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Purification of a Phosphorous-Containing Scheelite Ore Concentrate: A "Design-of-Experiment" Study

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ABSTRACT

A "design-of-experiment" (DOE) approach was used to study the purification of a scheelite ore concentrate in HCl. The ore concentrate contained about 65% $CaWO_4$, 18% $CaCO_3$, 14% $Ca_{10}(PO_4)_6(OH)_2$, and 3% SiO_2. In addition to these major phases, the ore concentrate also contained trace amounts of toxic elements such as arsenic, lead, and uranium. These elements were associated with the apatitic part of the ore. The results of DOE experiments indicated that calcite can be selectively removed with a low HCl concentration, and the resulting calcium-containing solution may be used for other applications. Apatite can then be removed with a high concentration of HCl. This solution contains toxic elements such as arsenic, lead, and uranium because of the association of these elements with apatite. High temperature seemed to enhance the dissolution of unwanted tungsten (scheelite part of the ore concentrate), perhaps due to the formation of P- and As-containing heteropoly anions of W, such as $PW_{12}O_{40}^{3-}$ and $AsW_{12}O_{40}^{3-}$ (formation of heteropoly anions may be favored at high temperature).

Key Words. Scheelite ore concentrate; Purification; Design of experiment

INTRODUCTION

Because of its high melting point, high density, good corrosion resistance, and the good thermal and electrical conductivity properties of its alloys, tungsten can be used advantageously in the production of numerous end-use items

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(1). For example, it is one of the most important refractory metals used in the manufacturing of crucial components of light sources (2). It is also used in the manufacturing of hard metals, i.e., cemented tungsten carbide, which are employed in the manufacture of tough and high wear-resistance materials such as machine tools (3).

Tungsten, in large part, is produced from the minerals wolframite and scheelite. The mineral scheelite (calcium tungstate) is normally found in quartz veins and in contact with so-called skarn ores of complex mineralogical composition (4). It is therefore associated with a large number of different minerals. These include main scarn minerals such as garnets, pyroxene, and amphibole, and other minerals such as calcite, apatite, quartz, etc. Different arsenopyrites and antimonites are also often found in skarn ores together with scheelite (4).

Scheelite ores can be classified into five different categories (5), i.e., 1) scheelite simple ore, 2) scheelite-sulfides ore, 3) scheelite-cassiterite ore, 4) scheelite-calcite-apatite ore, and 5) scheelite-powellite ore. The content of scheelite in a scheelite ore concentrate is normally expected to be more than 80% (tungsten content $\approx$ 56%). This is about 89% of the theoretical content of W in $CaWO_4$, which contains 63.8% W ($\approx$ 80.5% WO_3). However, low-grade ores with a WO_3 content as low as 13.9% have also been reported (6). Ore concentrates containing low concentrations of tungsten and high concentrations of calcium are associated with calcium phases other than scheelite such as calcite and calcium hydroxyapatite.

Tungsten processors, such as Osram Sylvania, use a large variety of feeds. Some feeds cannot be processed by normal methods. For example, the ore concentrates containing calcite and hydroxyapatite cannot be processed by typical hydrometallurgical methods (and require pretreatment to remove phosphorous). This is especially true when scheelite ore is processed via a caustic leaching process (7). In addition, it may be cheaper at times to buy ores containing certain impurities, or only ores with certain impurities may be available in the market. This suggests that the development of efficient methods for purification of tungsten ore concentrates (prior to typical processing methods) is important.

Although pretreatment methods of scheelite ore concentrates containing phosphorous (and other impurities) are known (7), no research work regarding the optimization and details of experimental parameters has been reported. So the purpose of this paper is to use a "design-of-experiment" (DOE) strategy for the optimization of experimental conditions used in the pretreatment of an ore concentrate in hydrochloric acid. DOE has proven to be the most efficient way of process optimization, as it is time- and cost-effective and often leads to interesting and new chemistry (8–11).

EXPERIMENTAL

Instrumentation

Phase identification of the ore sample (powdered to sieve through a 40-mesh screen) was carried out by powdered x-ray diffraction (XRD). Scanning electron microscopy with an energy dispersive x-ray analyzer (SEM-EDAX) was used for the microanalysis of individual particles (coated with Au) and morphological identification of different crystals. Wavelength-dispersive x-ray fluorescence spectrometry (WD-XRF) was used for quantitative chemical analysis. Analysis of trace concentrations of As and U was carried out by glow discharge mass spectrometry (GDMS).

