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Optimisation of Pure Stibnite Leaching Conditions by Response Surface Methodology

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ABSTRACT

In the present work chemical basic leaching of pure Stibnite (Sb_2S_3) by Na_2S and NaOH under different experimental conditions at 40°C, has been studied in order to optimise the reagent concentrations for the antimony dissolution process. Response Surface Methodology has been used to find the best experimental concentrations to maximise the Sb extraction yield. 98-100% of antimony recovery was obtained by using 1g Na_sS and 1g NaOH per gram of pure stibnite.

Keywords: Stibnite; Basic Leaching; Optimisation; Response Surface Methodology

1. INTRODUCTION

The recovery of antimony is generally realised by pyrometallurgical processes from sulphide ores. As a consequence, serious environmental problems of the atmosphere may be present if no-appropriate treatments of the gaseous emissions are considered. This indicates the need to develop and apply environmentally friendly hydrometallurgical processes to avoid toxicity for human health. Several leaching and bioleaching processes have been proposed in the literature (Abbruzzese et al., 1998; Solozhenkin et al., 1997; Ubaldini et al., 2000a,b) and different leaching agents can be used to solubilise Sb from stibnite ores (Sb_2S_3): mixture of hydrochloric and tartaric acids, mixture of nitric and tartaric acid and hot concentrated sulphuric acid (Havlik et al., 1991; Ubaldini et al., 2000b).

Stibnite can be leached by alkaline solutions of Na_2S and NaOH (Ubaldini et al., 2000b). Various studies have been published recently on the recovery of precious metals generally associated with this mineral (Ubaldini et al., 2000b; Robinson et al., 1992). Of the numerous antimony minerals, stibnite, tetrahedrite (Cu_3SbS_3) and lead ores are the major sources for Sb as far as commercial extraction is concerned.

Dissolution of the stibnite in alkaline solution involves the formation of various soluble species, such as antimonites, thioantimonites, oxothioantimonites, sulphites, thiosulphates, etc. Stibnite reacts with sodium sulfide and the reactions involved in the process can be found elsewhere (Ubaldini et al., 2000b) although we can consider the following as the main reaction:

$$Sb_2S_3 + 3\ Na_2S \rightarrow 2\ Na_3SbS_3 \qquad (1)$$

Generally, sodium hydroxide is added to prevent hydrolysis of Na_2S. Decomposition of stibnite in alkaline aqueous solutions yields compounds such as thioantimonide species: recently these ones were described by Mosselmans et al. (2000) (these solutions contain $[SbS_4]^{3-}$) demonstrating that the oxidation of Sb(III) to Sb(V) occurs after dissolution. The study

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provided new information on the thioantimonide species formation in these alkaline systems although the authors underline that further work should be addressed to better elucidate the stoichiometry.

Besides this last study, mainly aimed to geochemistry applications, Ubaldini et al. (2000b) have studied this leaching system to recover Sb from stibnite considering also the subsequent recovery of gold by cyanidation. This preliminary study demonstrated the technical feasibility, on laboratory scale, of an integrated process to treat a refractory auriferous stibnite: the recovery of Sb by Na_2S and NaOH leaching, the successive gold solubilisation by conventional cyanidation process and the recovery of Sb and Au from the respective leach solutions by electrowinning.

These preliminary results highlighted the possibility to optimise the alkaline leaching conditions to evaluate the best operating conditions mainly in terms of Na_2S and NaOH concentration.

The aim of this work was to optimise the leaching conditions of pure stibnite by using the Surface Response Method (RSM) arranged in a sequential manner: the response of the process was in all cases the Sb extraction yield; although real ores should be considered in an optimisation study, pure stibnite was considered in this work to eliminate other kind of chemical reactions associated to the accessory minerals.

2. MATERIALS AND METHODS

Pure Sb_2S_3 analytical grade (98%) was employed in the leaching experiments for optimisation purposes. A selected amount of pure stibnite with a mixed solution of Na_2S and NaOH according to the experimental procedure, was charged in different flasks placed in thermostatic Dubnoff shaker, and stirred at 200rpm. Temperature was regulated by thermostatic bath at 40°C according to previous results (Ubaldini et al., 2000b).

