Available online at www.sciencedirect.com

ScienceDirect

Trans. Nonferrous Met. Soc. China 22(2012) 675−685

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Modelling and process optimisation of antimony removal from a complex copper concentrate

Samuel Ayowole AWE[1], Mohammad KHOSHKHOO[1], Paul KRUGER[2], Åke SANDSTRÖM[1]

1. Division of Minerals and Metallurgical Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden;
2. Boliden Mineral AB, SE-936 81 Boliden, Sweden

Received 3 August 2011; accepted 6 December 2011

Abstract: The modelling and optimization for the alkaline sulphide leaching of a complex copper concentrate containing 1.69% Sb and 0.14% Sn were studied. Response surface methodology, in combination with central composite face-centred design (RSM-CCF), was used to optimise the operating parameters. The leaching temperature, sulphide ion concentration and solid concentration were chosen as the variables, and the response parameters were antimony and tin recovery, and the time required to achieve 90% Sb dissolution. It was confirmed that the leaching process was strongly dependent on the reaction temperature as well as the sulphide ion concentration without any significant dependence on the solid concentration. Furthermore, a mathematical model was constructed to characterise the leaching behaviour. The results from the model allow identification of the most favourable leaching conditions. The model was validated experimentally, and the results show that the model is reliable and accurate in predicting the leaching process.

Key words: alkaline sulphide hydrometallurgy; antimony; tetrahedrite; leaching optimization; response surface methodology; central composite face-centred design

1 Introduction

Antimony is a chalcophilic metalloid belonging to group 15 of the periodic table. It occurs naturally at a trace level in the environment. Antimony-bearing minerals are commonly found in small concentrations in many sulphide ore deposits. Tetrahedrite ($Cu_{12}Sb_4S_{13}$) is an antimony mineral which is often found in association with copper sulphide ores. Though, it is an important source of copper, it is more significant as a source of silver and antimony. Similarly, enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$) are minor sources of copper, and they result in arsenic reporting to the processing circuit in copper metallurgy. These antimony and arsenic minerals contain significant concentrations of mercury, bismuth, selenium, etc, which are unwanted impurity elements in the copper production process [1]. However, processing of future copper ores and concentrates will most likely involve the treatment of more complex, fine-grained minerals containing increased levels of impurity elements, which can be detrimental to the smelting process. Unfortunately, the prevalence of tetrahedrite, tennantite and enargite among the copper-bearing minerals will reduce their economic value due to their minor element content [2], which needs to be eliminated. The removal of impurities in copper metallurgy is crucial to the production of high-quality copper. The ability to efficiently remove impurities will become even more important in the future, because copper ores show a decreasing ore grade and increasing levels of impurities.

In Sweden, many of the complex sulphide mineral deposits found in the Boliden mining area are in association with impurity minerals like tetrahedrite and bournonite ($PbCuSbS_3$), which make it difficult to produce clean and high grade concentrates. Besides, the antimony, arsenic and bismuth of the complex sulphide mineral render it undesirable as a feed material for smelting because these impurities interfere with copper extraction. Also, they hamper copper electrorefining process by forming a scum on the electrolytic cells which allow impurities to be carried over to the cathodes [3,4]. Therefore, it is desirable to remove these impurities at an early stage of processing, since they may be difficult to remove from metallic copper. To increase the economic

---

Corresponding author: Åke SANDSTRÖM; Tel: +46-920-491290; Fax: +46-920-491199; E-mail: ake.sandstrom@ltu.se
DOI: 10.1016/S1003-6326(11)61231-4

value and metal grade of copper concentrates, it is therefore imperative to choose a pre-treatment processing route which can selectively remove these impurities prior to the smelting of the concentrate.

Interestingly, the recent study report submitted by the European Commission has listed antimony as a critical raw material needed by the European Union economy due to 1) the high supply risks for antimony to EU economy, 2) the lack of an effective substitute for its major application (flame retardant), and 3) its low degree of recycling because of the dissipative nature of its major usage [5]. However, it will be advantageous if the antimony content of copper concentrate can be removed as a saleable product at an early stage of processing instead of being stockpiled as a waste material from the final copper metallurgical process. In view of this, alkaline sulphide hydrometallurgical technology has been proven to be the best alternative route to selectively dissolve antimony from concentrates containing it [6−12], and to consequently produce a suitable feed for the copper smelter [12]. The efficiency of the process strongly depends on factors such as reaction temperature, concentration of sulphide ion, leaching time, particle size and the amount of solid leached. Antimony metal has been recovered from the pregnant solution via both diaphragm [13−15] and non-diaphragm [14,16] electrowinning processes, and also from autoclave oxidation of the pregnant solution [4,17,18].

Conventionally, the study of the effects of aforementioned factors, on the sulphide leaching of antimony-bearing copper concentrates, was conducted using an approach where one factor at a time was varied [6,19]. The effect of each experimental factor was investigated by altering the level of one factor at a time while keeping the levels of the other factors constant. However, if the aim of conducting a study is to determine the optimum operating conditions, response surface methodology (RSM) will be the appropriate method of performing the task. Conversely, RSM is an efficient methodology that all the experimental factors are varied simultaneously over a set of experimental runs. RSM is one of the relevant multivariate techniques that can deal with multivariant experimental design strategy, statistical modelling and process optimisation [20,21]. It is employed to study the relationship between one or more response variables and a set of quantitative or qualitative experimental factors. RSM is often used after the vital controllable factors are identified and to find the factor settings that optimise the response [22]. This type of experimental design is usually chosen when non-linear interactions between the experimental parameters and the response variables are suspected. Furthermore, the application of RSM reduces the number of experiments required for the analysis of the main effects and interactions between factors [22−24]. The objectives of the current research are to evaluate the influence of these experimental factors, reaction temperature, sulphide ion concentration and solid concentration, on the response variables and also model the behaviour of a complex copper concentrate in alkaline sulphide solution in order to determine the most favourable operating conditions.

2 Experimental

2.1 Material and characterisation techniques

Rockliden copper concentrate used in this investigation was a flotation concentrate obtained from Boliden Mineral AB, Sweden. Particle size distribution analysis of the concentrate showed that more than 80% of the mineral particles were smaller than 40 μm (Fig. 1). The chemical analysis of the concentrate is presented in Table 1.

