Optimization of gold recovery from copper anode slime by acidic ionic liquid

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Abstract−Hydrometallurgical gold recovery from primary or secondary sources is mainly based on a cyanide process, which is very dangerous for the environment due to the high toxicity levels. In view of the environmental effect, the present study proposes a new green solvent called 1-ethyl-3-methyl-imidazolium hydrogen sulfate (EmimHSO$_4$) ionic liquid (IL) to recover gold from copper anode slime (CAS). The optimum leaching conditions for maximizing gold recovery were determined by orthogonal array (OA) of Taguchi's experimental design method. OA L$_{16}$ (4^4) including four parameters with four levels each, was used to examine the effects of IL concentration (20%, 40%, 60%, 80% v/v), temperature (25, 50, 75, 95 °C), time (½, 1, 2, 4 h) and solid/liquid ratio (1/10, 1/15, 1/20, 1/25 g/mL) on leaching efficiency of the gold recovery. Statistical analysis of variance (ANOVA) was used to determine the relevance between experimental conditions and gold recovery. The selective leaching tests results showed that gold recovery up to 89.07% was attained on laboratory scale under the optimum leach conditions: 80% IL concentration, 75 °C, 4 h and 1/25 g/mL solid/liquid ratio. According to these results, EmimHSO$_4$ IL provides a very good ambiance for the oxidative leaching of gold and can be offered as an alternative leaching agent instead of harmful cyanide-based solvents.

Keywords: Ionic Liquid, EmimHSO$_4$, Anode Slime, Leach, Gold Recovery

INTRODUCTION

The world metal industry is seeking new methods to recover valuable metals in particular wastes with high efficiency and less damage to the environment [1]. Various industrial wastes are emerging in every metal production process. These wastes including valuable metals are called as a secondary source for several metals and gain importance increasingly. Copper anode slime (CAS) forming in step of electro-purification of anode copper is considered as the most valuable industrial waste due to the presence of valuable metals such as Au, Ag, Se, and Te [2,3]. Many researchers have focused on the recoveries of these valuable metals from the CAS by various methods: pyrometallurgical, hydrometallurgical or combination of them [4-9]. Since the nature of the slimes can vary from one refinery to another, CAS as a secondary source may have a complex chemical composition and physical morphology. Therefore, the applied method to recover the precious metals can be changed, depending on their chemical and morphological structures in the sources [10].

According to recent reviews [10,11] on the recovery of gold from secondary sources and conventional CAS, gold recovery from primary or secondary sources is mainly based on a cyanide process, which is very dangerous for the environment due to the high toxicity levels. In view of the environmental effects to substitute the cyanide for gold recovery, alternative leach chemicals have been sought for a long time. Common leaching agents have been extensively studied in the last three decades and used for the gold extraction from CAS: aqua-regia [12,13], thiourea [14,15], chlorina-

tion [16-18], thiocynate [19,20], thiosulfate [21], and ammonia [22]. However, they have many disadvantages, such as toxicity, corrosion, negative effects to the environment and their evaporations at high temperature [23]. Considering the negative effects of the present solvents, the ILs called "green solvents" with less vapor pressure, better thermal stability and without harmful effect to the environment have become the most promising solvents [24]. ILs as an alternative to the conventional organic solvents have a cationic and an anionic part and are used to adjust hydrophobic or hydrophilic properties [25]. However, recent studies [26,27] reported that ILs based on imidazolium are poorly bio-degradable and can stay in the aquatic environment. On the other hand, some researchers [28] revealed that the growth of micro-organisms in the environment containing imidazolium ILs is slowed down but not completely stopped, and micro-organisms continue to grow at low levels. Fortunately, recyclability and reusable of ionic liquids are very important properties to overcome environmental concerns like bio-degradation. As described in previous studies [29,30], ILs based on imidazolium cation can be recycled by different methods such as extraction of non-volatile products, distillation of volatile impurities etc., and reused several times after the leaching process without any change in their structures and impurities.

A limited number of studies have indicated that ILs play a significant role as a solvent or an electrolyte for recovery of precious metals in the extraction or separation processes. For the first time, 1-butyl-3-methyl-imidazolium hydrogen sulfate (BmimHSO$_4$) IL by mixing thiourea for gold and silver extraction from gold bearing ores was used by Whitehead et al. [30], who have also made a comprehensive study on the usage of 1-alkyl-3-methyl-imidazolium ILs and their derivatives in order to leach sulfidic copper, gold and silver ores [31]. Dong et al. leached the chalcopyrite concentration in the temperature range of 50-90 °C by using Brønsted acid (BmimHSO$_4$)

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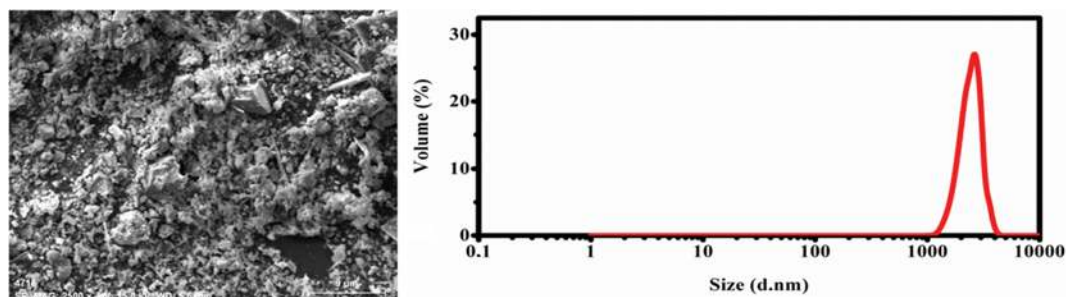E-mail: aydinrusen@kmu.edu.tr, aydinrusen@hotmail.com

Fig. 1. Particle size distribution of the CAS with scanning electron microscope (SEM) image.