Several solution samples have been collected to monitor the dissolution of antimony during the leaching test.

Quantitative chemical analyses of the sampled liquid solutions during the leaching were conducted by atomic absorption technique after filtration/centrifugation procedures.

Leaching tests were carried out by NaOH and $Na_2S.9\ H_2O$ reagent grade. Deionised water was used in all experiments.

3. RESULTS AND DISCUSSION

Chemical leaching of pure stibnite has been studied in order to optimise the concentration of the used reagents in the basic leaching (Ubaldini et al., 2000b). A centred 2^3 full factorial design has been planned in order to evaluate the effect of Na_2S, NaOH and ore concentrations on the Sb extraction yield. Table 1 shows factors and levels investigated, whereas Table 2 shows the treatments of the selected experimental design.

Table 1
Factors and levels investigated: temperature 40°C

Code	Factor	Low level -1	Central point 0	High level 1
A	Na_2S, g/100ml	1	2.5	4
B	NaOH, g/100ml	1	2.5	4
C	Mineral, g/100ml	4	6	8

Figure1 shows the experimental results expressed in terms of Sb extraction yield for the first 8 tests, whereas Table 3 shows the Sb extraction yield in the replicated tests carried out in the central point after 1h of leaching: this last test was performed in order to have an estimation of the experimental error (Montgomery, 1991).

Table 2
Treatment of the centred full-factorial design

Test No	A	B	C
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
Central point	0	0	0

Table 3
Experimental results obtained in the central point:
S^2_{err}, variance of the experimental error; d.f., degree of freedom

No	Sb extraction yield (%) after 1h
R1	59.69
R2	63.54
R3	64.51
R4	64.51
R5	63.54
R6	66.43
S^2 err	4.97 (d.f.)

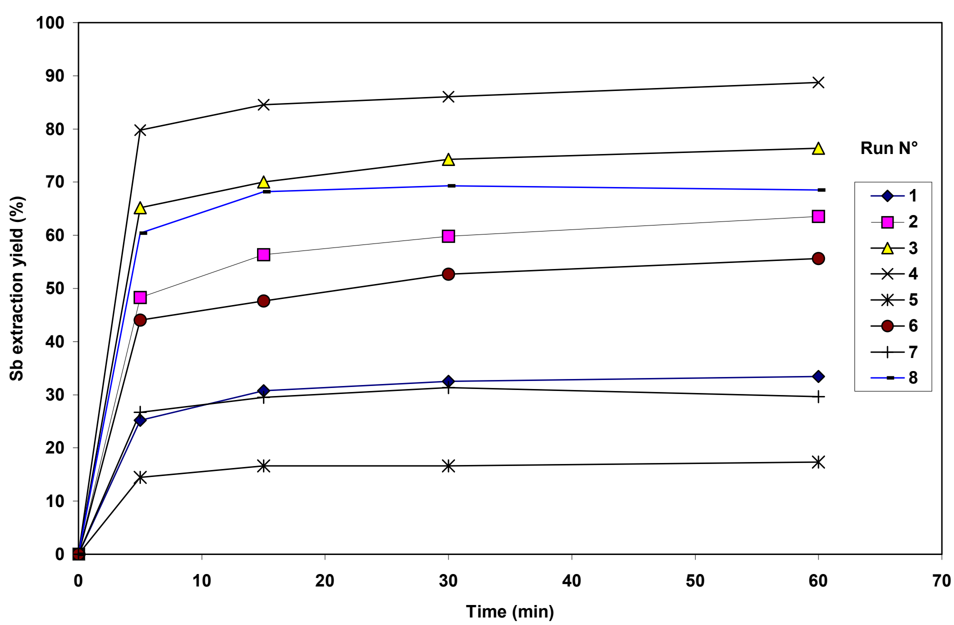

Figure 1. Sb extraction yield vs. time: temperature 40°C, experimental conditions reported in Table 2