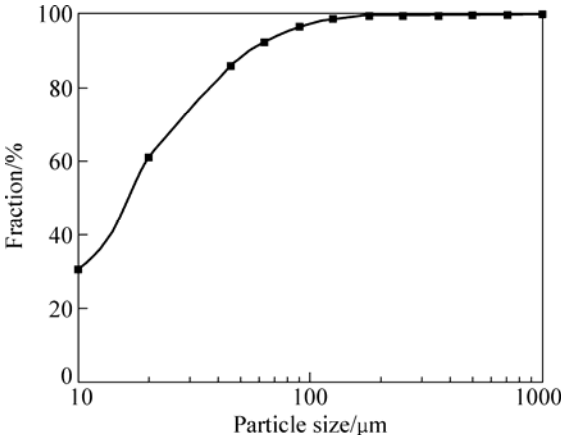

Fig. 1 Particle size distribution of concentrate

Table 1 Elemental analysis of complex copper concentrate (mass fraction, %)

Cu	Fe	Pb	Zn	Sb	Sn
17.8	27.1	7.1	5.7	1.69	0.14

As	Se	Hg	Ag	S
0.42	0.06	0.03	0.08	>15

A representative sample was taken from the concentrate for scanning electron microscopy (SEM) examination using a SEM JEOL JSM5900LV equipped with an EDS-analyser. The sample was embedded in epoxy, polished and coated with carbon prior to the analysis. X-ray powder diffraction (XRD) was used to characterize the complex copper concentrate using a Siemens D5000 automatic diffractometer equipped with a continuous scanning device. Patterns were collected between 2θ angles of 10°−90° (at Cu K_α radiation of 40 kV, 30 mA). Mineral phases were identified using the Joint Committee for Powder Diffraction Standards

(JCPDS) file of the instrument.

2.2 Leaching procedure

The leaching experiments were performed by dissolving the Rockliden complex sulphide copper concentrate samples in 800 mL of lixiviant solutions. The lixiviant solution was prepared by dissolving sodium sulphide ($Na_2S·3H_2O$) in sodium hydroxide (NaOH) solution. The concentration of sodium hydroxide used at each run of the test was 20% (mass fraction) of the sodium sulphide concentration used. The whole experiments were conducted in a batch mode using a 1 L five-necked round bottomed glass reactor. The contents of the reactor were mechanically homogenized using a paddle stirrer at a constant stirring rate of 300 r/min and heated on auto-regulated device. All the leaching experiments lasted for 6 h. The lixiviant was first added to the reactor, and when the desired temperature was reached, the solid sample was added. At predetermined time intervals, slurry sample was taken from the reactor for the analysis of dissolved metals. All reagents used for leaching and chemical analysis were of analytical grade and used without further purification. Leaching results were evaluated by means of elemental determinations on the leach products using inductively coupled plasma-atomic emission spectrometry (ICP-AES)/sector field mass spectrometry (ICP-SFMS).

2.3 Experimental design

The experiments were designed using response surface methodology (RSM) approach. RSM is a particular set of mathematical and statistical methods that includes experimental design, model fitting and validation, and condition optimisation [24]. Experimental runs were designed in accordance with central composite face-centred design (CCF), which allows a full quadratic model for each response under investigation. A detailed discussion of CCF design is documented elsewhere [20,21].

MODDE 8.0 Umetrics software was used in the design and analysis of the experiment. The effect of the following three factors on the efficiency of the leaching process was investigated: reaction temperature (X_1), sulphide ion concentration (X_2) and solid concentration (X_3). The interaction between the effects of the various variables was also examined. According to the previous work conducted by the authors [6,25,26] as well as the practical considerations in order to industrialise the process, the levels (minimum and maximum) of each of the factors were chosen as follows: temperature (80 and 100 °C), sulphide ion concentration (41 and 82 g/L) and solid concentration (100 and 300 g/L). The response variables were the recoveries of antimony (Sb) and tin (Sn), and leaching time t_{90}, which is the time required to leach out 90% of antimony from the concentrate by alkaline sulphide lixiviant. The recoveries of antimony and tin were computed based on the solid residues analysis, Eq. (1), whilst t_{90} was estimated from antimony leaching kinetic profiles which is fitted to the exponential equation.

$$\eta = \frac{f-r}{f} \times 100\% \tag{1}$$

$$C_t = C_0 \exp(kt) \tag{2}$$

where η represents the recovery of Sb or Sn; f and r are the amount of Sb or Sn in the feed and residue, respectively; C_0 is the initial concentration of Sb in the feed material; C_t is the concentration of antimony in the residue after time t of leaching; k is the rate constant. Since the mass difference between the feed and leach residue was negligible, Eq. (2) was used to simplify the relationship between the leaching time and the amount of metal leached.

Table 2 shows the actual values of the independent variables at which the experiments were performed to estimate the response variables. The table contains the measured values of antimony and tin recoveries, as well as the calculated t_{90} from Eq. (2). The experiments were conducted in randomized order, to avoid any occurring systematic time trend which could cause error in the model. The original design, that involved replicates of the reference mixture for estimating the pure error, was augmented with replicates of random runs so that the homogeneity of variance error could be checked. The model fitting was investigated by using multiple linear regression (MLR) method.

The experimental results obtained from the CCF model were described in the form presented in Eq. (3),

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j \tag{3}$$

where Y is the predicted response; β_0, β_i, β_{ii} and β_{ij} are constant coefficients, linear coefficients, interaction coefficients and the quadratic coefficients, respectively; X_i and X_j are the coded levels of the factors investigated. The model fitting was evaluated by checking the coefficients of determination R^2, R^2_{adj} and Q^2 values, which indicate the fraction of the variation of the response explained by the model, the fraction of the variation of the response described by the model adjusted for degrees of freedom and the fraction of the variation of the response predicted by the model, respectively. The validity of the model was examined at 95% confidence interval.

Table 2 Central composite face-centred design arrangements and responses for complex concentrate leaching by alkaline sulphide solution

Exp. No.	Run order	Experimental factor			Response variable		
		Temperature, X_1/°C	S^{-2} conc., X_2/(g·L^{-1})	Solid conc., X_3 /(g·L^{-1})	Sb recovery, η(Sb)/%	Sn recovery, η(Sn)/%	Leaching time, t_{90}/h
N1	13	80	41	100	43	34	26.5
N2	2	100	41	100	78	39	8.9
N3	10	80	82	100	94	36	4.4
N4	3	100	82	100	97	68	3.5
N5	1	80	41	300	39	35	29.9
N6	12	100	41	300	76	31	9.8
N7	8	80	82	300	94	38	4.4
N8	4	100	82	300	96	83	3.5
N9	5	80	61.4	200	87	32	6.5
N10	16	100	61.4	200	91	39	5.3
N11	9	90	41	200	63	33	13.8
N12	6	90	82	200	96	49	3.9
N13	15	90	61.4	100	91	33	5.3
N14	14	90	61.4	300	88	34	6.1
N15	11	90	61.4	200	89	33	5.7
N16	17	90	61.4	200	92	34	5.2
N17	7	90	61.4	200	91	32	5.3

3 Results and discussion

3.1 Mineralogical study

The mineralogical composition of the concentrate was investigated by XRD and SEM-EDS analytical techniques. Figure 2 presents the result of XRD analysis performed on the concentrate. The main mineralogical phases identified in the XRD pattern were tetrahedrite, chalcopyrite, sphalerite, galena, iron sulphide and pyrite.