Design of Experiments (DOE)

A 2-levels 3-factors design was used. The following parameters (factors) were included in the experimental design: 1) slurry density (g ore concentrate per 100 mL HCl), 2) HCl concentration (M), and 3) temperature (°C). Data were processed by Design-Expert Version 5.0.4 software. The range for design parameters is presented in Table 1.

Procedure

The appropriate amount of ore sample was weighed into an Erlenmeyer flask. A specified amount of acid was then added, and the stoppered flask was placed in a constant temperature bath and agitated. After 2 hours the slurry was filtered. Samples of the filtrate were submitted for elemental analysis. After washing with water, the solid samples were dried at 110°C, weighed accurately, and submitted for XRF, XRD, and GDMS analyses.

RESULTS

Characterization

The x-ray diffractogram and WD-XRF analysis indicated that the ore concentrate contained about 65% $CaWO_4$, 18% $CaCO_3$, 14% $Ca_{10}(PO_4)_6(OH)_2$,

TABLE 1
Design Parameters and Their Chosen Values

	Chosen values	
Parameters/factors	Low	High
A. Slurry density (g/100 mL)	24	72
B. HCl concentration (M)	0.1	3.0
C. Temperature (°C)	20	60

TABLE 2
DOE Results of the Dissolution of Ore Concentrate in HCl: Factors and Responses

Design ID	Slurry density (g ore/100 mL): Factor A	HCl concentration (M): Factor B	Temperature (°C): Factor C	P (mg/L) response	% P removal response	As (mg/L) response	Weight (g) response	W (mg/L) response	W efficiency[a] (%)	W (%) response
1	24	0.1	20	0	0.0	0	20.85	0	>99.9	44.4
2	72	0.1	20	0	0.0	0	65.05	0	>99.9	41.7
3	24	3	20	6,500	104.2	15	14.98	1,700	98.2	58.9
4	72	3	20	11,000	58.8	43	55.45	610	99.8	50.1
5	24	0.1	60	1.3	0.0	0	21.66	0	>99.9	41.8
6	72	0.1	60	0.64	0.0	0	69.30	0	>99.9	44.4
7	24	3	60	6,300	101.0	12	14.98	2,100	96.9	55.5
8	72	3	60	9,400	50.2	33	52.73	980	99.7	51.6

[a] Efficiency is defined as: [(weight of W in recovered ore)/(weight of W in recovered ore + weight of W in filtrate)].

and 3% SiO_2 (12). WD-XRF and GDMS analyses indicated that in addition to these major phases, the ore concentrate also contained trace amounts of toxic elements such as arsenic, lead, and uranium. These elements were associated with the apatitic part of the ore (12).

Design Analysis

Design factors and responses are presented in Table 2. Design-Expert software was utilized to calculate the factor effects relative to dissolved phosphorous (P), arsenic (As), and tungsten (W) in HCl under various experimental conditions. Factorial effect is defined as the change in average response when a factor goes from its low level to its high level.

Figure 1 presents the half-normal percent probability plot for the analysis of phosphorus. This plot is used to sort the significant (vital) effects from error (negligible effects). Negligible effects will fall to near zero on the straight line while significant effects will be outliers. As can be seen (Fig. 1), Factor B was selected as a significant effect. The probability of a zero difference between error and the selected effect was less than 0.1% (Table 3). The coefficient estimate (defined as one-half of the coded factorial effect) for selected effect is also listed in Table 3.

The effect of HCl concentration (Factor B) on phosphorous (P) concentration (dissolved in HCl) can be seen in Fig. 2. It is clear that P, i.e., the apatitic part of the ore concentrate, dissolved only in a high (3.0 M) concentration of HCl. At a low concentration of HCl (0.1 M), apatite remained completely undissolved, as all the acid was consumed to dissolve $CaCO_3$. This was confirmed by XRD analysis and the sample weight loss. A substantial amount