The Analysis of the Variance (ANOVA) was carried out by Yates' method (Montgomery, 1991) on the Sb extraction yield after 1h of leaching to evaluate the influence of the selected factors on this response: Figure 2 summarises the results of this analysis (major details of the ANOVA analysis are not been reported here). From the ANOVA analysis it is possible to confirm the positive effect of the increase of the Na_2S and NaOH concentration on the Sb extraction yield whereas an increasing of the ore concentration produces a decreasing of the Sb dissolution yield. Moreover some two-interaction effects were also statistically significant: as well described elsewhere (Montgomery, 1991) two factors interact when the effect of a first factor changes with the changing of the second one. Figure 3 shows the interaction AB as an example (Montgomery, 1991). In this case it is possible to observe that the positive effect of the NaOH concentration on the Sb extraction yield, is reduced increasing the Na_2S concentration (the two straight lines are not parallel in Figure 3).

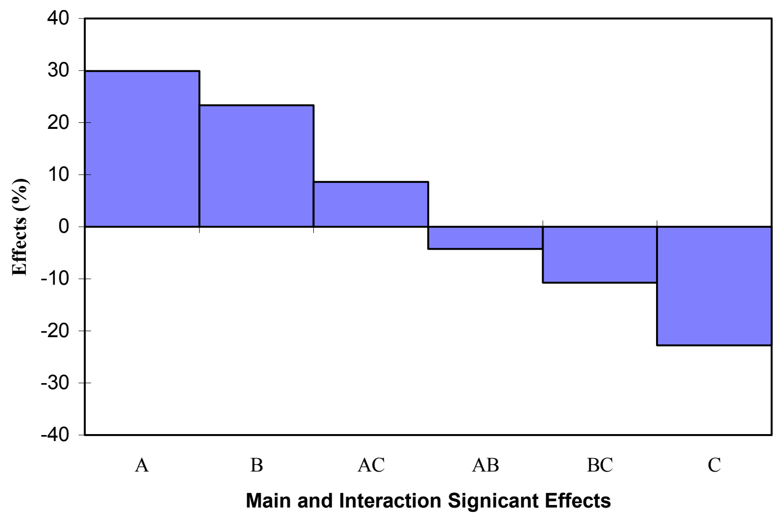

Figure 2. Results of the ANOVA analysis

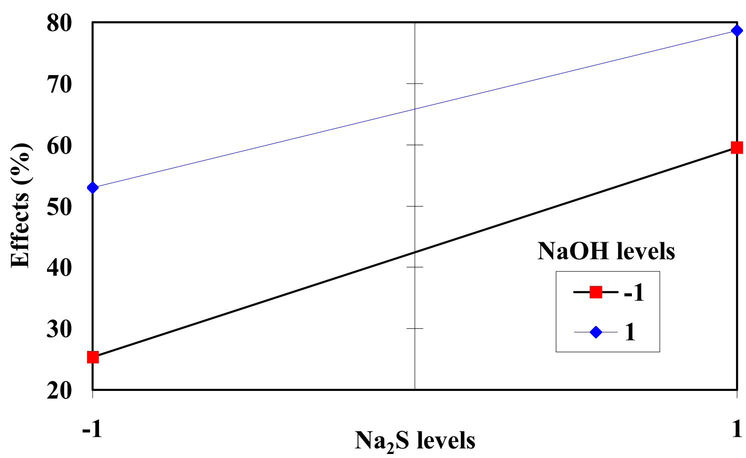

Figure 3. Significant two-interaction effect AB

According to the Surface Response Method (SRM) and its sequential experimental approach (Montgomery, 1991), a curvature tests was carried out in order to verify if a first order model might be able to describe the experimental results: i.e. the Sb extraction yield for a selected leaching time, as a function of the Na_2S, NaOH and ore concentration. Table 4 shows the results of this analysis: the very high significant difference between the $SS_{Pure\ Quadratic}$ and S^2_{error} (Montgomery, 1991) indicates that a first order model is not suitable to describe the experimental data and more trials have to be carried out in order to develop a second order model (Montgomery, 1991). In this manner a star design has to be carried out. According the

RSM, factors and levels shown in Table 5 were considered in further tests and added to the experimental results obtained in the first centred factorial design: Table 5 also shows the experimental results corresponding to these treatments.