Table 1. Chemical composition of CAS in mass fraction

Element	Cu	Sn	Pb	S	Ba	Au (ppm)	Ag (ppm)
%	23.10	20.51	15.42	4.11	5.87	21.9	2204.2
Element	Ni	Sb	Sr	Zn	Bi	Se (ppm)	Te (ppm)
%	0.82	0.24	0.14	0.13	0.11	413	83

and its aqueous solutions [32]. Recovery of the base and precious metals from gold ores by using BmimHSO$_4$ and BmimCl ILs saturated with potassium sulfate (K$_2$SO$_4$) solution in the presence of oxidant (Peroxymonosulfate) was investigated by Whitehead et al. [33]. A recent study [34] on dissolving and recovery of gold in the presence of ILs indicated that deep eutectic solvent (DES) ILs mixing with choline chloride and urea/thiourea are convenient to recover gold from sulfides (galena and chalcopyrite). All these studies showed that gold can be recovered up to 85% by IL media from chalcopyrite based ores.

Several papers have described the extraction of gold from sulfidic ores (chalcopyrite and galena) by using ILs; nevertheless, no study related to recovery of gold from anode slime known as secondary source has been reported so far. This is the first study reported in the literature to focus on the gold recovery from CAS by using ILs. In this study, the optimum leaching conditions for gold recovery were determined by using Taguchi experimental design method. Being simple and systematic, this method has been widely used, especially in engineering and chemistry, for product design and process optimization in last decades [35-40]. Many researchers have studied to specify the optimum parameters to recover metals such as copper [41,42], zinc [43,44] and lead [45,46]. Therefore, in the present study, optimization of the crucial parameters (concentration of solvents, temperature, reaction duration, solid/liquid ratio) affecting the leaching efficiency was performed to attain the maximum gold recovery from CAS. In addition, ANOVA was applied to find whether leaching parameters are statistically significant. By this way, EmimHSO$_4$ IL can be offered as a possible green leaching agent to recover gold from CAS under the optimum condition.

EXPERIMENTAL PART

1. Characterization of the Sample

CAS used in this study was provided from Er-bakır copper plant in Turkey. Before leaching experiments and characterization, the CAS was pulverized to obtain a homogeneous particle size. Fig. 1

indicates the particle size distribution of the CAS with scanning electron microscope (SEM) image, obtained by using Malvern Particle Sizer (Zetasizer Nano ZS), is from 1 to 5 μm. In addition, Z-Average mean known as 'harmonic intensity averaged particle diameter' of the CAS was determined as 2,807 nm.

Chemical analysis of the CAS was by fire assaying method (cupellation) for precious metals and inductively coupled plasma mass-spectrometry (ICP-MS) for other base metals. Chemical composition of CAS in mass fraction is given in Table 1.

From the literature, it is known that CASs have different chemical structures depending on their local characteristics and refinery processes. Typical CAS contains 5-41%Cu, 0.004-1.4% Au, 0.73-24% Ag, 0.2-7% Te and 0.2-3% Se [47]. However, the precious metal contents of the CAS used in this study was lower than that of the conventional ones due to the usage of scrap in the plant.

Mineralogical analysis of CAS was by an X-Ray diffractometer (XRD, Bruker D8 Advance with Da Vinci) with Cu Kα radiation at 30 kV, at a scanning rate of 0.4° min^{-1}. According to the mineralogical analysis, CAS was mainly composed of PbSO$_4$, SnO$_2$ and Cu$_2$O. Other minor components were detected as BaSO$_4$, SbAsO$_4$ and SiO$_2$.

The sample surface's topography and composition were revealed by SEM (Zeiss Evo LS10 model available in the Metallurgical and Materials Engineering Department of Karadeniz Technical University) equipped with energy dispersive X-ray spectroscopy. Since elemental color mapping obtained by SEM-EDS is generally used to specify distribution of the constituents in a sample, it was applied to the original CAS. Fig. 2 shows the elemental maps with SEM photograph and EDS result for selected image area. Each color in the maps represents a separate element (Cu=red, Sn=green, Pb=dark blue, S=pink, Ba=light blue, and O=yellow).