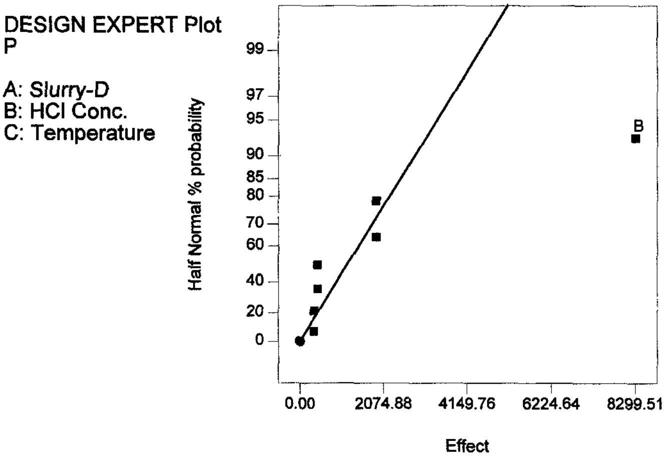

FIG. 1 Half-normal probability plot for the analysis of phosphorus (P).

TABLE 3
ANOVA Results and Coefficient Estimates for the Analysis of Phosphorous

Source	Sum of squares	*DF*	Mean square	*F* value	Probability > *F*
Model	1.4×10^8	1	1.4×10^8	52.5	0.0004
Residual	1.6×10^7	6	2.6×10^6		
Cor. total	1.5×10^8	7			
Root MSE	1620		R^2	0.8975	
Dep mean	4150		Adjusted R^2	0.8804	
C.V. %	39.0		Predicted R^2	0.8177	
PRESS	2.8×10^7		Adequate precision	10.2 (desired > 4)	

Factor	Coefficient estimate	*DF*	Standard error	*t* for H_0, coefficient = 0	Probability > |*t*|
Intercept	4150	1	573		
B, HCl concentration	4150	1	573	7.3	0.0004

(>60%) of calcite dissolved in low (0.1 M) acid concentration. This is a significant finding indicating that calcite can be selectively dissolved from the ore concentrate with a dilute HCl solution. The dissolution of calcite from the ore concentrate can be explained on the basis of the following chemical reactions:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2CO_3 \quad (1)$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \quad (2)$$

$$CaCO_3 + HCO_3^- \rightarrow CaHCO_3^+ + CO_3^{2-} \quad (3)$$

It is clear from the above that the reaction of HCl with calcite produces soluble calcium chloride and carbonic acid which further reacts with calcite to form other soluble calcium species.

Dissolution of apatite (P) occurred only in 3 M HCl. A combined effect of Factors A (slurry density), B (HCl concentration), and C (temperature) (Fig. 3) indicated that apatite (along with calcite) was quantitatively dissolved under the conditions of Runs 3 and 7 (Table 3) i.e., in 3.0 M HCl with a slurry density of 24 g per 100 mL. The dissolution of apatite can be explained on the basis of the following chemical reaction:

$$Ca_{10}(PO_4)_6(OH)_2 + 20HCl \rightarrow 10CaCl_2 + 6H_3PO_4 + 2H_2O \quad (4)$$

Analysis of dissolved arsenic (As), depicted in Figs. 4 and 5, was similar to that of phosphorous. This suggested that As was associated in the ore concentrate with P. Because As and other elements dissolved in 3.0 M HCl from apatite are highly toxic, this discard solution requires careful waste disposal.

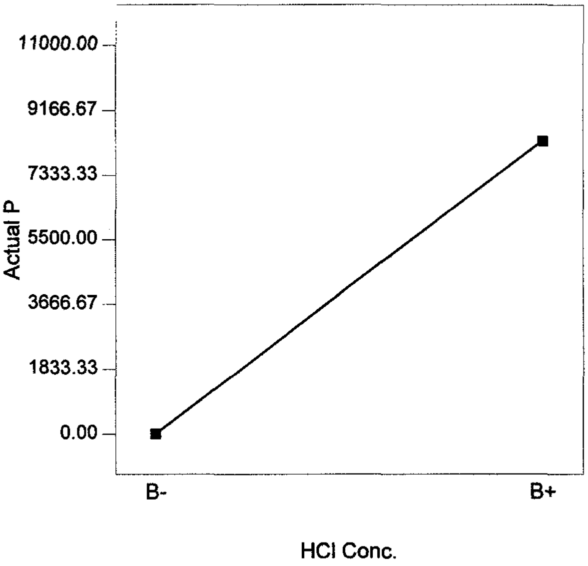

FIG. 2 The effect of Factor B, HCl concentration, on dissolved P (mg/L).