Table 4
Curvature tests (Montgomery, 1991)

$SS_{Pure\ Quadratic}$	375.2
S^2_{error}	5.12
F-test	73.32
Significant, %	99.998

Table 5
Factor and levels (in coded form) carried out to complement the first centred factorial design; related experimental results in the fourth column

Test No	A levels	B levels	C levels	Sb extraction yield after 1h of leaching
9	-1.682	0	0	36.35
10	1.682	0	0	79.94
11	0	-1.682	0	15.78
12	0	1.682	0	83.29
13	0	0	-1.682	83.25
14	0	0	1.682	42.96

Considering these results, a new empirical model (second order model) has been considered to relate the Sb extraction yield (Y) with the Na_2S, NaOH and mineral concentrations (X_1, X_2 and X_3 respectively – in coded form). The empirical model is reported as follows:

$$Y = a_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} c_i X_i^2 + d_1 X_1 X_2 + d_2 X_1 X_3 + d_3 X_2 X_3 \qquad (2)$$

where a_o, b_i, c_i and d_i (i=1 to 3) represent the empirical constants found by linear regression analysis.

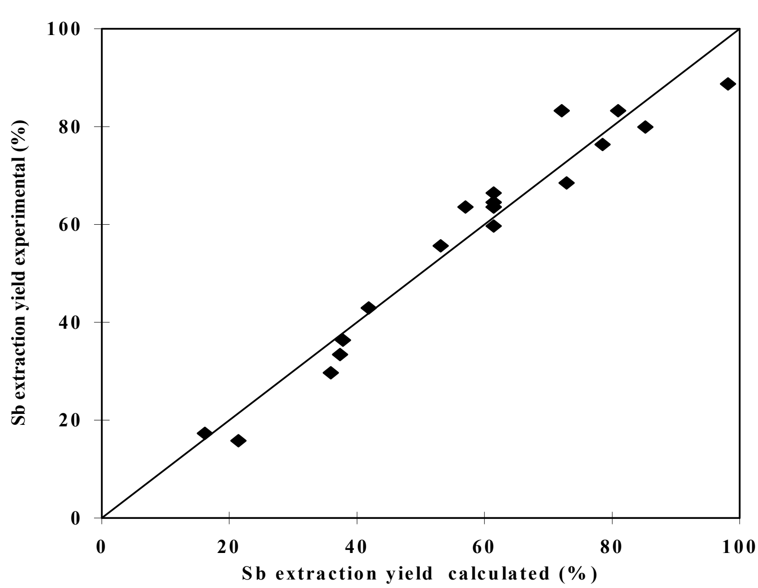

Figure 4. Scatter diagram of the regression analysis carried out on the model (2)

The statistical analysis of the model carried out by partial t-tests (Himmelblau, 1978) permits to establish that the empirical coefficient of X_1^2, X_3^2 e $X_1 \cdot X_2$ are not significant ($p < 0.05$) and so they can be eliminated from the model. A further linear regression analysis was carried out with the new model and these results are summarised in Table 6. Figure 4 shows the scatter diagram in which calculated and experimental Sb extraction yield have been reported. This analysis permitted to establish that the proposed empirical model was able to fit the experimental results without any significant bias. The final model can be so written as reported in the following equation:

$$Y = 61 + 14X_1 + 15X_2 - 12X_3 - 5X_2^2 + 4X_1X_3 - 5X_2X_3 \tag{3}$$

Considering this empirical equation, the response surface can be plotted to give a graphical representation of the leaching process (Figures 5a, b). In any case it is possible to observe that large Sb extraction yields can be obtained by using both reagents and, although NaOH is added to prevent the hydrolysis of the solubilised forms of antimony, it can be also considered as reagent of the dissolution process of Sb_2S_3 (see Figures 5a, b).