The result of SEM-EDS analysis shown in Fig. 3 corroborates the result obtained from the XRD analysis. This method identifies a much wider range of minor minerals (Table 3) that are below the detection limit for

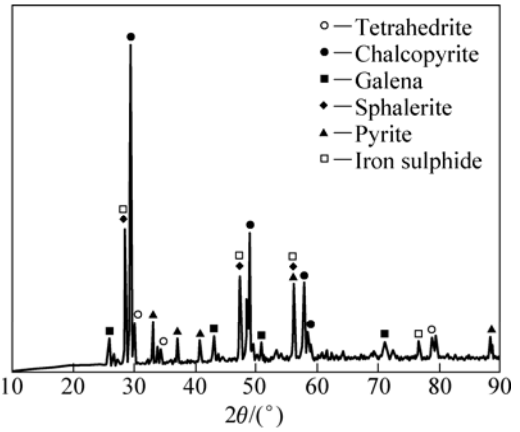

Fig. 2 XRD pattern of concentrate

Table 3 Mineralogy and composition of selected microanalyses of Rockliden copper concentrate defined by SEM-EDS analysis

No.	Composition (mole fraction)/%									Mineral
	Cu	Fe	Zn	Pb	Sb	As	Sn	Ag	S	
1	35.4	5.4			30.9			1.3	27.0	Tetrahedrite
2	34.4	5.6	2.5		30.6			1.3	25.6	Tetrahedrite
3	33.7	5.8	1.6		31.3			2.0	25.6	Tetrahedrite
4	34.1	6.2	2.0		30.1			1.3	26.2	Tetrahedrite
5	34.4	5.3	1.8		30.8			1.6	26.1	Tetrahedrite
6	34.1	6.1			30.1			3.2	26.6	Tetrahedrite
7	12.5	1.1		38.8	27.1				20.6	Bournonite
8	13.1	0.8		39.0	26.1				20.9	Bournonite
9	12.5	1.4		38.4	26.3				21.4	Bournonite
10	27.2	12.6					29.1		31.1	Stannite
11	28.6	12.5					28.0		30.9	Stannite
12	1.0	32.9				44.8			21.3	Arsenopyrite
13		33.5				46.1			20.4	Arsenopyrite
14	33.2	30.0							36.8	Chalcopyrite
15	32.7	30.2							37.1	Chalcopyrite
16		1.3		83.1					15.6	Galena
17		8.1	55.6						36.3	Sphalerite
18		44.2							55.8	Pyrite
19		58.8							41.2	Pyrrhotite

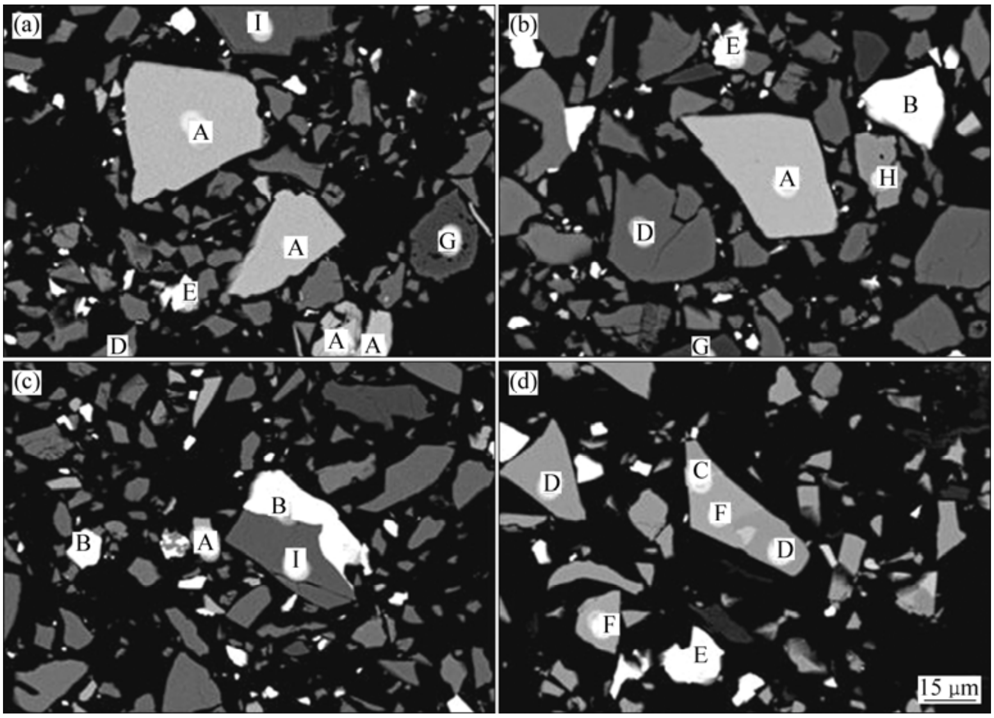

Fig. 3 SEM-EDS micrographs of concentrate: A—Tetrahedrite; B—Bournonite; C—Stannite; D—Chalcopyrite; E—Galena; F—Sphalerite; G—Pyrite; H—Arsenopyrite; I—Pyrrhotite

XRD. Apart from tetrahedrite, the SEM result (Fig. 3) shows that antimony was also found as bournonite ($PbCuSbS_3$) while tin and arsenic were present as stannite (Cu_2FeSnS_4) and arsenopyrite, respectively. Table 3 shows that silver is bound in the tetrahedrite structure, which enhances the value of the concentrate.

3.2 Data evaluation and RSM model analysis

The distributions of the data for all the responses were inspected for normality, and it was observed that the responses needed to be transformed in order to obtain improved models. Negative logarithmic transformation was carried out for Sb recovery, and power transformation was performed for both Sn recovery and t_{90} as detailed in Table 4. Evaluation of the raw data revealed that the replicate errors were satisfactorily small for all of the output responses.

Table 4 Transformation of responses

Response	Transformation
$\eta(\mathrm{Sb})/\%$	$-\lg(100-\eta(\mathrm{Sb}))$
$\eta(\mathrm{Sn})/\%$	$\eta^{-1}(\mathrm{Sn})$
t_{90}/h	$t_{90}^{-0.5}$

The model was fitted using multiple linear regression (MLR) method, and the overall result of the model fitting is displayed in Fig. 4. A model can be judged as good if $R^2-Q^2<0.2-0.3$, $Q^2>0.5$, model validity >0.25 and reproducibility is greater than 0.5 [21]. The predictive power (Q^2) values for the responses of Sb recovery, t_{90} and Sn recovery are 0.93, 0.91 and 0.55, respectively. It is observed that the Q^2 of the models ranges from excellent to good. All models also show high model validity, which indicates no lack of fit.

