary to them, the neutralization rate with coarse marble waste (MCF) is twice slower.This can be explained by the significantly lower content of calcium carbonate (~ 64

Table 6. Conditions and results of neutralization with different types of reagents.

No	Reagent (mass, g)	Time, min	Sludge,		V, ml	Filtrate		
			Mass, g	S_{SO_4},%		H_2SO_4 g l^{-1}	Fe^{3+} g l^{-1}	Fe^{2+} g l^{-1}
1	CaCO3 (extra pure) (4.30 g)	15	5.72	43.20	116	27.12	50.76	1.34
2		30	6.54	58.57	110	26.12	54.43	0.87
3		60	5.78	57.97	104	23.52	56.10	1.23
4		120	6.18	59.90	98	24.68	56.34	1.34
5	Limestone “Velikan” (4.64 g)	30	5.01	57.60	116	53.90	43.38	1.12
6		60	6.32	58.03	104	46.35	48.30	1.17
7		120	6.48	61.78	112	14.12	48.33	1.17
8	Marble waste FF (4.56 g)	30	4.30	63.98	118	41.65	43.38	1.12
9		60	6.27	60.15	110	46.55	49.42	1.23
10		120	6.30	64.93	118	14.83	43.65	1.17
11	Marble waste CF* (4.32 g)	30	2.70	60.09	116	39.2	46.21	1.17
12		60	2.84	60.15	104	39.4	47.10	1.10
12		120	2.90	61.33	98	49.0	47.81	1.15

Table 7. Feed parameters of solutions subjected to the precipitation process.

Reagent	Mass g	Ratio S:L	Chemical composition of solution			
			H_2SO_4 g l^{-1}	Fe$_{общо}$ g l^{-1}	Fe(III) g l^{-1}	Fe(II) g l^{-1}
$CaCO_3$	4.65	1:20	28.24	51.91	51.80	0.11
Limestone	4.65	1:20	32,48	53,97	53,88	0,08
Marble waste FF	4.56	1:20	30.36	50.30	50.19	0.11
Marble waste CF	6.34	1:27	26.83	50.26	50.09	0.17

%) and higher share of coarse particles in it (Table 4).

Fig. 4 shows the rates of sedimentation of gypsum precipitates, produced in analogous conditions: temperature 323 K, reaction time of 120 minutes and 70 % extent of sulfuric acid neutralization. They have been calculated as a ratio of the volume of the clarified liquid per unit of time (cm^3 s^{-1}), for the duration of the reaction.

The feed parameters of precipitation such as solid/liquid ratio and chemical composition, characterizing the density and viscosity of the solution, are provided in Table 7. The precipitation rate is determined with a graduated cylinder with a volume of 100 ml. It is evident that for the three reagents: pure calcium carbonate, limestone and marble waste fine fraction, the solid:liquid ratio has one and the same value. The lower solid:liquid ratio when using marble coarse fraction as a neutralizer, is the reason for the lower quantity of gypsum, formed in the neutralization process. This is attributable to the lower percentage grade of calcium carbonate in this reagent (~ 67 %).

It is evident that more significant differences in the precipitation rates are observed in the first 240 seconds (~ 4 minutes). The most significant of them are for gypsum particles, formed after neutralization with pure calcium carbonate and the marble waste coarse fraction.

CONCLUSIONS

On the basis of the test work performed, it has been ascertained that for partial neutralization of solutions, obtained after autoclave treatment of pyrite concentrate, the following reagents can be used: limestone (Velikan deposit) and marble cutting waste, fine fraction. Both reagents have a high grade of calcium carbonate (> 92 %).The gypsum formed is with high chemical activity. The gypsum recovery is > 96 %.

It has been established, that the use of marble waste coarse fraction as a neutralizer is not acceptable for the following reasons: the gypsum recovery is almost two times lower, compared to the recovery achieved when using limestone or MFF; the process has a very low rate and the solution is enriched with magnesium ions. This is due to the significantly lower percentage grade of calcium carbonate (67.79 %) in MCF, high share of coarse particles and high content of magnesium carbonate (33.51 %).

The following optimal parameters of the process of partial neutralization have been determined: the process of neutralization should be conducted up to pH = 0.9 - 1.1 (neutralization of about 70 % of the initial acid), at temperature of neutralization 323 K. This allows the formation of gypsum with low impurities content (< 0.05 % Fe and < 0.02 % Cu). The total content of other impurities is less than 0.001 %.

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