Table 6
Significant parameters of the empirical model (2): summary of the statistical analysis

Parameters	value	s.d.	t value	Significativity (αvalue)	Low Lim. (95%)	Sup. Lim. (95%)
Intercept	61	1.71	35.82	$2\ 10^{-14}$	57.7	65.1
X_1	14	1.62	8.72	$9\ 10^{-7}$	10.6	17.7
X_2	15	1.62	9.37	$4\ 10^{-7}$	11.7	18.7
X_3	-12	1.62	-7.17	$7\ 10^{-6}$	-15.1	-8.1
X_2^2	-5	1.57	-3.34	0.005	-8.7	-1.9
$X_1 \cdot X_3$	4	2.12	2.04	0.05	-0.2	8.9
$X_2 \cdot X_3$	-5	2.12	-2.53	0.03	-9.9	-0.8

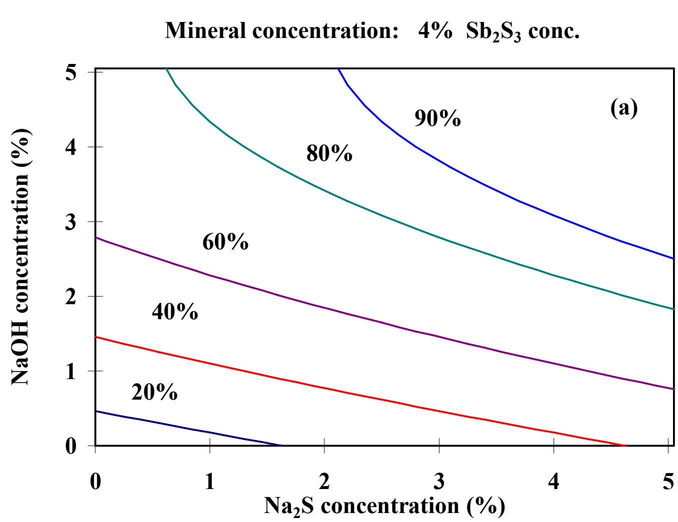

Figure 5. Sb extraction yield as a function of the investigated process parameters (X_1, X_2 and X_3)

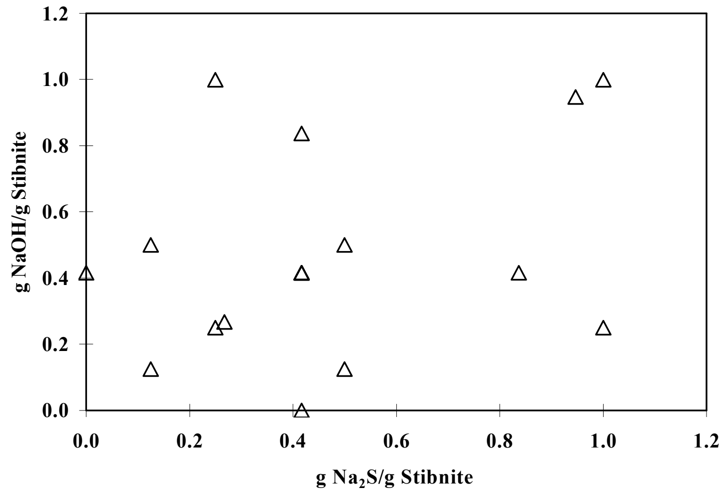

Figure 6. Experimental conditions by using specific amount of reagents

To obtain a more useful and practical relationship to establish the Na_2S and NaOH concentration per gram of stibnite, the same experimental data were processed by linear regression analysis. In this manner X_1 and X_2 independent variables represent in this case the amount (g/g) of Na_2S and NaOH per gram of stibnite respectively. With the new independent variables (X_1 and X_2) the experimental design is not orthogonal (Montgomery, 1991) but in any case it can be useful to evaluate their correlation with Y (Sb extraction yield): as well reported elsewhere (Montgomery, 1991) if the design is not orthogonal the effects of the investigated factors can not be evaluated independently. As an example, the main effect of the factor A can be related to the choice of the levels of the factor B. Figure 6 shows the experimental plane obtained eliminating the factor C (ore concentration – see Table 1) and introducing the new two specific independent variables; Table 7 reports the significant parameters of the empirical model formulated in the last manner (specific concentrations: i.e. g of Na_2S per g of ore). A scatter diagram (not shown here), in which calculated and experimental Sb extraction yield have been reported and the statistical analysis reported in Table 7, permitted to establish that the proposed empirical model was able to fit the experimental results without any significant bias. Considering this empirical equation (reported in the follo), the response surface can be plotted to give a graphical representation of the leaching process (Figure 7):

$$Y = -11 + 117X_1 + 117X_2 - 5 - 71X_1^2 + 4 - 63X_2^2 \qquad (4)$$

Table 7
Significant parameters of the empirical model expressed with X_1 and X_2 as amount (g/g) of Na_2S and NaOH per gram of stibnite respectively: summary of the statistical analysis

