Optimized Leaching Conditions for Selenium from Sar-Cheshmeh Copper Anode Slimes

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ABSTRACT: *The recovery process of selenium from Iranian Sar-Cheshmeh copper anode slimes employing hydrometallurgical methods has been investigated. The copper anode slimes are made up of those components of the anodes, which are not soluble in the electrolyte. They contain varying quantities of precious metals like gold, silver, selenium and tellurium. They are being extracted as a by product in the copper production process.*
In this paper, some parameters affecting the leaching conditions of anode slimes in nitric acid are studied. Taguchi experimental design method is used to find out the effect of acid concentration, temperature and time.
The statistical results of the experiments show that the above parameters are important in the leaching of -10 microns fraction. The optimum conditions determined are: T = 90^o C, acidity = 4 M and the leaching time = 60 min. Under these conditions, 99 % of the selenium is leached out.

KEY WORDS: *Sar-Cheshmeh mine, Copper anode slimes, Hydrometallurgy, Selenium extraction*

INTRODUCTION

Anode slimes refer to the residual materials generated at the bottom of the electrolysis cells during the refining of copper. Copper anode slimes from Sar-Cheshmeh (a mine in the Southeast of Iran) are black in colour and are extremely fine-grained. According to Abdollahy [1], the copper anode slimes, from Sar-Cheshmeh are composed mainly of 9.41 % selenium, 12.86 % copper, 3.35 % silver, 0.1 % gold and about 45% barite, plus lead, tellurium, antimony, sulphur, silica,with small amounts of nickel, iron, zinc, bismuth and traces of arsenic, cadmium, cobalt and manganese.

In the periodic table, selenium is located between sulphur and tellurium, therefore it shares characteristics of both elements. Selenium's proximity to tellurium results in important separation problems when these two element co-exist in solution. Both are readily precipitated

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from soltion with sulphur dioxide. However, reduction of tellurium from solution with sulphur dioxide is inhibited in strongly acidic chloride solution. Dilute sulphuric and hydrochloric acid do not attack selenium.

Hydrometallurgical processes are designed to recover precious metals, such as gold, silver, selenium and tellurium etc., from the anode slimes with small amounts of impurities. More recently increasing attention has been paid to improving the recovery of by products. These processes are economic, and energy saving as well as pollution free. They comprise three stages: (a) leaching, where the valuable elements are dissolved in the aqueous solution, (b) solvent extraction, where metals are recovered and purified, (c) reduction, where metallic ions are precipitated from solution [2].

Hoffmann [3] has described the various separation and recovery processes for selenium from copper anode slimes based on the chemistry of selenium. It is concluded that there is no one best process, because the optimum selenium technology processes depends on many factors including copper refinery location, environmental and regulatory conditions, local markets for selenium or selenium chemicals and other plant processes.

The initial separation of tellurium from selenium in solution is carried out by neutralisation [4]. Tellurium precipitates as TeO_2 whereas selenium remains in solution as selenious acid. Selenium is later reduced by sulphur dioxide as amorphous selenium.

$$H_2SeO_3 + 2SO_2 + H_2O \rightarrow Se + 2H_2SO_4$$

An entirely hydrometallurgical process has been described by Subramanian et al. [5] to recover silver and other valuable elements such as Se, Te, Ni and precious metals from copper and nickel anode slimes. The authors have proposed a method to avoid or minimise the need for Dore′ smelting. In another route, similar treatment is carried out by Subramanian et al. [5]. In addition to the recovery of silver and selenium, the treatment of other elements such as tellurium and precious metals, in particular, Au, Pt, and Pd has been studied.

Another hydrometallurgical process has been published by Heimala et al. [6] for the recovery of silver, selenium and tellurium from the anode slimes, in which the decopperised slimes are sulphated in an iron tank containing concentrated sulphuric acid at about 180 °C for four hours. The silver, selenium and tellurium are dissolved in the sulphuric acid, also nickel is sulphated.