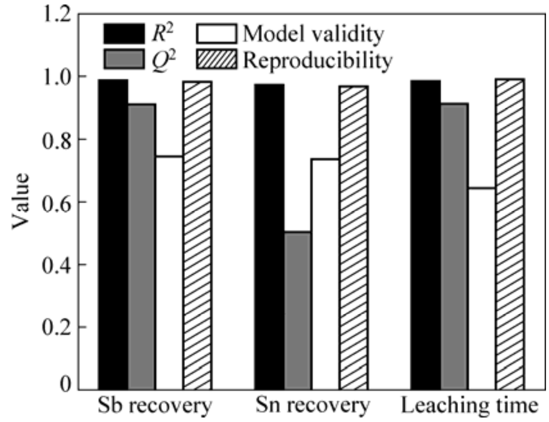

Fig. 4 Summary of fit plot of initial modelling

Figure 4 shows that Sb recovery and t_{90} models satisfied the model performance indicator conditions while the Sn recovery model did not. The lower Q^2 value of Sn recovery model could be due to the presence of irrelevant terms contained in the regression model.

The regression coefficient plots of the models were examined and the statistically non-significant terms were eliminated. Thus, the models were refined and simplified. The summary of fit plot of the refined models is presented in Fig. 5. It can be seen from Fig. 5 that all three Q^2 values have increased, and now amount to 0.97, 0.97 and 0.74 for Sb recovery, t_{90} and Sn recovery, respectively. The refined models show improved model validity. The outcome of the normal probability plot of the residuals after refinement (Fig. 6) reveals that the models look satisfactory, except for the deviating behaviour of experiment 2 in Sn recovery model. Subsequently, experiment 2 was critically scrutinized for any possible error, but it was found to be well fitted into the other models; therefore, the experiment cannot be removed from the model. Due to satisfactory R^2 and Q^2 of Sn recovery model, it may be assumed that experiment 2 is a weak outlier which does not influence the model decisively. In order to obtain information concerning how the input variables affect the responses, regression coefficient plots of the refined models were made and interpreted (Fig. 7). These plots show that reaction temperature and sulphide ion concentration have a strong effect on the three responses but that solid concentration has an insignificant effect on all the three responses.

Furthermore, the analysis of variance (ANOVA) of the refined models shown in Table 5 reveals that all the

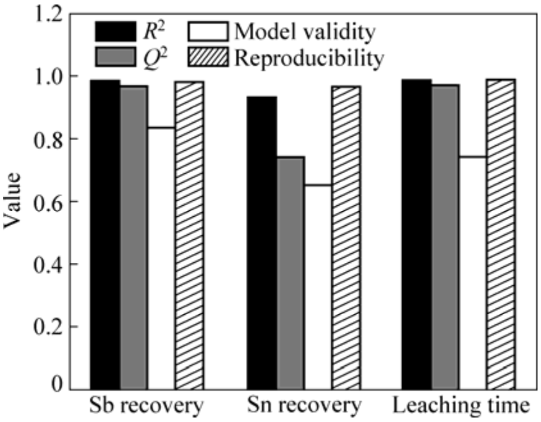

Fig. 5 Summary of fit plot of refined modelling

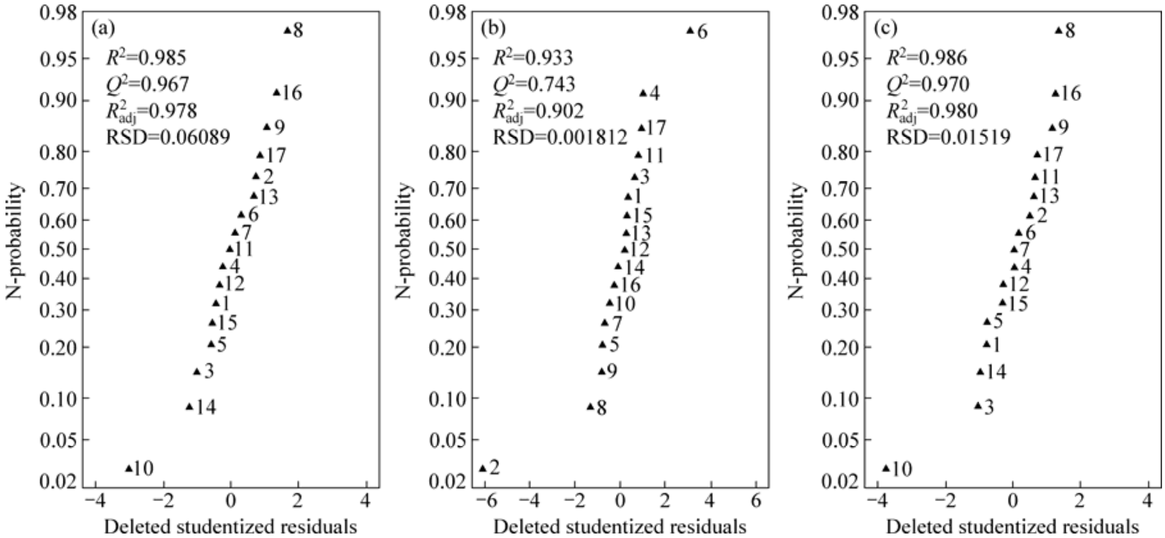

Fig. 6 Normal probability plots of residuals after model refinement: (a) Sb recovery with experiment number tables; (b) Sn recovery with experiment number tables; (c) Leaching time with experiment number tables