As seen in the color mapping of the representative CAS sample given in Fig. 2, the CAS was predominantly composed of Sn, Pb, Cu, S, O and Ba elements. Additional element, Ca, was also detected by EDS analysis. The color mapping of the CAS indicated that all the elements were homogeneously scattered in the CAS, indicat-
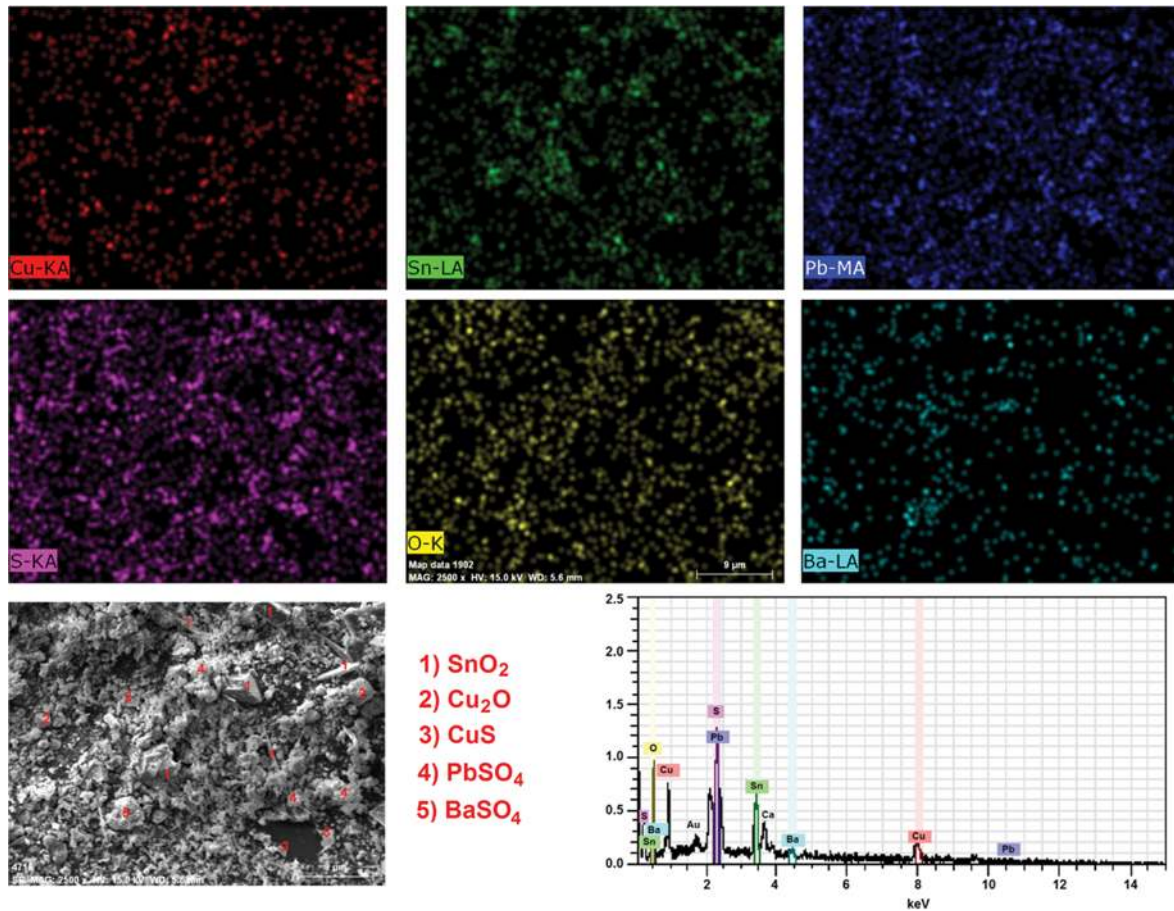
Fig. 2. SEM elemental color mapping with EDS spectra for the selected area of CAS.

ing high concentration of the elements in some points where corresponding to all phases determined by XRD analysis.

2. Optimization Method

In this study, in order to determine the optimum parameters for gold recovery from CAS by Taguchi Method, experimental leaching conditions were selected as (a) solvent concentration, (b) temperature, (c) time and (d) solid/liquid ratio. These four factors with four levels for leaching of CAS are summarized in Table 2. Experimental parameters were investigated by using the orthogonal array (OA) experimental design method with L_{16} (4^4) given in Table 3 with experimental results.

In this study, to maximize recovery of gold from the CAS, the performance statistics of OA were evaluated by using the follow-ing equation (Eq. (1)) [48]:

$$(S/N)_L = -10\log\left(\frac{1}{N}\sum_{i=1}^{n}\frac{1}{x_i^2}\right), \text{ "larger is better"} \quad (1)$$

where $(S/N)_L$ is the performance statistic corresponding to signal-noise ratios of "*larger is better*," n is the number of repetitions for an experimental combination, and x_i is the performance value of ith experiment.

3. Leaching Experiments

ILs as an alternative to the conventional organic solvents have a cationic and an anionic part and are used to adjust hydrophobic or hydrophilic properties. According to the study by Whitehead et al. [31], when ILs based on methylimidazolium are used as a leaching agent to recover gold from primary ores, the amount of gold extraction decreases by increasing the length of the alkyl chain, which results in significant increase in its viscosity. Also, HSO_4 is more advantageous for gold recovery among the possible anion groups with its acidic properties, low cost and the stronger non-oxidizing anion [31]. Therefore, $EmimHSO_4$ IL was selected as a leaching agent based on methylimidazolium with the shortest alkyl chain as a cation group and HSO_4 as an anion group. $EmimHSO_4$ IL was commercially supplied from Merck Co. with high quality (>98%) as a new solvent to recover the gold from CAS.

After the OA experimental design, all leaching experiments were

Table 2. Experimental parameters and their levels for leaching of CAS

Parameters		Levels			
		1	2	3	4
A	IL concentration (v/v)	20	40	60	80
B	Temperature (°C)	25	50	75	95
C	Time (h)	0.5	1	2	4
D	S/L ratio (g/mL)	1/10	1/15	1/20	1/25

conducted in closed glass flask placed on a temperature controlled heater with a magnetic stirrer. The leaching tests were carried out at a solid-liquid ratio of 1/10 to 1/25 g/mL, using the constant volume of leaching solution (50 ml) in the temperature range of 25 to 95 °C. In all the experiments, the leach solution was magnetically stirred at 600 rpm. The IL concentration (v/v) of EmimHSO$_4$ was prepared as aqueous solutions in the range of 20% to 80% with the increment of 20% by mixing sufficiently deionized water. After each of the leaching tests, the solid and liquid parts were separated from each other by means of a filtration system equipped with a vacuum pump. Then, the amount of gold in leach liquor was ana-

lyzed by using Perkin Elmer PinAccle 900T model atomic absorption spectroscopy (AAS). Lastly, Minitab 17 Statistical Software package and ANOVA were used to analyze the collected data and to determine the effect of each parameter on the optimization criteria.