Wang et al. [2] presented a new hydrometallurgical process for recovering precious metals from copper refinery anode slimes. The unit operations used were mainly leaching, liquid-liquid extraction and reduction. The author employs decopperised slimes to extract silver, selenium, tellurium and gold. The decopperised anode slime is first leached with nitric acid at a concentration of about 4 to 9 M and at an elevated temperature between 40-115 °C to obtain a leach solution, in which, silver, selenium and tellurium are dissolved, whereas gold and other impurities remain in the residue. Silver in the leach solution is recovered in the form of silver chloride by adding stoichiometric proportions of hydrochloric acid.

Another method proposed by Hoffman [7], is to remove selenium after decoppering, prior to leaching for silver. A variety of processes have been developed for the removal of selenium from anode slimes, the most commonly applied, are sulphation roasting methods. Silver which is present in the sulphated slimes calcine as silver sulphate, can then be recovered by leaching with calcium nitrate according to the following reactions:

$$Ag_2Se + 4H_2SO_4 \rightarrow Ag_2SO_4 + SeO_2 + 4H_2O + 3SO_2 \qquad (1)$$

$$Ag_2SO_4 + Ca\,(BO_3)_2 \rightarrow 2AgNO_3 + CaSO_4 \qquad (2)$$

Because calcium sulphate is much less soluble than silver sulphate, the sulphate ion is precipitated from solution resulting in the formation of the highly soluble silver nitrate. The silver nitrate bearing solution contains other impurity elements present in the sulphated slimes, particularly, Se, Sb, As, Pb, Cu. To purify the silver bearing solution, advantage is taken of the difference in pH at which Ag and the various impurities hydrolyse. All impurities except lead hydrolyse at least two to three pH units lower than the pH at which silver would begin to hydrolyse. To further decrease the concentration of the impurity metals in solution, ferric ion, either as ferric nitrate or ferric sulphate is added to the solution. Finally the purified solution of silver nitrate can be electrolysed to recover elemental silver.

Recovery and separation of Se, and Te was again proposed by Morrison [8] using alkaline pressure leaching in the presence of oxygen to extract selenium and tellurium at higher efficiencies, followed by purification and a reduction process.

Finally the leach solution contaminated with impurities, is treated by a liquid – liquid extraction technique to separate selenium from other impurities.

The slimes are the raw materials from which more than 90 % of selenium is produced in the world [9]. Anode slimes, on the other hand, are considered to be the first source of selenium. In this research work the possibility of selenium extraction from Sar–cheshmeh copper anode slimes was being studied.

MATERIALS AND EQUIPMENTS

Nitric acid obtained from Merck GmbH (Darmstadt, Germany) was used here to dissolve and extract selenium. The reaction vessel was a 1000 ml flanged pyrex glass vessel consisting of a five necked top and a flat bottom connected by a metallic clip. A magnetic stirrer was utilised for agitation. A thermometer and isothermal electric heating mantle were applied for monitoring and controlling temperature and heating, respectively.

SAMPLE PREPARATION

Raw copper anode slimes, as received from Sar-Cheshmeh, were first analysed by various methods including atomic absorption (AAS) and X-ray diffraction (XRD) both qualitatively and quantitatively to determine the percentage of major elements, table 1. The anode slimes also comprise of the following major phases:

$$Se,\ BaSO_4,\ \alpha\text{-}SiO_2,\ \beta\text{-}Ag_2Se,\ CuAgSe,$$

The specific gravity of the slimes were found to be 4.7 g/cm^3.

According to Abdollahy [1], about 62 % by weight of the total product was below 10 μm. The chemical analysis showed that the barium sulphate was the major compound in the + 10 μm, whereas more than 90 % of the precious metals such as selenium, silver, copper and gold was concentrated in the ultrafine fraction (-10 μm). Therefore - 10 μm fraction was separated for leaching.

In the leaching study of anode slimes, in order to find the factors affecting the process, the Taguchi method in the experimental design was used. The three main factors, i.e., temperature, time and the acidity were studied in a 3^3 design. The three levels of factors were selected according to the preliminary test and the previous researcher as being found in the literature [1-8].