Parameters	value	s.d.	t value	Significativity	Low Lim. (95%)	Sup. Lim. (95%)
Intercept	-11	7.27	-1.52	0.15	-26.5	4.5
X_1	117	22.33	5.25	10^{-4}	69.6	164.8
X_2	117	22.33	5.26	10^{-4}	69.8	165.0
X_1^2	-71	19.78	-3.61	0.003	-113.6	-29.3
X_2^2	-63	19.78	-3.16	0.006	-104.7	-20.3

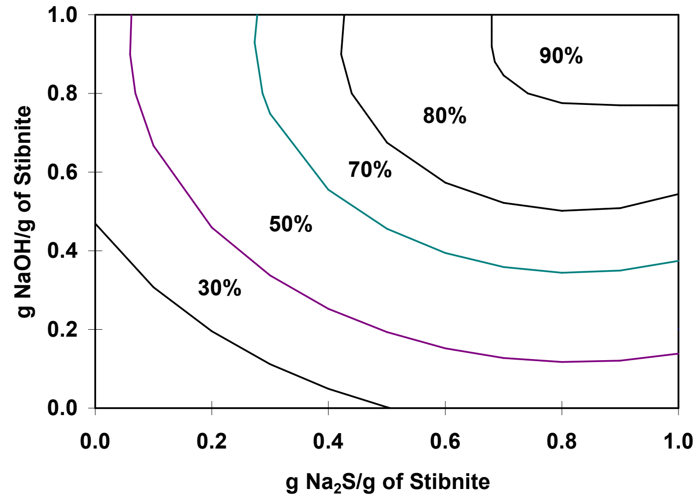

Figure 7. Surface response plot (Sb extraction yield) by using specific concentration of the chemical reagents

where X_1 and X_2 are the specific concentration of both Na_2S and NaOH per gram of pure stibnite respectively. The reported experiments have permitted to establish the experimental stoichiometry of the process considering the action of both reagents (Na_2S and NaOH) as well as the possible interactions (that have been evaluated in the ANOVA analysis).

To give a fine relationship in the region of maximum Sb extraction yield, a further centred factorial design has been planned and carried out. Table 8 reports the factors and levels investigated whereas Table 9 shows the investigated treatments organised according to the RSM for three factors (Montgomery, 1991). Also in this case a linear regression analysis has been carried out: all the statistical tools showed a good data fitting (t-tests, R^2 value, ANOVA, confidence intervals, scatter diagram etc. – data not reported here). The final empirical model is reported as follows:

$$Y = 96 + 2X_1 - 4X_1^2 - 4X_2^2 - 3X_3^2 \quad (5)$$

Table 8
Factors and levels investigated in the region of maximum yield

Factors	Levels in coded form	-1.682	-1	0	+1	+1.682
g_{Na2S}/g_{min}	X_1	0.58	0.75	1	1.25	1.42
g_{NaOH}/g_{min}	X_2	0.58	0.75	1	1.25	1.42
Min. conc., %	X_3	1.32	2	3	4	4.68

where X_1 and X_2 are the specific concentration of both Na_2S and NaOH per gram of pure stibnite respectively, and X_3 is the mineral concentration in the leaching suspension (all the independent variables have been expressed in coded form).

From these results it is possible to verify that very large extraction yield have been obtained in these experimental conditions.

It is possible to find the best condition by eq. (5) to maximise the Sb extraction yield (X_1=0.25 and X_2=0 for X_3=0 in coded form and about 1g Na_2S/g ore, 1g NaOH/g ore respectively as specific concentration). In this manner, this model can be used to evaluate the levels of reagent concentrations required to obtain a selected Sb extraction yield.