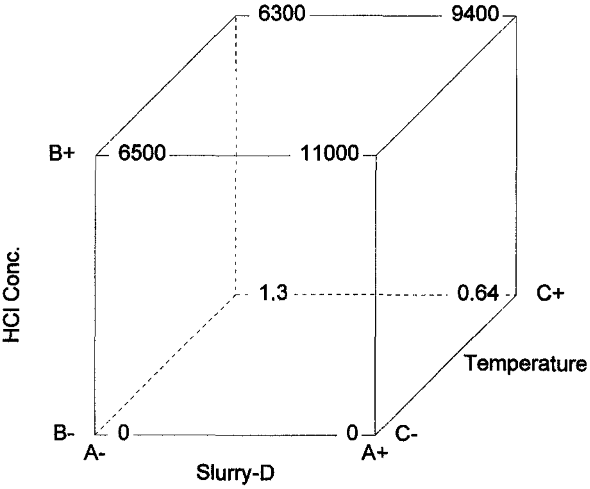

FIG. 3 Combined effect of Factors A, slurry density; B, HCl concentration; and C, temperature on dissolved P (mg/L).

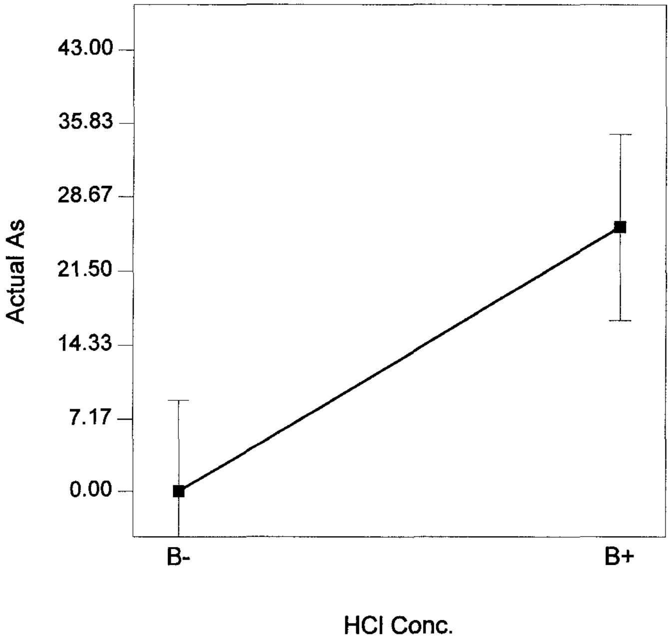

FIG. 4 The effect of Factor B, HCl concentration, on dissolved As (mg/L).

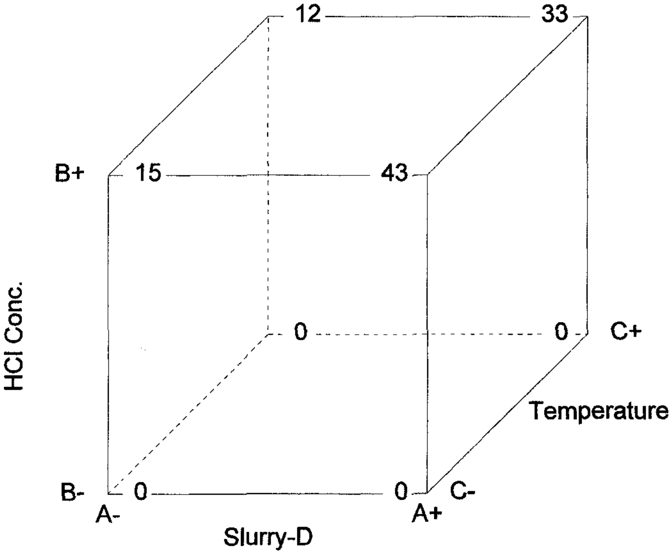

FIG. 5 Combined effect of Factors A, slurry density; B, HCl concentration; and C, temperature on dissolved As (mg/L).

DISCUSSION

The DOE results presented in this paper indicate that if an ore concentrate contains both calcite and apatite, calcite can be selectively removed using a low HCl concentration. Apatite can then be dissolved in a high HCl concentration, and this toxic solution can be carefully disposed of. According to the published literature (7), removal of P from the ore is carried out in two steps; however, an explanation of this effect was not provided.