STATISTICAL DESIGN OF EXPERIMENTS

It should be first emphasized that experimental design, factorial design and Taguchi method, is merely a tool and will not replace technical judgment or creativity in experimental work. In a broad way, the purpose of statistical experimental analysis is to investigate the significance of systematic effects. The application of this kind of experiments requires careful planning, prudent layout of experiment, and expert analysis of results. Based on years of research and applications, Taguchi has standardized methods for each of these design of experiments application steps.

Generally, statistical project consists of five fundamental steps:

1-Problem definition
2- System identification
3- Statistical model formulation
4- Data collection
5- Statistical analysis and results

The scope of the above five steps can be summarized as follows:

Problem definition

The basic purpose of this phase is to specify the scope of the problem to be investigated. This can be done by stating the objective or the study of the major assumptions made concerning the particular conditions that define the environment in which a set of experiments will be conducted to perform the corresponding data analysis. Often a correct solution cannot be found for a problem as a result of an incomplete definition.

System identification

A system can be defined as a collection of elements acting and interacting in order to perform a common function. The specific purpose of this phase is to identify the variables and the levels that are believed to be significant in the study.

The variables can be grouped into two major classifications: (a) independent variables or factors, (b) dependent variables or responses.

Table 1: Chemical analysis of SarCheshmeh copper anode slimes (major elements)

Fraction	Barium Sulphate, %	Silver, %	Selenium, %	Gold, %
Raw slimes	52.05	3.35	9.41	0.10
-10 μm	39.69	5.51	15.34	0.16

Statistical model formulation

A model is an ideal representation of a system. In the case of statistical experiments, a model is a mathematical relationship that describes the value of a random observation in terms of collection of components with assignable causes and a random error which by definition does not have an assignable cause.

Data Collection

Data are collected for each of the experimental conditions of a system in order to assess the significance of each term having an assignable cause in the statistical model. The assignable cause can be either a factor or an interaction among several factors. For proper use of experimental data, the following three basic principles of the design of experiments must be observed. [10,11]

Randomization

Replication

Local control

Statistical Analysis

The random error term of the statistical model can not be predicted for a single observation, but it approaches zero in the long run. On the basis of a random sample it is possible to estimate the value of each term of the model. The aim of the statistical analysis is to compare the estimate of each systematic effect to that of the random error to establish if the term with assignable cause is or is not significant. This test is generally known as a significance which the replication makes it possible.

Taguchi Method

Experimental designs were first introduced by Fisher as an agricultural research tool in the 1920s [12]. His primary aim was to obtain the most information possible about a process with the least number of experiments. Experimental designs and optimization methods for chemists and other engineering branches were reviewed by Bayne and Rubin [13], Debets [14] and Duckworth [15].

Taguchi [16,17] simplified the application of experimental design by using standardized library of basic designs called orthogonal arrays, along with some simple methods to modify these layout to fit individual situations. His methodology was also developed within an industrial environment and favoured productivity and cost effectiveness over the statistical rigor.

Orthogonal arrays were used to assign factors to a series of experimental combinations which results could then be analyzed by using a common mathematical procedure. The main effect of these factors and preselected interactions between the factors were independently extracted. The identification of controlling factors and the quantitation of the magnitude of the effects was emphasized rather than just the identification of statistically significant effects. The number of trial chosen for an experimental design was based on the resolution desired. In a factorial design, one could study main effects as well as interactions between factors. This latter characteristic was a major advantage of the technique but a major disadvantage of one-at-a-time variable testing. Main effects and interactions could be confounded, with one another if the experimental design of low resolution were chosen [18].

In the present paper, applications of the experimental design based on the Taguchi methods are described in detail. A major failing of this technique occurs when interactions that confound the observed variance with a main factor are not identified. But in a full resolution design, all main effects and all interactions are resolved. In the full resolution in order to study x factors at Z levels, Z^x experiments are required.