Table 9
Treatments and experimental results of the second experimental design: Sb extraction yield after 1h of leaching at T=40°C

Runs N°	X_1	X_2	X_3	Na_2S, %	NaOH, %	Sb_2S_3, %	Sb extract. yield (%)
1	-1	-1	-1	1.5	1.5	2	83.14
2	+1	-1	-1	2.5	1.5	2	87.70
3	-1	+1	-1	1.5	2.5	2	85.91
4	+1	+1	-1	2.5	2.5	2	87.77
5	-1	-1	+1	3	3	4	80.01
6	+1	-1	+1	5	3	4	84.77
7	-1	+1	+1	3	5	4	82.03
8	+1	+1	+1	5	5	4	87.37
9	-1.682	0	0	1.74	3	3	78.60
10	+1.682	0	0	4.26	3	3	86.20
11	0	-1.682	0	3	1.74	3	82.16
12	0	+1.682	0	3	4.26	3	83.44
13	0	0	-1.682	3	3	1.32	85.18
14	0	0	+1.682	3	3	4.68	85.21
R1	0	0	0	3	3	3	93.60
R2	0	0	0	3	3	3	97.64
R3	0	0	0	3	3	3	100.00
R4	0	0	0	3	3	3	98.43
R5	0	0	0	3	3	3	92.41
R6	0	0	0	3	3	3	93.50
R7	0	0	0	3	3	3	97.74
R8	0	0	0	3	3	3	97.05
R9	0	0	0	3	3	3	95.86

R1-R9: replicated tests in the central point (Montgomery, 1991)

4. CONCLUSIONS

The experimental results obtained and the related data analysis have permitted to study the influence of the Na_2S and NaOH concentration in the stibnite dissolution at 40°C for different mineral concentrations. The best operative conditions have been obtained in the investigated experimental conditions. The empirical models obtained permit to quantify the reagent concentrations in ore leaching knowing the stibnite content in the ore. Obviously it is necessary to carry out also some experimental tests with real ores because interaction with the gangue may be possible. Previous work reported elsewhere has demonstrated that this information may be helpful in the interpretation of leaching data obtained with real ores (Ubaldini et al., 2000b).

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REFERENCES

Abbruzzese, C., Ubaldini, S., Veglio', F., Behaviour of phyrrotite, arsenopyrite and stibnite to biooxidation. Acta Metallurgica Slovaca, 1998, **4**, 1, pp.19-24.

Havlik, T., Skrobian, M., Balaz, P., A Study of Stibnite Acid Oxidative Leaching. Rudy, 1991, Vol.**39**, N.5-6, pp.100-102.

Himmelblau, D. M. Process Analysis by Statistical Methods. John Wiley & Sons, Inc. 1978.

Montgomery D.C., Design and Analysis of Experiments. J. Wiley & Sons, third edition, 1991, Singapore.

Mosselmans, J. F. W., Heltz, G.R., Pattrik, R.A.D., Charnock, J.M., Vaughan, D.J., A study of speciation of Sb in bisulphide solutions by X-ray absorption spectroscopy. Applied Geochemistry, 2000, **15**, pp.879-889.

Robinson, J., Williams, C., Gold recovery from a Golden Spec stibnite concentrate by aqueous pressure techniques. Publ. Australas. Inst. Min. Metall., 1992, Vol.**9**, pp.333-337.

Solozhenkin, P., Nebera, V., Abdulmanov, I., The technology of direct processing of antimony-bearing materials for obtaining of antimony compounds. Proceedings of the XX IMPC, 1997, Vol. **4**, pp.227-234, Aachen.

Ubaldini, S., Vegliò, F., Fornari, P., Abruzzese, C., Process flow-sheet for gold and antimony recovery from stibnite. Hydrometallurgy, 2000a, **57**, pp.187-199.

Ubaldini, S., Veglio', F., Toro, L., Abbruzzese, C., Combined bio-hydrometallurgical process for gold recovery from refractory stibnite. Mineral Engineering, 2000b, **13**, No.14-15, pp.1641-1646.