Recovery of cyanide in gold leach waste solution by volatilization and absorption

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Abstract

In this study, the effects of pH, time and temperature in regeneration of cyanide in the leaching waste solution of gold production from disseminated gold ore by cyanidation process were investigated and the optimum conditions, consumptions and cyanide recovery values were determined.

The sample of waste solution containing 156 mg/l free CN^- and 358 mg/l total CN^-, that was obtained from Gümüşhane–Mastra/Turkey disseminated gold ores by cyanidation and carbon-in-pulp (CIP) process under laboratory conditions was used in the experiments. Acidification with H_2SO_4, volatilization of hydrogen cyanide (HCN) with air stripping and absorption of HCN in a basic solution stages were applied and under optimum conditions, 100% of free cyanide and 48% of complex cyanide and consequently 70% of the total cyanide in the liquid phase of gold leach effluent are recovered.
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1. Introduction

The cyanidation process for the extraction of gold from ore has been employed for nearly a century. Recently, this process has been developed to recover the low-grade gold ores sized down to 10 μm grain size.

The overall reaction for the dissolution of gold by cyanide in alkaline solution is known as Elsner's equation:

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O = 4\,Au(CN)_2^- + 4\,OH^- \quad (1)$$
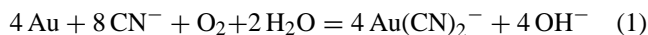
Relatively dilute cyanide solutions can be used because of the strong complex formed between cyanide and gold. The ability of cyanide to form complexes makes cyanide able to dissolve gold. However, cyanide forms complexes with other metals, such as mercury, zinc, copper, iron and nickel, which partially account for consumption of cyanide in gold extraction, and creates waste solutions that are difficult to treat [1].

The wastes including cyanide ions are those coming from leaching residues of the adsorption of gold, that was transferred to the liquid phase as anionic cyanide complex ion during leaching operation, to the activated carbon by carbon-in-pulp (CIP), carbon-in-leach (CIL) or carbon-in-column (CIC) processes. The free cyanide (CN^-) ions or simple cyanide compounds giving free CN^- ions readily and weak metal–cyanide complex ions, that can be present in leaching wastes, are highly toxic. This toxicity decreases towards strong metal–cyanide complexes. For instance, the cyanide in very stable complex structures such as $[Fe(CN)_6]^{4-}$ can be degraded or decomplexated only under very specific conditions and these kinds of compounds are much less toxic. Thiocyanide (SCN^-) ions may also be present in wastes in
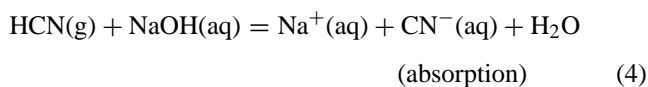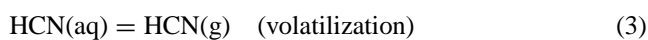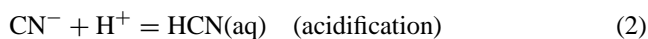
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the case of sulfur containing ores. Cyanate (OCN^-) ion may form during adsorption to activated carbon and it is not hazardous for environment [2,3].
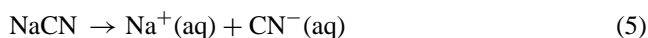
Natural degradation (waste ponds) or chemical destruction methods are employed for preventing or minimizing the hazardous environmental effects of gold production process waste, which contains 100–500 ppm cyanide and have a pH value of approximately 10.5 or more. Other alternatives of cyanide removal from waste effluents are regeneration of cyanide, complex forming, precipitation, ion exchange, biodegradation and adsorption on the active carbon [4,5].

Cyanide is recovered from leach wastes through acidification with SO_2 or H_2SO_4, volatilization of hydrogen cyanide (HCN) with air stripping and absorption of HCN in a basic solution. The simplified chemistry of the process is presented in the following reactions [6,7].
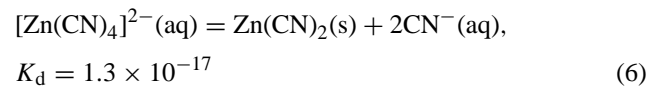
$$CN^- + H^+ = HCN(aq) \quad \text{(acidification)} \tag{2}$$

$$HCN(aq) = HCN(g) \quad \text{(volatilization)} \tag{3}$$

$$HCN(g) + NaOH(aq) = Na^+(aq) + CN^-(aq) + H_2O$$
$$\text{(absorption)} \tag{4}$$

The cyanide (CN^-) ions in the leaching wastes of gold ores are originated mainly from readily dissolution of simple cyanide compounds of alkali metals, such as NaCN and KCN, and, in very low ratios, from dissociation of weak cyanide complexes such as $[Zn(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$, and, in much lower ratios, even negligibly, from dissociation of strong cyanide complexes such as $[Co(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$, $[Ni(CN)_4]^{2-}$ and $[Ag(CN)_2]^-$. Especially the strong cyanide complexes have very small values of dissociation equilibrium constants, so their dissociation can be considered as negligible. Some examples to dissociation reactions and their dissociation constant in neutral media (H_2O) at 25 °C are given below:
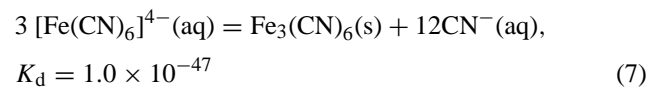
Simple cyanide compounds,

$$NaCN \rightarrow Na^+(aq) + CN^-(aq) \tag{5}$$

Weak metal–cyanide complexes,

$$[Zn(CN)_4]^{2-}(aq) = Zn(CN)_2(s) + 2CN^-(aq),$$
$$K_d = 1.3 \times 10^{-17} \tag{6}$$