For this research work, the extraction of selenium from Sarcheshmeh anode slimes by nitric acid leaching was carried out by the Taguchi method for statistical design of experiments. In choosing a design, we took into account 3 factors in a $L_{27}(3^{13})$ design, in which up to 13 factors (and the interactions) affecting the process could be studied at 3 levels. In addition to the 3 factors chosen,

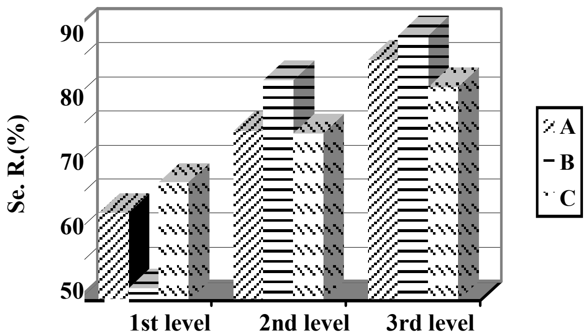

Fig. 1: The effects of different levels of factors on the selenium recovery

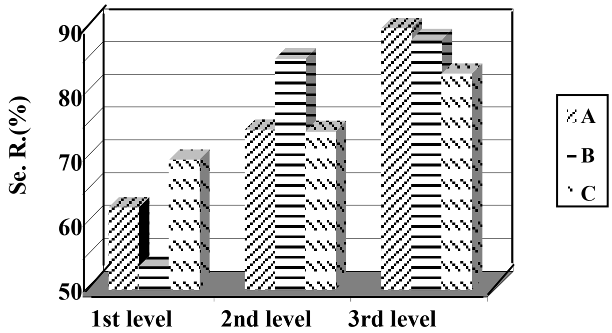

Fig. 2: The effect of different levels of factors on the selenium recovery for the L_9 design experiment

we expected three interactions between the 3 factors and the other columns for the determination of errors. The factors and levels considered for this experiment are shown in table 2. And the selenium recoveries for different conditions of the design are shown in table 3.

RESULTS AND DISCUSSION

Effect of acid concentration

The effect of nitric acid concentration was investigated over the range from 2.0 to 4.0 M.

Preliminary tests showed that when leaching was carried out with 2.0 M HNO3 at 80 °C for 20 minutes, the extraction of selenium was low (32.20 %). It was found that with increasing acid concentration, the dissolution of selenium increased. At the higher temperatures, the higher acidity increases the rate of reaction, resulting in the reduction of leaching time. In other words, more than 90 % of the selenium was dissolved with 4.0 M HNO_3 at 90 ^{0}C for 20 minutes.

Effect of temperature

The effect of temperature was studied over the range from 80 to 100 °C. Higher temperatures showed a beneficial effect on the dissolution of the metals. Consequently, the maximum extraction of selenium was achieved with higher temperature and acidity and time.

The selenium recoveries for the 27 trials have been analyzed by using the analysis of the variance (ANOVA) which is tabulated in table 4. Insignificant effects and interactions are pooled with error, and the F ratios of the variances are computed. Taguchi also computed a term called the "purified sum of squares", S' which is the sum of squares minus the variance caused from errors. Finally, a term used by Taguchi called, rho %, defined as the relative contribution of S,' is calculated for each factor, interaction, or error to the total S' for all possible causes.

As it is seen, all 3 factors affect the selenium recovery and the F ratios show the consistency in the mentioned factors. It is also concluded that comparing with the main factors, the interactions have less effect on the recovery and the factor B, i.e. the temperature, has the highest effect on the selenium recovery.

The variation of selenium recovery against the different levels of independent factors is shown in Fig. 1. As it is noted the highest level of the 3 factors gives the maximum recovery for selenium.

To compare the results with other design, a L_9 Taguchi design are chosen, the results of which is shown in table 5. In this design the evaluation of the interactions is impossible.