RESULTS AND DISCUSSION

1. Determination of Optimal Conditions

In the IL system, Taguchi design of experiment method was performed to obtain the maximum gold recovery with lowest amount of impurities. The results of gold recovery with investigated condi-

Table 3. L$_{16}$ (4^4) OA and experimental results of gold recovery

| Exp. no.	Experimental parameters and their levels				Gold recovery (%)	[S/N]$_L$
	IL conc. (% v/v)	Temperature (°C)	Time (h)	S/L ratio (g/L)		
1	20	25	0.5	1/10	15.80	23.97
2	20	45	1	1/15	25.40	28.10
3	20	75	2	1/20	30.80	29.77
4	20	95	4	1/25	38.85	31.79
5	40	25	1	1/20	50.15	34.01
6	40	45	0.5	1/25	57.50	35.19
7	40	75	4	1/15	23.92	27.58
8	40	95	2	1/10	29.60	29.43
9	60	25	2	1/25	63.96	36.12
10	60	45	4	1/20	52.12	34.34
11	60	75	0.5	1/15	40.50	32.15
12	60	95	1	1/10	23.45	27.40
13	80	25	4	1/15	49.56	33.90
14	80	45	2	1/10	31.45	29.95
15	80	75	1	1/25	82.20	38.30
16	80	95	0.5	1/20	51.30	34.20
				[S/N]$_{mean}$		31.46
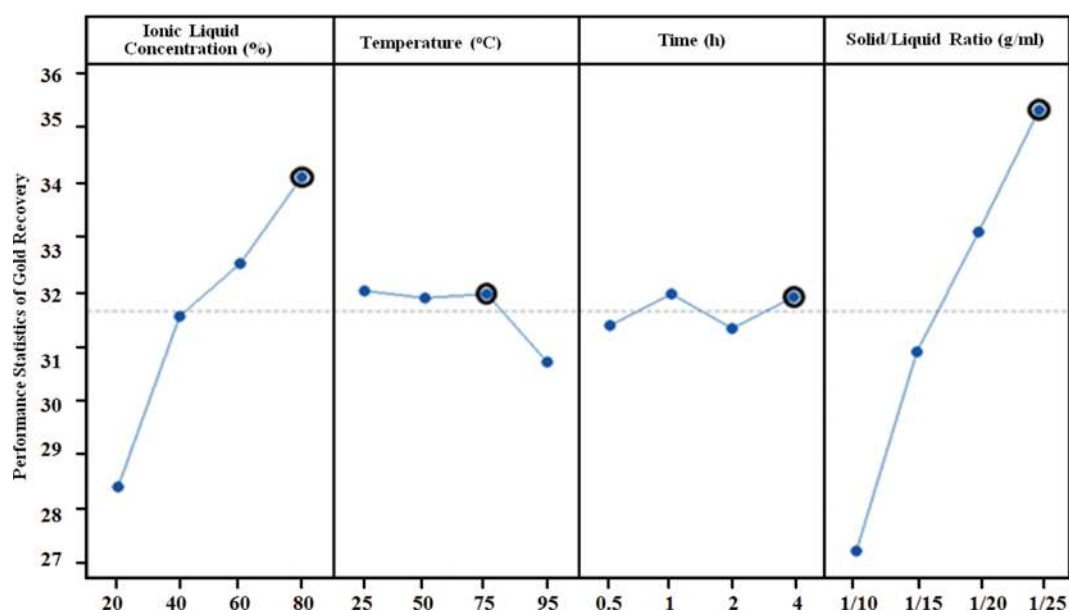
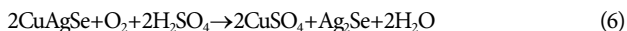**Fig. 3. Main effects of each parameter on the performance statistics for Au recovery.**
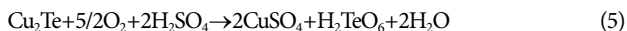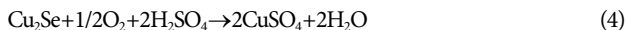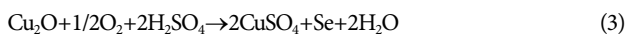
tions and main effects plots of each parameter on the performance statistic are displayed in Table 3 and Fig. 3, respectively. Selected experiments were repeated to verify the results under similar conditions. There is a fairly good agreement between the two experimental results. The experimental average values obtained at the same conditions are displayed in Table 3.

In the Taguchi method, the graphs of marginal means for each parameter are always used to show only the trend of the each factor. The numerical value of the maximum point in each graph marks the best value of that particular parameter. According to main effect plots in Fig. 3, the optimum condition for gold recovery by using EmimHSO$_4$ can be determined as IL concentration: 80%, Temperature: 75 °C, Time: 4 hours and Solid/Liquid ratio: 1/25 g/mL. That is, the experimental parameter values for the optimum condition correspond to A$_4$, B$_3$, C$_4$ and D$_4$.

From the experimental results, the leaching of CAS by using concentrated ILs was easier when compared to leaching by its diluted aqueous solution. Because, concentrated ILs have more acidic properties. Degree of acidity of the EmimHSO$_4$ and its aqueous solutions were determined by using a pH meter. At first, pH values of the original IL solutions were measured between 0.7 and 1.2 depending on the IL concentration from 20 to 80 (v/v). Increasing IL concentration would cause enhancement of the H$^+$ ions in the solution as well as pH values of the IL solution, which helped to dissolve minerals or compounds in the CAS.