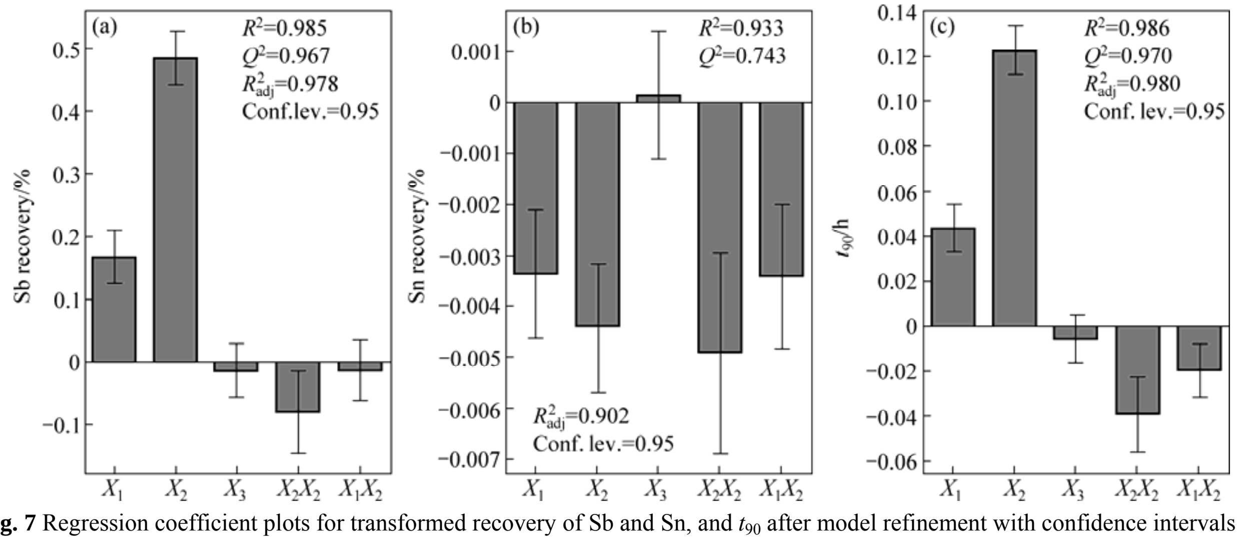

Fig. 7 Regression coefficient plots for transformed recovery of Sb and Sn, and t_{90} after model refinement with confidence intervals

Table 5 ANOVA for quadratic models predicted for each response variable

Response variable	Source	DF	SS	MS (variance)	F_0	F_{critical} ($\alpha = 0.05$)	*P*-value
Sb recovery	Total corrected	16	2.7026	0.1689			
	Regression	5	2.6619	0.5324	143.58	3.20	0.000
	Residual	11	0.0408	0.0037			
	Lack of fit (model error)	9	0.0347	0.0039	1.28	19.37	0.514
	Pure error (replicate error)	2	0.0060	0.0030			
Sn recovery	Total corrected	16	0.0005	3.37×10^{-5}			
	Regression	5	0.0005	1.01×10^{-4}	30.61	3.20	0.000
	Residual	11	3.61×10^{-5}	3.29×10^{-6}			
	Lack of fit (model error)	9	3.39×10^{-5}	3.77×10^{-6}	3.36	19.37	0.251
	Pure error (replicate error)	2	2.24×10^{-6}	1.12×10^{-6}			
t_{90}	Total corrected	16	0.1823	0.0114			
	Regression	5	0.1798	0.0360	155.78	3.20	0.000
	Residual	11	0.0025	0.0002			
	Lack of fit (model error)	9	0.0023	0.0003	2.16	19.37	0.356
	Pure error (replicate error)	2	0.0002	0.0001			

DF—Degree of freedom; SS—Sum of squares; MS—Mean square

regression models are statistically significant with a 95% confidence level. For all the response variables, F_0 values are greater than F_{critical} values, and *P*-values are smaller than 0.05. According to the results displayed in the ANOVA table (Table 5), it can be inferred that the model error of the original model is of the same magnitude as the replicate error for all the responses, because their *P*-values are greater than 0.05 and $F_0<F_{\text{critical}}$ at 95% confidence level. Hence, the models have small error and good fitting power, meaning that the models show no lack of fit.

Moreover, Fig. 8 illustrates that the observed responses correlated very well with the predicted values. Thereby, the models are considered adequate for the predictions and optimisation of the process. The regression models describing the relation of the three transformed responses and the parameters investigated are given as:

$$-\lg(100-\eta(\text{Sb})) = -1.002+0.168X_1+0.485X_2-0.013X_3-0.079X_2^2 \quad (4)$$

$$\eta^{-1}(\text{Sn}) = 0.030-0.003X_1-0.004X_2+0.0001X_3-0.005X_2^2-0.003X_1X_2 \quad (5)$$

$$t_{90}^{-0.5} = 0.422+0.044X_1+0.123X_2-0.006X_3-0.039X_2^2-0.020X_1X_2 \quad (6)$$

In the regression models, the low level, centre level and high level of all the experimental parameters were coded as −1, 0 and 1, respectively; where X_1 is the reaction temperature, X_2 is the sulphide ion concentration, X_3 is the solid concentration, and $(X_2)^2$ and X_1X_2 are the square and interaction of the main factors, respectively. The presence of significant square and interaction terms in the regression equations confirms quadratic behaviour and non-linear combining effects of the variables.

3.3 Interpretation of data by response surface modelling

According to the empirical models explained in Eqs. (4)−(6), response surface plots were developed, which provide a better understanding of the effect of the experimental parameters on the response variables. Figure 9 displays the contour plots at various solid concentrations where antimony recovery is represented by varying simultaneously the leaching temperature from 80 °C to 100 °C and sulphide ion concentration from 41 to 82 g/L. The figure shows that antimony recovery increases with the increase of both sulphide ion concentration and reaction temperature. The effect of both leaching temperature and sulphide ion concentration on antimony recovery can be explained by the fact that tetrahedrite, the antimony mineral, is refractory in nature. Therefore, high sulphide concentration and reaction temperature are needed to enhance antimony dissolution by the lixiviant. Besides, tetrahedrite dissolution in alkaline sulphide solution is controlled by chemical reaction with a relatively high activation energy [6], hence, higher lixiviant concentration as well as increasing leaching temperature would favour its dissolution.

Figure 10 presents the effect of leaching temperature and sulphide concentration on Sn recovery. It is seen that these independent variables have significant effects on Sn dissolution. Like antimony, Sn extraction is observed to increase with increasing the

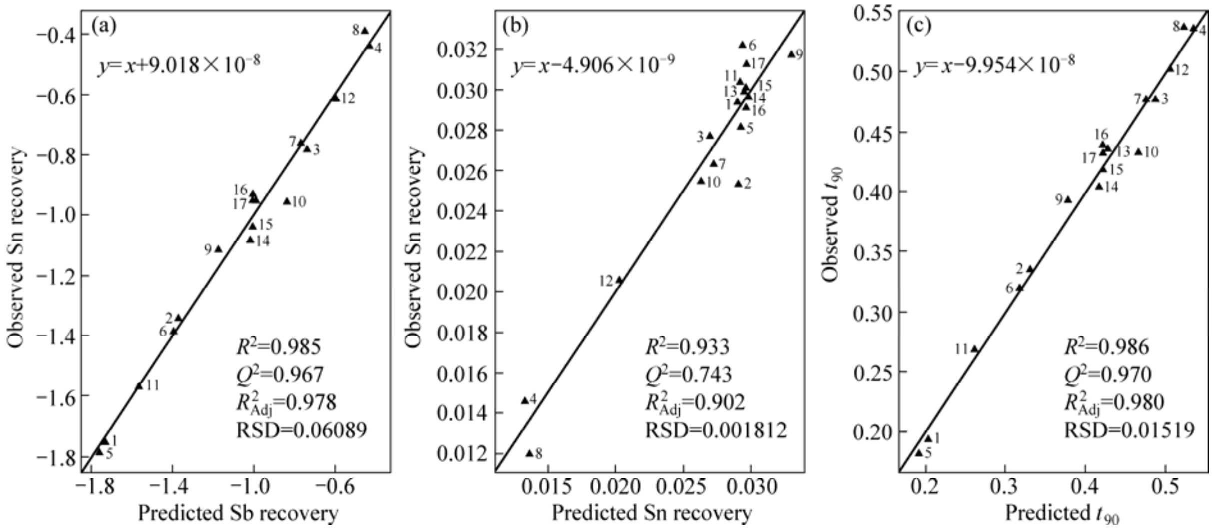

Fig. 8 Relationship between observed and predicted values for response variables of Sb and Sn recoveries and t_{90}