The selenium recoveries for the 9 trials are also analyzed by using analysis of the variance (ANOVA) which is tabulated in table 6. As it is seen the factor B, the temperature is the most significant factor which is affecting the selenium recoveries. The variation of selenium recovery against the different levels of independent factors is shown in Fig. 2. It is noted that the same as the $L_{27}(3^{13})$ design, the highest level of the 3 factors gives the maximum recovery for selenium.

CONCLUSIONS

Using Taguchi's method an experimental design was developed which includes 3 level factors. The results and analysis of the variance show that all three factors,

Table 2: Factors and levels for selenium leaching experiments

Code	Factors	Levels		
A	Acidity, M	2	3	4
B	Temp. , C	80	90	100
C	Time. , min	20	40	60

Table 3: Selenium recoveries at different conditions of the $L_{27}(3^{13})$ design

Run	A	B	A*B		C	A*C		B*C		e				Se recovery %
	1	2	3	4	5	6	7	8	11	9	10	12	13	
1	1	1	1	1	1	1	1	1	1	1	1	1	1	32.20
2	1	1	1	1	2	2	2	2	2	2	2	2	2	40.53
3	1	1	1	1	3	3	3	3	3	3	3	3	3	50.48
4	1	2	2	2	1	1	1	2	3	2	2	3	3	49.28
5	1	2	2	2	2	2	2	3	1	3	3	1	1	72.71
6	1	2	2	2	3	3	3	1	2	1	1	2	2	83.72
7	1	3	3	3	1	1	1	3	2	3	3	2	2	72.06
8	1	3	3	3	2	2	2	1	3	1	1	3	3	82.32
9	1	3	3	3	3	3	3	2	1	2	2	1	1	86.69
10	2	1	2	3	1	2	3	1	1	2	3	2	3	45.12
11	2	1	2	3	2	3	1	2	2	3	1	3	1	51.21
12	2	1	2	3	3	1	2	3	3	1	2	1	2	57.67
13	2	2	3	1	1	2	3	2	3	3	1	1	2	79.85
14	2	2	3	1	2	3	1	3	1	1	2	2	3	81.32
15	2	2	3	1	3	1	2	1	2	2	3	3	1	88.80
16	2	3	1	2	1	2	3	3	2	1	2	3	1	83.17
17	2	3	1	2	2	3	1	1	3	2	3	1	2	92.13
18	2	3	1	2	3	1	2	2	1	3	1	2	3	94.85
19	3	1	3	2	1	3	2	1	1	3	2	3	2	54.80
20	3	1	3	2	2	1	3	2	2	1	3	1	3	57.87
21	3	1	3	2	3	2	1	3	3	2	1	2	1	77.17
22	3	2	1	3	1	3	2	2	3	1	3	2	1	93.99
23	3	2	1	3	2	1	3	3	1	2	1	3	2	94.57
24	3	2	1	3	3	2	1	1	2	3	2	1	3	97.40
25	3	3	2	1	1	3	2	3	2	2	1	1	3	95.23
26	3	3	2	1	2	1	3	1	3	3	2	2	1	98.34
27	3	3	2	1	3	2	1	2	1	1	3	3	2	99.11

Table 4: Analysis of the variance for the selenium design experiment

Factor	f	S	V	F	S'	rho %
A	2	2269.01	1134.50	***116.00***	2249.45	21.41
B	2	7037.26	3518.63	***359.77***	7017.70	66.79
C	2	877.38	438.69	***44.85***	857.82	8.16
A*B	4	60.50	15.12			1.40
A*C	4	147.27	36.82	***3.76***	147.27	
B*C	4	106.28	26.57			
e1	8	229.58	28.70			
(e)	(16)	(156.48)	(9.78)		234.68	2.23
Total	26	10506.91			10506.91	100.00

f, the degree of freedom; S, the sum of squares; V, the variance; F, F ratio of variances, S', "purified sum of squares"; rho, % relative contribution of factors, interactions or errors to the observed variance.
F(0.05,2,16)=3.63