Several studies have mentioned that the EmimHSO$_4$ IL is acidic in aqueous solutions and the dissolved oxygen present in the solution acts as an oxidant [31,32]. Also, it has been stated that as the ionic liquid concentration increases, the rate of dissolved oxygen in the solution increases, but the amount of dissolved oxygen decreases with increasing temperature. For this reason, in the present study, significant change in the recovery of gold was not observed as the temperature went up. It even fell at very high temperatures.

Since the presence of hydrogen sulfate anion in IL is responsible for acidity, possible reactions between acidic IL and copper bearing compounds in the CAS much resembled H$_2$SO$_4$ as follows (Eqs. (2)-(6)) [49]:

$$Cu+1/2O_2+H_2SO_4 \rightarrow CuSO_4+H_2O \qquad (2)$$

$$Cu_2O+1/2O_2+2H_2SO_4 \rightarrow 2CuSO_4+Se+2H_2O \qquad (3)$$

$$Cu_2Se+1/2O_2+2H_2SO_4 \rightarrow 2CuSO_4+2H_2O \qquad (4)$$

$$Cu_2Te+5/2O_2+2H_2SO_4 \rightarrow 2CuSO_4+H_2TeO_6+2H_2O \qquad (5)$$

$$2CuAgSe+O_2+2H_2SO_4 \rightarrow 2CuSO_4+Ag_2Se+2H_2O \qquad (6)$$

2. Comparison of Predicted and Confirmation Experiment Results

After selecting the optimal level for each factor, the next step is to predict and confirm the gold recovery from CAS under this optimum working condition. Considering the design layout of L$_{16}$ (4^4) experimental table given in Table 3, it can be noticed that the experiment corresponding to the optimum condition (A$_4$, B$_3$, C$_4$ and D$_4$) was not performed during the experimental trials. Therefore, the value belonging to the optimum conditions should be estimated by means of the balanced characteristic of OA. In this manner, the predicted [S/N] ratio under the optimum experimental condition

Table 4. Arithmetical mean of [S/N]$_L$ ratios at the optimal level for each studied parameters for gold recovery

Parameter	Level 1	Level 2	Level 3	Level 4
IL concentration	28.41	31.55	32.50	34.09
Temperature	32.00	31.90	31.95	30.70
Reaction time	31.38	31.95	31.32	31.90
Solid/liquid ratio	27.23	30.89	33.08	35.35

of the studied parameters can be calculated theoretically by the Eq. (7) as an additive model [50-53]:

$$\left[\frac{S}{N}\right]_{Predicted} = \left[\frac{S}{N}\right]_{mean} + \sum_{i=1}^{n}\left(\left[\frac{S}{N}\right]_i - \left[\frac{S}{N}\right]_{mean}\right) \qquad (7)$$

where [S/N]$_{mean}$ is the arithmetical mean of the whole experimental [S/N]$_L$ ratios, [S/N]$_I$ is the arithmetical mean of [S/N]$_L$ ratios at the optimal level for each studied parameters given in Table 4, and n is the number of the factor that affects the gold recovery from CAS. By this way, the value estimated for optimum condition could be comparable with the result of confirmation experiment.

The obtained value of [S/N]$_{mean}$ from Table 3 for gold recovery is 31.46, and the values of [S/N]$_i$ for the optimum condition A$_4$, B$_3$, C$_4$ and D$_4$ can be found from Table 4 as 34.09, 31.95, 31.90, and 35.35, respectively. The [S/N]$_{predicted}$ value could be obtained after the substitution of these values into the Eq. (7); [S/N]$_{predicted}$=38.38, which can be used to estimate the gold recovery at the optimum experimental condition by substituting into Eq. (1). Thus, Eq. (1) can be rewritten as 38.38=−10log(1/(y)^2). By solving this equation, the predicted gold recovery ratio under the experimental conditions was calculated as 82.97%. On the other hand, a confirmation experiment was carried out at the same optimum condition to verify the predicted result. Quantities of the gold recoveries (%) confirmed experimentally and predicted theoretically with the level of optimum conditions for each studied parameters are summarized in Table 5.

As can be seen in Table 5, under the optimum condition the predicted percentage of the gold extraction was 82.97% and the gold recovery obtained from the confirmation experiment corresponds to 89.07%. According to these results, it can be concluded that good agreement exists between the predicted and confirmed leaching efficiencies of gold.

In last three decades, several leaching agents have been used in

Table 5. Confirmed experimentally and predicted theoretically recovery of gold quantities (%) under the optimum condition

Symbol parameters	Optimum experimental conditions	
	Value	Level
A IL concentration (v/v)	80	4
B temperature (°C)	75	3
C time (h)	4	4
D solid/liquid ratio (g/L)	1/25	4
Confirmed recovery quantity (%) Au	89.07	
Predicted recovery quantity (%) Au	82.97	

Table 6. The gold leaching efficiencies from CAS by using different leach agents

Leach agent	Leach efficiency (%)	Ref.
Cyanide	>98%	[54,55]
Agua regia	80-95%	[12,13]
Thiourea	90-95%	[14,15]
Chlorination	70-99%	[16-18]
Thiocyanate	>95%	[19,20]
Thiosulfate	65-88%	[21]
Ammonia	80-90%	[22]
EmimHSO$_4$	89%	This study result

gold extraction from anode slime to substitute the cyanide. Table 6 summarizes the comparison of leaching efficiencies of gold from CAS by EmimHSO$_4$ with those by other agents.

When compared to the leaching efficiency by EmimHSO$_4$ obtained under the optimum condition with those by other methods, most of them have reached relatively higher gold recovery values than that of the present study. However, with various oxidant additives into EmimHSO$_4$ ionic liquid solution, the gold recovery ratios can be raised at high levels [33,56,57].