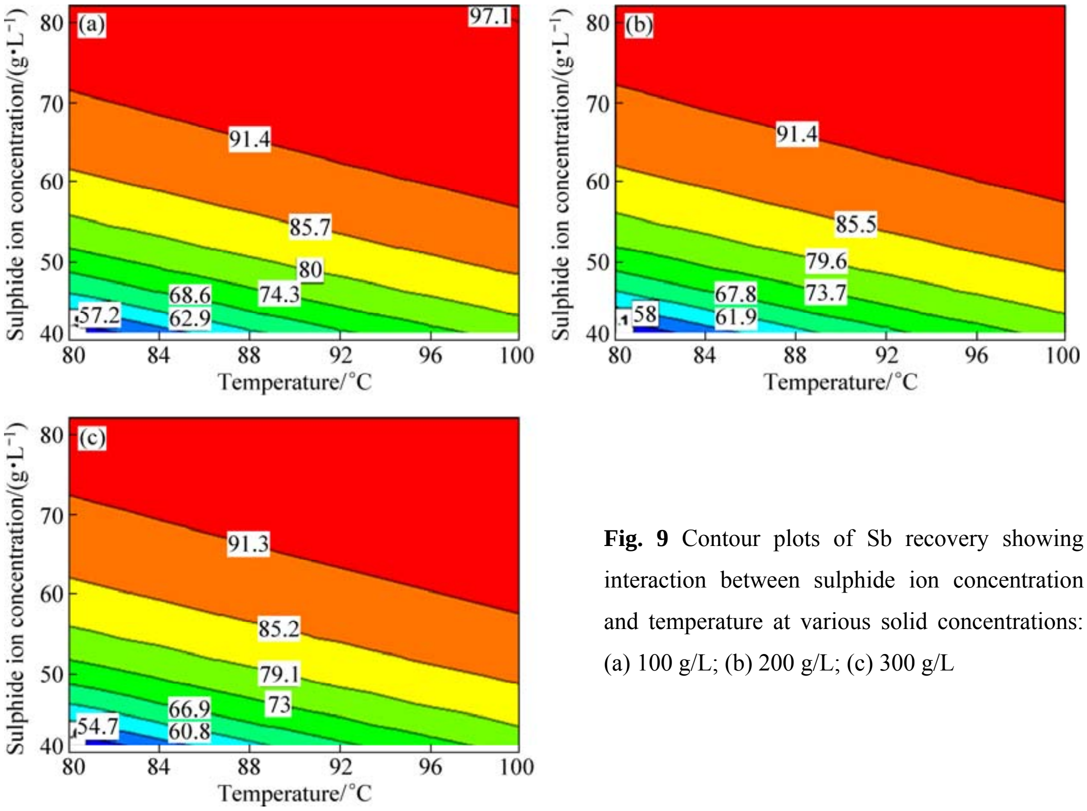

Fig. 9 Contour plots of Sb recovery showing interaction between sulphide ion concentration and temperature at various solid concentrations: (a) 100 g/L; (b) 200 g/L; (c) 300 g/L

temperature and sulphide concentration. At a lower leaching temperature and sulphide concentration, there is no appreciable amount of tin dissolving into the lixiviant. The reason could be that the tin mineral, stannite (Cu_2FeSnS_4), may be refractory to the lixiviant, as the case for the tetrahedrite mineral. Consequently, higher concentrations of sulphide and temperature would be needed to decompose the mineral for effective dissolution of tin. Under the studied condition, it is evident from Figs. 9 and 10 that the concentration of the solid leached does not influence tin or antimony recovery. For example, at 82 g/L sulphide ion concentration and 100 °C leaching temperature, tin recovery is 64.7%, 69.5% and 68.5% at 100, 200 and 300 g/L solid concentration, respectively.

Figure 11 shows the influences of temperature and sulphide concentration on the time required to dissolve 90% Sb from the copper concentrate. It can be seen from the contour plots that the time needed to leach out 90% Sb decreases with increasing temperature and sulphide concentration, with an insignificant effect of solid concentration. The model reveals that it is possible to

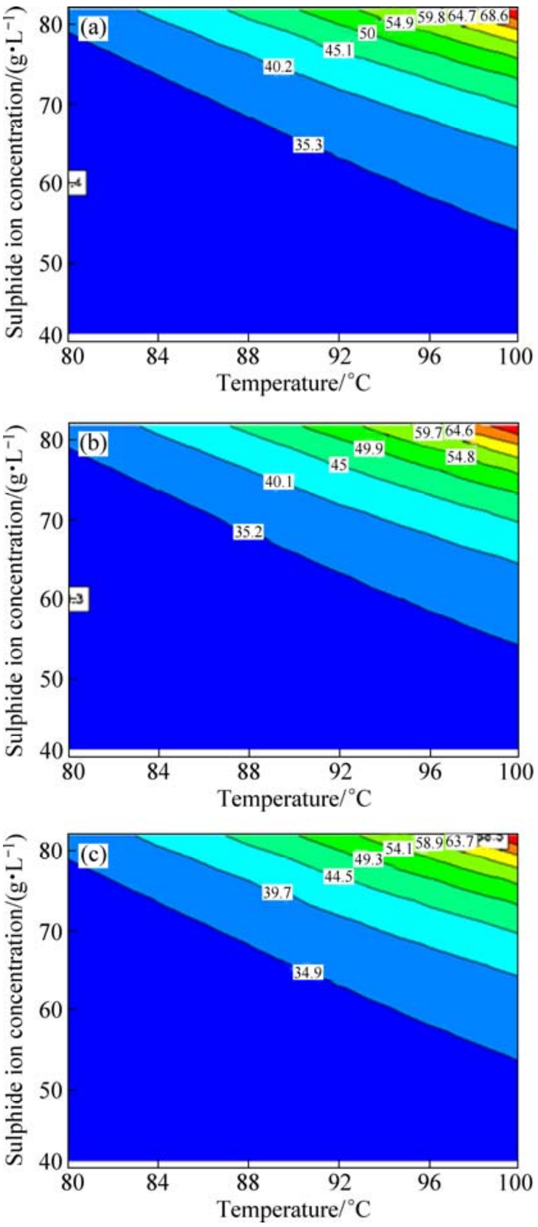

Fig. 10 Contour plots of Sn recovery showing interaction between sulphide concentration and temperature at various solid concentrations: (a) 100 g/L; (b) 200 g/L; (c) 300 g/L