The work presented herein also indicates that there might be a benefit to carrying out the purification of calcite-apatite-scheelite ore concentrate in two steps. Calcium solution produced via selective dissolution of calcite can be used for other applications (as this solution does not contain toxic elements such as As, Pb, U, etc.). This selective removal of calcite as a calcium solution will also make the dissolution of apatite in a high HCl concentration more efficient. This is because high levels of calcium (produced via the dissolution of calcite), if not removed, would inhibit the dissolution of apatite by the common ion effect as well as by the reprecipitation of phosphate ions (as calcium phosphate) produced through the dissolution of apatite. The latter was confirmed by XRD analysis of solids obtained at the end of Run 4 (Table 2) which indicated the presence of a trace concentration of a calcium phosphate phase other than apatite.

One other notable result of this work was that high temperature is not desired as it seemed to facilitate the dissolution of unwanted scheelite (for example, compare the W efficiency in Runs 3 and 7, Table 2). This may perhaps be due to the formation of P- and As-containing heteropoly anions (such as $PW_{12}O_{40}^{3-}$ and $AsW_{12}O_{40}^{3-}$) which consume 12 atoms of W with each atom of P and As. The formation of these compounds is favored at high temperature.

CONCLUSION

For efficient preliminary purification of a scheelite ore concentrate (i.e., to remove selectively calcium phases other than scheelite), its accurate phase characterization is required. Purification of an ore concentrate containing calcite and apatite (as in a calcite-apatite-scheelite ore concentrate) should be carried out in two steps: 1) to remove selectively calcite at a low HCl concentration and 2) to remove selectively apatite at a high HCl concentration. Use of high temperature (higher than ambient) is not desired. In fact, high temperature would have a negative effect as it facilitates the dissolution of unwanted scheelite phases. The work reported herein could lead to the development of more efficient methods for the purification of scheelite ore concentrate.

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REFERENCES

1. E. B. Amey, in *Encyclopedia of Chemical Processing and Design, Vol. 59* (J. J. McKetta, Ed.), Dekker, New York, NY. 1997, pp. 130–153.
2. G. Eichelbronner, *Int. J. Refract. Met. Hard Mater.*, *16*, 5–11 (1998).
3. L. J. Prakash, *Ibid.*, *13*, 257–264 (1995).
4. "Chapter I: Rhenium, Molybdenum, and Tungsten," in *Rare Earths*, 3rd ed. (Translated from Russian by the Israel Program for Scientific Translation, O. A. Songina, Ed.), Jerusalem, 1970, pp. 15–71.
5. M. Shamsuddin and H. Y. Sohn, in *Extractive Metallurgy of Refractory Metals* (H. Y. Sohn, O. N. Carlson, and J. T. Smith, Eds.), (Proceedings of 110th AIME Annual Meeting, Chicago, IL, February 22–26, 1981). AIME, New York, NY, 1981, pp. 205–230.
6. P. B. Queneau, D. K. Huggins, and L. W. Beckstead, *Ibid.*, pp. 237–267.
7. S. W. H. Yih and C. T. Wang, *Tungsten: Sources, Metallurgy, Properties and Applications*, Plenum Press, New York, NY, 1981, Chapter 2, pp. 79–128.
8. I. J. Barnabas, J. R. Dean, W. R. Tomlinson, and S. P. Owen, *Anal. Chem.*, *67*, 2064–2069 (1995).
9. S. Ubaldini, L. Piga, P. Fornari, and R. Massidda, *Hydrometallurgy*, *40*, 369–379 (1996).
10. G. K. Das, S. Acharya, S. Anand, and R. P. Das, *Ibid.*, *39*, 117–128 (1995).
11. M. J. Anderson and P. J. Whitcomb, *Chem. Eng. Prog.*, pp. 51–60 (December 1996).
12. R. P. Singh and M. J. Miller, in *Light Metals 1998* (B. J. Welch, Ed.), (Proceedings of the Technical Sessions Presented by the TMS Aluminum Committee at the 127th TMS Annual Meeting, San Antonio, TX, February 15–19, 1998), TMS, Warrendale, PA, 1998, pp. 1343–1347.

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