After filtration of the leaching mixture of the confirmation ex-

periment, maximum Au content in the pregnant solution could be obtained with minimum amount of impurities by using the proposed statistical method. Under the optimum condition, impurities content in the filtrate were analyzed by AAS and their dissolution ratios are summarized in Table 7.

Several studies [31,32,57] have shown that ILs with acidic property have the ability to dissolve different types of minerals such as oxidic, sulfidic etc. Unfortunately, in this study, beside Au, some elements such as Cu, Sb, Ba, Se or Te in the CAS could be solved in acidic EmimHSO$_4$ during the leaching process. Nonetheless, other impurity elements (especially Sn and Pb) present in a large amount in the CAS could not dissolve in the IL solution due to insolubility of PbSO$_4$ and SnO$_2$ in the acidic media. In addition, the low silver solubility value after the EmimHSO$_4$ IL leaching at optimum condition may be attributed to reaction 6.

Comparing the XRD pattern of the leach residue obtained from confirmed experiment at the optimum condition with the pattern of the original CAS sample (Fig. 4), the sulfidic and oxidic copper structures disappeared and peaks of the SnO$_2$ and PbSO$_4$ remained unchanged.

3. Analysis of Variance (ANOVA) Results

The purpose of the ANOVA is to investigate which of the process parameters significantly affect the performance characteristics.

Table 7. Dissolution ratios of impurities for confirmation experiment at the optimum condition

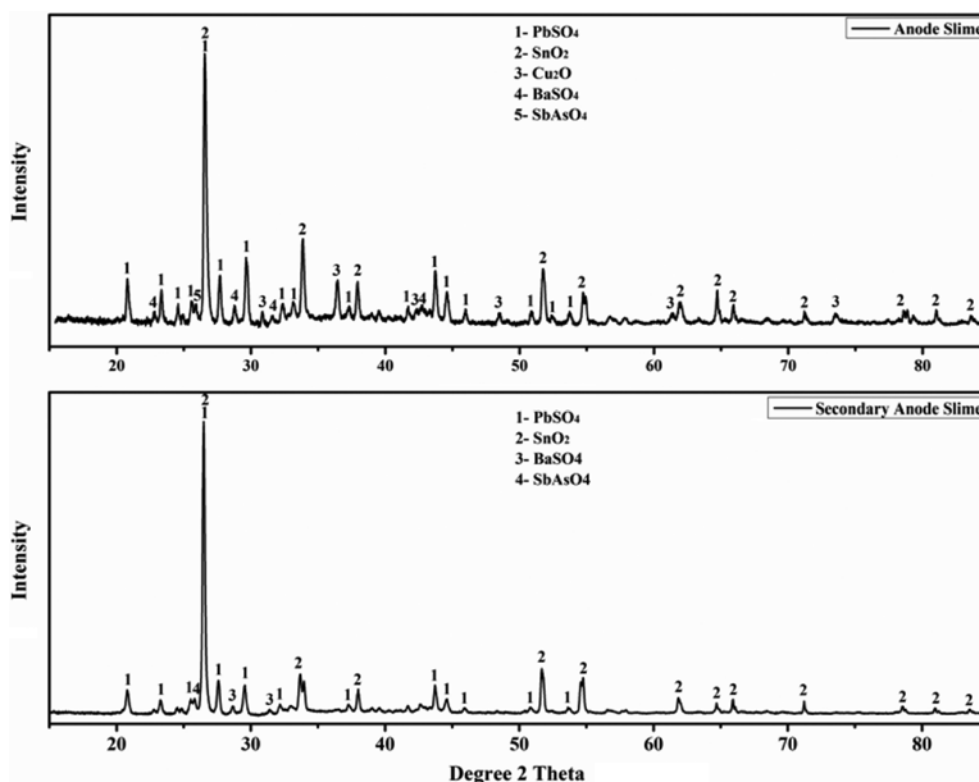| Element	Ag	Cu	Sn	Pb	Ba	Ni	Zn	Sb	Sr	Bi
Dissolution rate (%)	1.12	30.22	0.12	0.07	63.07	10.26	19.14	29.47	25.93	26.63

Fig. 4. XRD pattern of the leach residues belonging to optimum and original samples.

Table 8. ANOVA results of gold recovery

Source	df	SS	MSS	F-ratio	Cr (%)
IL concentration	3	1403.32	467.77	23.77	30.34
Temperature	3	207.57	69.19	3.52	4.49
Time	3	84.11	28.04	1.42	1.81
Solid/liquid ratio	3	2930.80	976.93	49.65	63.36
Error	3	59.03	19.68		
Total	15	4672.30			

Statistically, the F-Test is used to specify which process parameter has a significant effect on the performance characteristic. Usually, the larger F value has the greater effect on the performance characteristic due to the change of the process parameter [58]. The results of the ANOVA applied in the light of such information for gold recovery from CAS are summarized in Table 8.

According to Table 8, the solid/liquid ratio and IL concentration are the most significant process parameters for gold recovery with 63.36% and 30.34% contribution rate, respectively. These results are supported from the performance statistic for Au recovery (Fig. 3) that the gold recovery sharply increased with increasing IL concentration and solid/liquid ratio. The changes of the leaching temperature and duration (see Table 8) have not significant effect on the performance characteristic of gold recovery with lower than 5% contribution rates.

Ultimately, it can be stated that the gold recovery from CAS by EmimHSO$_4$ IL is a possible hydrometallurgical technique under the optimum condition. The maximum gold recovery with lowest amount of impurities could be yielded by Taguchi design of experiment method. However, obtaining the Au from this leach solution depends on the gold form in the solution. Filtrate can be processed to extract gold by several methods, such as solvent extraction with different extractants, cementation with zinc dust, ion exchange with some resins, and adsorption of Au with carbon or magnetite nanoparticles [23,59]. Electrodeposition of gold from ILs is also a new applicable method proposed by several researchers [42,43,60,61]. Since Pb and Sn have not passed through the solution as contaminants, the recovery of Au from the solution will be easier.