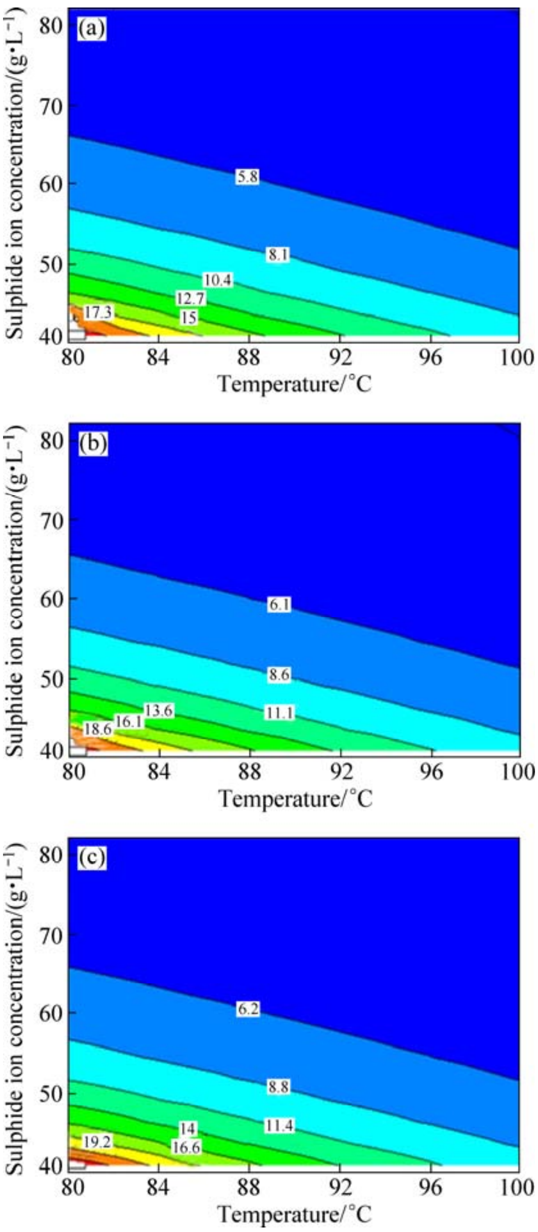

Fig. 11 Contour plots for t_{90} showing interaction between sulphide ion concentration and temperature at various solid concentrations: (a) 100 g/L; (b) 200 g/L; (c) 300 g/L

leach at lower sulphide concentration and temperature, which is beneficial to the process and still ensures high metal recovery over an extended leaching time. For instance, the lower left corners of the plots in Fig. 11 state the leaching conditions, at which 90% Sb can be obtained over 22 h duration of leaching, while the lixiviant concentration and temperature are at the minimum levels.

3.4 Model validation

In order to test the validity of the model with regards to the response variables of recovery of Sb and Sn, and t_{90}, a separate leaching experiment was performed at the conditions predicted by the model, as shown in Table 6 for 24 h. The results, as given in Table 6, indicate a close agreement with the values predicted by the model. Consequently, the model from a response surface methodology is considered to be accurate and reliable, for predicting the leaching of antimony and tin from the complex copper concentrate, and also good at predicting the time needed to recover 90% of the antimony from the concentrate.

3.5 Process optimization and economic implications

Furthermore, optimization of the factors affecting the leaching process can be carried out depending on what is expected from the process. If high recoveries of

Table 6 Validation of model

Temperature/°C	Sulphide ion concentration/(g·L^{-1})	Solid concentration/(g·L^{-1})	Sb recovery/%		Sn recovery/%		t_{90}/h	
			Predicted	Observed	Predicted	Observed	Predicted	Observed
80	45	290	48−64	52	30−35	26	16−22	20

Sb and Sn are desirable in as short as possible leaching time and at any cost, one might opt for leaching at a maximum temperature and sulphide ion concentration as displayed in Figs. 9 and 10. On the other hand, if for practical and economic reasons, low production cost due to heating energy and reagent cost, and less electrowinning problems due to high sulphide concentration, are desirable. A compromise must be made among these factors in order to have desirable leaching conditions. For instance, higher concentration of sodium sulphide would enhance antimony recovery. But, an excessive concentration of sodium sulphide would result in the formation of sodium polysulphide and sodium thiosulphate which will consequently lower the current efficiency of the onward electrolytic process, and thus adversely affecting the productivity and quality of the by-product [9]. As a result, a compromise must be established based on the properties of raw materials and solvent, and also with consideration of power consumption so as not to create problems during onward processing. Conversely, lower temperature and sulphide concentration can be used (Fig. 11) to set the factors in such a level to obtain a high recovery of Sb (min. 90%) by extending the leaching time.

The three parameters considered in this study affect the economics of the process in various ways. Increasing the leaching temperature accelerates the leaching kinetics, resulting in a smaller volume for the leach tanks. For temperatures above 90° C, filtration will have high maintenance costs due to material constraints, necessitating the use of additional cooling equipment prior to filtration. Therefore, the preferable leaching temperature is 90 °C. There exists a strong correlation between the soluble sulphide (free ion) concentration and the leaching rate. However, raising the sulphide concentration could reduce the tank volumes at the expense of an increase in sulphide losses to the bleed stream. So any savings in capital expenditure is likely to be offset by an increase in operating cost. In practice, the process would have a large recycle stream and a small bleed stream, to minimise the loss of sulphide lixiviant. Another effective means of reducing the tank volumes is to increase the solids concentration. The result would be an increase in the solution metal concentrations reporting downstream, which would improve the recovery of antimony. Further work is in progress in order to determine the maximum solid concentration that is technically feasible. This will be communicated in our subsequent publication.

4 Conclusions

1) Modelling and optimisation of alkaline sulphide leaching of a complex copper concentrate containing 1.69% Sb and 0.14% Sn were conducted using response surface methodology−central composite face-centred design (RSM−CCF).

2) It was demonstrated that the leaching process was strongly dependent on the reaction temperature as well as the sulphide ion concentration with insignificant dependence on solid concentration within the experimental range studied.

3) A strong mathematical model with no lack of fit was developed and the validity of the model was confirmed experimentally. The result shows that the model is reliable and accurate for predicting the leaching process.