Table 5: Selenium recoveries at different conditions for L_9 design

Run	A	B	C	e	Se recovery %
1	1	1	1	1	32.20
2	1	2	2	2	72.71
3	1	3	3	3	86.69
4	2	1	2	3	51.21
5	2	2	3	1	88.80
6	2	3	1	2	83.17
7	3	1	3	2	77.17
8	3	2	1	3	93.99
9	3	3	2	1	98.34

Table 6: A nalysis of variance for the L_9 design experiment

Factor	f	S	V	F	S'	rho%
A	2	1124.34	562.17	*15.02*	1049.47	28.03
B	2	2202.51	1101.26	*29.42*	2127.63	56.83
C	2	267.54	133.77			
e1	2	31.97	15.98			
(e)	(4)	(149.75)	(37.44)		567.05	15.14
Total	8	3744.15			3744.15	100.00

F(0.05,2,6)=6.94

i.e., acidity, temperature and time, are important for the selenium extraction in leach solutions. It was also concluded that the recoveries increase as the levels of the factors increase.

Limitations to the experimental design seem obvious, and worth of being stated, neglecting them often leads to the failing of this approach:

1. The variance observed for a factor or interaction is only valid over the range studied for that factor.

2. Confounding an interaction with a main effect could negate the benefit of minimizing the number of experiments through the use of the fractional factorial design.

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REFERENCES

[1] Abdollahy, M., The Treatment of Sar-Cheshmeh Copper Anode Slimes, Ph.D. Thesis, Leeds University, U.K., (1996).

[2] Wang et. al., Hydrometallurgical Process for Recovering Precious Metals from Anode Slimes, US. Patent 4293332 (1981).

[3] Hoffmann J. E., Recovery of Selenium from Electrolytic Copper Refinery Slimes, Precious Metals: Mining, Extraction and Processing, *Metallurgical Soc. Of AIME*, Warrendale, p.495 (1984).

[4] Habashi F., Recent Methods for the Treatment of Anodic Slimes of Copper Electrolysis, *Metallurgia* **12**, p.257 (1965).

[5] Subramanian K. N., Process for the Recovery of Metal Values from Anode Slimes, US. Patent 4229270 Oct. 21, (1980).

[6] Heimala S. O. et al., Hydrometallurgical process for the recovery of valuable components from the anode slimes produced in the electrolytic refining of copper, *US. Pat. 4002544*, (1977).

[7] Hoffmann J. E., "Hydrometallurgical Processing of Refinery Slimes at Phelps Dodge", Theory to Practice Hydrometallurgy 94 , SC, London p. 69-105 (1994).

[8] Morrison B.H., "Recovery and Separation of Se and Te by Pressure Leaching of Copper Refinery Slime", International Symposium on Unit Processes in Hydrometallurgy, Gordon and Breach Sci. pub., New York, pp. 227-49 (1963).

[9] Kudryavtsev A. A., The Chemistry and Technology of Selenium and Tellurium, Collet's Ltd, London (1974).

[10] Hicks, C. R., Fundamental concept in the Design of Experiments. 3rd end, Holt, Rinehart and Winston, In C.New York (1982).

[11] Kac. M., what is random? *American Scientist*, **71**, 405 (1983).

[12] Fisher, R. A., & yates, F., "Statistical Tables for Biological, Agricultural, and Medical Research", 4th Ed.,Oliver and Boyd, Edinburgh (1953).

[13] Bayne, C., & Rubin, I., "In practical Experimental Designs and Optimization Methods for Chemists", VCH Publisher Inc., New York, NY (1986).

[14] Debets, H.J.G., *J. Liq. Chromatogr.* **8**, 2725 (1985).

[15] Duckworth W. E., "Statistical Techniques in Technological Research": An aid to research productivity, London, Methuen, (1968).

[16] Genichi Taguchi, "System of Experimental Design", Vol.1, KRAUS International publisher, (1987).

[17] Genichi Taguchi, "System of Experimental Design", Vol.2, KRAUS International publisher, (1987).

[18] Montgomery Doglas C., "Design and Analysis of Experiments", John Willy & Sons, (1991).