As described in the previous studies [29,30], ILs based on imidazolium cation can be recycled and reused several times without any change in structure and impurity of ILs. By this way, most of the ionic liquid used in the leaching process can be sent back to the system for metal extraction without polluting the waste water. Therefore, ILs have an important role to overcome the environmental concern of conventional solvents. Nowadays, the bulk production costs of imidazolium-based ionic liquids are between $2.96 and $5.88 per kg [62], which is only two times of conventional solvents such as cyanide, thiourea and so on. As their prices fall depending on the technological improvements, imidazolium-based ILs can be widely used for metal recovery as an environmentally sensitive solvent.

CONCLUSIONS

Taguchi method was used for determining optimum leaching conditions for gold recovery from CAS in the IL system. Leaching parameters (IL concentration, leaching time, temperature and solid/liquid rate) were investigated with orthogonal experimental design, L$_{16}$ (4^4). To maximize gold amount in the solution by using EmimHSO$_4$, IL concentration (A$_4$): 80% (v/v), temperature (B$_3$): 75 °C, duration (C$_4$): 4 hours and the solid/liquid ratio (D$_4$): 1/25 g/mL were selected as the optimum conditions. Under this condition, gold recovery obtained from confirmation experiment (89.07%) and predicted theoretical value (82.97%) indicated an excellent relation between them. Statistical analysis of variance (ANOVA) revealed the relationship between experimental conditions and gold recoveries. Experimental trials on gold recovery indicated that the most effective parameters were solid/liquid ratio (63.36%), IL concentration (30.34%), temperature (4.49%), and time (1.81%), respectively. According to results, we concluded that the hydrometallurgical leaching process in the presence of EmimHSO$_4$ ILs can be successfully applied to maximize the gold recovery from CAS.

REFERENCES

1. B. Kıyak, A. Özer, H. S. Altundoğan, M. Erdem and F. Tümen, *Waste Manage.*, **19**(5), 333 (1999).
2. A. Agrawal, K. K. Sahu and B. D. Pandey, *Resour. Conserv. Rec.*, **42**(2), 99 (2004).
3. Y. Kılıç, G. Kartal and S. Timur, *Int. J. Miner. Process*, **124**, 75 (2013).
4. W. Liu, T. Yang, D. Zhang, L. Chen and Y. Liu, *Int. J. Miner. Process*, **128**, 48 (2014).
5. B. Dönmez, C. Çelik, S. Çolak and A.Yartaşi, *Ind. Eng. Chem. Res.*, **37**, 3382 (1998).
6. A. Khaleghi, S. Ghader and D. Afzali, *Int. J. Min. Sci. Technol.*, **24**, 251 (2014).
7. J. Hait, R. K. Jana, V. Kumar, P. Dasgupta, M. Bandyopadhyay and S. K. Sanyal, *Int. J. Environ. Waste Manage.*, **216** (1998).
8. W. A. Dutton, A. J. V. Steen and N. J. Themelis, *Metall. Trans.*, **2**, 3091 (1971).
9. A. M. Amer, *Waste Manage.*, **23**, 763 (2003).
10. A. Chen, Z. Peng, J. Y. Hwang, Y. Ma, X. Liu and X. Chen, *JOM*, **67**(2), 493 (2015).
11. S. Syed, *Hydrometallurgy*, **115**, 30 (2012).
12. W. K. Wang, Y. C. Hoh, W. S. Chuang and I. S. Shaw, *US Patent*, 4,293,332 (1981).
13. M. H. Dehghanpoor, M. Zivdar and M. Torabi, *J. South. Afr. Inst. Min. Metall.*, **116**(2), 1153 (2016).
14. R. Ranjbar, M. Naderi, H. Omidvar and G. Amoabediny, *Hydrometallurgy*, **143**, 54 (2014).
15. Ö. Yavuz and R. Ziyadanoğulları, *Sep. Sci. Technol.*, **35**(1), 133 (2000).
16. K. S. Nam, B. H. Jung, J. W. An, T. J. Ha, T. Tran and M. J. Kim, *Int. J. Miner. Process.*, **86**(1), 131 (2008).
17. B. Dönmez, Z. Ekinci, C. Çelik and S. Çolak, *Hydrometallurgy*,

52(1), 81 (1999).