Acknowledgement

The authors would like to appreciate the following organisations, VINNOVA, Boliden Mineral AB, LKAB and the Adolf H. Lundin Charitable Foundation, for their financial supports. The contribution from the Centre of Advanced Mining & Metallurgy (CAMM) is gratefully acknowledged.

References

[1] RIVEROS P A, DUTRIZAC J E. The leaching of tennantite, tetrahedrite and enargite in acidic sulphate and chloride media [J]. Canadian Metallurgical Quarterly, 2008, 47: 235−244.

[2] MIHAJLOVIC I, STRBAC N, ZIVKOVIC Z, KOVACEVIC R, STEHERNIK M. A potential method for arsenic removal from copper concentrates [J]. Minerals Engineering, 2007, 20: 26−33.

[3] BALÁŽ P, ACHIMOVIČOVÁ M. Selective leaching of antimony and arsenic from mechanically activated tetrahedrite, jamesonite and enargite [J]. International Journal of Mineral Processing, 2006, 81: 44−50.

[4] FILIPPOU D, ST-GERMAIN P, GRAMMATIKOPOULOS T. Recovery of metal values from copper-arsenic minerals and other related resources [J]. Mineral Processing and Extractive Metallurgy Review, 2007, 28: 247−298.

[5] CATINAT M. Report for the Ad-hoc working group on defining critical raw materials [R]. European Commission-Enterprise and Industry. Brussels, 2010: 85.

[6] AWE S A, SAMUELSSON C, SANDSTRÖM Å. Dissolution kinetics of tetrahedrite mineral in alkaline sulphide media [J]. Hydrometallurgy, 2010, 103: 167−172.

[7] ANDERSON C G, NORDWICK S M, KRYS L E. Processing of

antimony at the Sunshine mine [C]//Residues and Enffluents: Processing and Environmental Considerations. The Minerals, Metals and Materials Society, 1991: 349−366.

[8] BALÁŽ P, KAMMEL R, VILLACHICA C. As and Sb leaching from polymetallic sulfide concentrates [J]. Metall (Berlin, West), 2001, 55: 196−200.

[9] ZHAO Tian-cong. The metallurgy of antimony [M]. Changsha: Central South University of Technology Press, 1988. (inChinese)

[10] ANDERSON C G, KRYS L E. Leaching of antimony from a refractory precious metals concentrate [C]// HISKEY J B, WARREN G W. Hydrometallurgy Fundamentals, Technology and Innovations, Salt Lake City, Utah, 1993: 341−362.

[11] ANDERSON C G, TWIDWELL L G. Hydrometallurgical processing of gold-bearing copper enargite concentrates [J]. Canadian Metallurgical Quarterly, 2008, 47*:* 337−346.

[12] NADKARNI R M, KUSIK C L, HEISSNER H P. Method of removing arsenic and antimony from copper ore concentrate: US3911078 [P]. 1975.

[13] NORDWICK S M, ANDERSON C G. Advances in antimony electrowinning at the Sunshine mine [C]//HISKEY J B, WARREN G W. Hydrometallurgy Fundamentals, Technology and Innovations. Salt Lake City, Utah, 1993: 1107−1128.

[14] ANDERSON C G, NORDWICK S M, KRYS L E. Antimony separation process: US5290338 [P]. 1994.

[15] HOLMES W C. How electrolytic antimony is made at the Sunshine plant [J]. Engineering and Mining Journal, 1944, 145: 54−58.

[16] LINDSTROM NFR. Method for the electrolytic recovery of Sb, As, Hg and/or Sn: US4017369 [P]. 1977.

[17] DAYTON S. Equity silver on line with leach plant: How Sb and As are purged from a high-silver copper concentrate before smelting [J]. Engineering and Mining Journal, 1982, 183: 78−83.

[18] EDWARDS C R. Engineering the Equity concentrate leach process [C]//Complex Sulfides — Processing of Ores, Concentrates and By-products. San Diego, Califonia, 1985: 197−219.

[19] AWE S A, SANDSTRÖM Å. Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution [J]. Minerals Engineering, 2010, 23: 1227−1236.

[20] MONTGOMERY D C. Design and analysis of experiments [M]. John Wiley & Sons, Inc, 2009.

[21] ERIKSSON L, JOHANSSON E, KETTANEH-WOLD N, WIKSTRÖM C, WOLD S. Design of experiments—Principles and applications [M]. UMETRICS AB, Umeå, 2008.

[22] ZHANG Z, PENG J, SRINIVASAKANNAN C. Leaching zinc from spent catalyst: Process optimization using response surface methodology [J]. Journal of Hazardous Materials, 2010, 176: 1113−1117.

[23] MEHRABANI J V, NOAPARAST M, MOUSAVI S M, DEHGHAN R, GHORBANI A. Process optimization and modelling of sphalerite flotation from a low-grade Zn−Pb ore using response surface methodology [J]. Separation and Purification Technology, 2010, 72: 242−249.

[24] GARCÍA V, LANDABURU-AGUIRRE J, PONGRÁCZ E, PERÄMÄKI P, KEISKI R L. Dehydration of water/ dichloromethane/n-butanol mixtures by pervaporation; optimisation and modelling by response surface methodology [J]. Journal of Membrane Science, 2009, 338: 111−118.

[25] AWE S A, SANDSTRÖM Å. Leaching mechanism of tetrahedrite in alkaline sulfide solution [C]//Conference in Minerals Engineering. Luleå, Sweden, 2010: 13−24.

[26] AWE S A, SANDSTRÖM Å. Upgrading of an impure copper concentrate for pyrometallurgical processing [C]//Proceedings of European Metallurgical Conference. Dusseldorf, Germany, 2011: 15−31.

复杂铜精矿除锑的建模与工艺优化

Samuel Ayowole AWE[1], Mohammad KHOSHKHOO[1], Paul KRUGER[2], Åke SANDSTRÖM[1]

1. Division of Minerals and Metallurgical Engineering, Department of Civil, Environmental and
Natural Resources Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden;
2. Boliden Mineral AB, SE-936 81 Boliden, Sweden

摘　要：对一种含 1.69% Sb 和 0.14% Sn 的铜精矿进行碱性硫化物浸出以除去 Sb 和 Sn，对浸出条件建立数学模型，并对工艺条件进行优化。采用响应面方法并结合面心立方中央复合设计来优化工艺参数。选取浸出温度、硫化物浓度和固体含量作为变量参数，而将 Sb 和 Sn 的浸出率和达到浸出 90% Sb 所需时间作为响应参数。结果表明：温度和硫化物浓度对 Sb 和 Sn 的浸出影响显著，而固体含量的影响不显著。建立了一个数学模型来描述浸出条件，实验验证了该模型是可靠与准确的。

关键词：碱性硫化物湿法冶金；锑；黝铜矿；浸取优化；响应面方法；面心立方中央复合设计

(Edited by YUAN Sai-qian)