18. B. Dönmez, F. Sevim and S. Çolak, *Chem. Eng. Technol.*, **24**(1), 91 (2001).

19. A. G. Kholmogrov, O. N. Kononova, G. L. Pashkov and Y. S. Kononov, *Hydrometallurgy*, **64**, 43 (2002).

20. A. J. Monhemius and S. P. Ball, *Trans. Inst. Min. Metall., Sect. C*, **104**, 117 (1995).

21. B. Xu, Y. Yang, Q. Li, W. Yin, T. Jiang and G. Li, *Hydrometallurgy*, **164**, 278 (2016).

22. X. Meng and K. N. Han, in *Hydrometallurgy Fundamentals*, Ed. J. B. Hiskey and G. W. Warren, Colorado (1993).

23. G. Tian, J. Li and Y. Hua, *Trans. Nonferrous Met. Soc. China*, **20**(3), 513 (2010).

24. J. Park, Y. Jung, P. Kusumah, J. Lee, K. Kwon and C. K. Lee, *Int. J. Mol. Sci.*, **15**(9), 15320 (2014).

25. N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, **37**(1), 123 (2008).

26. K. M. Docherty, J. K. Dixon and C. F. Kulpa, *Biodegradation*, **18**, 481 (2007).

27. A. Jordan and N. Gathergood, *Chem. Soc. Rev.*, **44**(22), 8200 (2015).

28. A. Romero, A. Santos, J. Tojo and A. Rodriguez, *J. Hazard. Mater.*, **151**(1), 313 (2008).

29. J. A. Whitehead, G. A. Lawrance and A. McCluskey, *Green Chem.*, **6**, 313 (2004a).

30. K. Huang, W. U. Rui, C. A. O. Yan, L. Huiquan and W. Jinshu, *Chin. J. Chem. Eng.*, **21**(5), 577 (2013).

31. J. A. Whitehead, J. Zhang, N. Pereira, A. McCluskey and G. A. Lawrance, *Hydrometallurgy*, **88**(1-4), 109 (2007).

32. T. Dong, Y. Hua, Q. Zhang and D. Zhou, *Hydrometallurgy*, **99**(1-2), 33 (2009).

33. J. A. Whitehead, J. Zhang, A. McCluskey and G. A. Lawrance, *Hydrometallurgy*, **98**(3-4), 276 (2009).

34. G. R. Jenkin, A. Z. Al-Bassam, R. C. Harris, A. P. Abbott, D. J. Smith, D. A. Holwell and C. J. Stanley, *Miner. Eng.*, **87**, 18 (2016).

35. W. H. Wang and Y. S. Tarng, *J. Mater. Process. Technol.*, **84**, 122 (1998).

36. J. A. Ghana, I. A. Choudhury and H. H. Hassan, *J. Mater. Process. Technol.*, **145**, 84 (2004).

37. M. Yeşilyurt, *Chem. Eng. Process.*, **43**, 1189 (2004).

38. Z. Guo, F. Pan, X. Xiao, L. Zhang and K. Jiang, *Trans. Nonferrous Met. Soc. China*, **20**, 2000 (2010).

39. V. A. Beşe, N. O. Ata, C. Çelik and S. Çolak, *Chem. Eng. Process.*, **42**, 29 (2003).

40. M. S. Safarzadeh, D. Moradkhani, M. O. Ilkhchi and N. M. Golshan, *Sep. Purif. Technol.*, **58**, 367 (2008).

41. S. Shariati and M. Golshekan, *J. Anal. Chem.*, **69**(3), 248 (2014).

42. O. N. Ata, S. Çolak, Z. Ekinci and M. Çopur, *Chem. Eng. Technol.*, **24**(4), 409 (2001).

43. P. Ashtari and P. Pourghahramani, *J. Inst. Eng. (India): Series D.*, **96**(2), 179 (2015).

44. B. Behnajady, A. Babaeidehkordi and J. Moghaddam, *Metall. Mater. Trans. B*, **45**(2), 562 (2014).

45. H. Huang, G. Cheng, L. Chen, X. Zhu and H. Xu, *Water, Air, Soil Pollut.*, **203**(1-4), 53 (2009).

46. N. M. S. Kaminari, D. R. Schultz, M. J. J. S. Ponte, H. A. Ponte, C. E. B. Marino and A. C. Neto, *Chem. Eng. J.*, **126**(2), 139 (2007).

47. T. T. Chen and J. E. Dutrizac, *Can. Metall. Q.*, **28**(2), 127 (1989).

48. G. Taguchi, *System of Experimental Design, Quality Resources*, New York, Vol. 1 (1987).

49. S. R. Rao, Resource Recovery and Recycling from Metallurgical Wastes, 1st Ed., Elsevier, Amsterdam, Netherland (2006).

50. S. M. Kim, K. S. Park, K. K. Do, S. D. Park and H. T. Kim, *J. Ind. Eng. Chem.*, **15**(6), 894 (2009).

51. K. K. Do, D. N. Han and H. T. Kim, *Chem. Eng. J.*, **104**(1), 55 (2004).

52. R. Torkaman, M. Soltanieh and H. Kazemian, *Chem. Eng. Technol.*, **33**(6), 902 (2010).

53. M. Edrissi, M. Soleymani and M. Adinehnia, *Chem. Eng. Technol.*, **34**(11), 1813 (2011).

54. G. Tong, *Precious Met.*, **3**, 4 (2001).

55. Y. Shouming, Z. Yongwei and Z. Shenyou, *Gold*, **4**, 18 (2003).

56. A. Kılıçarslan, M. N. Sarıdede, S. Stopic and B. Fredrich, *Int. J. Miner., Metall. Mater.*, **21**(2), 138, (2014).

57. J. Huang, M. Chen, H. Chen, S. Chen and Q. Sun, *Waste Manage.*, **34**(2), 483 (2014).

58. C. Y. Nian, W. H. Yang and Y. S. Tarng, *J. Mater. Process. Technol.*, **95**(1), 90 (1999).

59. N. R. Sahraie, J. P. Paraknowitsch, C. Göbel, A. Thomas and P. Strasser, *J. Am. Chem. Soc.*, **136**(41), 14486 (2014).

60. J. A. Whitehead, G. A. Lawrance, M. P. Owen and A. McCluskey, *Molten Salts XIV: Proceedings of the International Symposium* (Ed. A. Mantz) p. 901-910, October 3-8, Honolulu, Hawaii (2004).

61. T. Oyama, T. Okajima and T. Ohsaka, *J. Electrochem. Soc.*, **154**(6), 322 (2007).

62. L. Chen, M. Sharifzadeh, N. M. Dowell, T. Welton, N. Shah and J. P. Hallett, *Green Chem.*, **16**, 3098 (2014).