Strong cyanide complexes,

$$3[Fe(CN)_6]^{4-}(aq) = Fe_3(CN)_6(s) + 12CN^-(aq),$$
$$K_d = 1.0 \times 10^{-47} \tag{7}$$

As can be seen from the values of dissociation constants, the CN^- amounts originated from the cyanide complexes are on very low levels. However, when the formed CN^- ions are converted to hydrocyanic acid and removed as hydrogen

cyanide gas, the position of equilibrium will lie to the right in the reactions. As a result, significant increases will occur in dissociation in relation to several factors such as temperature, kind of the complex, volatilization rate and time. Although the metal cyanide compounds formed from dissociation of the weak metal cyanide complexes, that are insoluble in water in neutral conditions, become more soluble under acidic conditions, the dissociation of CN^- ions from the very stable metal cyanide compounds such as $Fe_3(CN)_6$ may be possible only at much more specific conditions such as very strong acids, UV radiation and addition of some reagents such as Cu_2Cl_2, $MgCl_2$ and $CuSO_4$ in order to facilitate the dissociation [8,9].

In this study, the aim was to remove the environmentally harmful cyanides in the leach waste of an epithermally formed finely disseminated gold ore including SiO_2 in high amounts and also to recover these cyanides economically. For this purpose, especially the highly toxic free cyanides were ought to be recovered and the complexated cyanides which could be dissociated to CN^- ions due to the ambient conditions were also recovered partially. The effects of pH, time and temperature in regeneration of cyanide were also investigated; and the optimal conditions, consumptions and recovery values were determined.

2. Materials and methods

The experiments were carried out on cyanide wastes generated by laboratory scale work that had been done at MTA (General Directorate of Mineral Research and Exploration of Turkey) for the recovery of gold from Gümüşhane–Mastra ore by cyanidation. These ore samples contain 8.97 g/ton Au and high percentage of SiO_2 (>90%). Chemical analysis results of the representative ore sample are seen in Table 1. Ore formation shows epithermal property. Finely disseminated gold (in size of <40 μm) are dispersed to the overall ore [10,11].

Cyanide regeneration experiments were performed in the setup shown in Fig. 1 by using a waste solution containing

Table 1
Results of analysis of ore sample

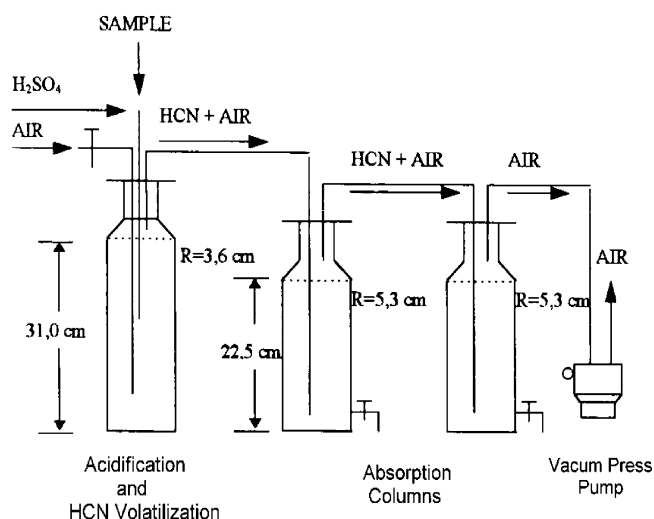| Optical spectrographic analysis (semiquantitative analysis)	Percentage	Chemical analysis	
Cr	0.02	SiO_2	90.50%
Pb	0.07	Al_2O_3	4.00%
Ag	0.001	Fe_2O_3	2.50%
Ca	0.015	Pb	0.30%
Fe	2	S	0.34%
Cu	0.02	Cu	0.02%
Ti	0.04	As	220 mg/kg
Mg	0.04	Zn	60 mg/kg
Si	>10	Hg	1 mg/kg
Mn	0.003	Sb	50 mg/kg
Ba	0.2	Cd	<10 mg/kg
Al	>1	Ag	8.2 mg/kg

Fig. 1. Setup for regeneration of cyanide.

156 mg/l free CN^- and 358 mg/l total CN^-, which was obtained by filtration of the pulp coming from leaching waste of CIP process.

Experimental studies and analyses were performed with parallels (double) and they were repeated in the case of inconsistency of the results.

The recovering setup of cyanide in liquid phase by regeneration consists of two parts made from glass. In the first part of the apparatus, acidification to form HCN and volatilization of formed HCN was performed. In the second part, HCN gas was absorbed in two columns of NaOH solution. The second column is to trap the hydrogen cyanide gas that may escape in the case of saturation of the first column by cyanide absorption. The NaCN formed in this second column in very low amounts was also taken into account in efficiency calculations. This will be explained in results and discussion part. A vacuum pump was used for volatilization and transport of HCN gas through the absorption columns. Ninety-six percent (w/w) concentrated sulfuric acid was used for acidification. In all cyanide regeneration experiments, air flow rate was held constant at 10 l/h, NaOH concentration in absorption columns was held constant as 0.025 M and the volume ratio of waste solution (amount of sample) in acidification–volatilization column to sodium hydroxide solution in absorption columns (V_{vol}/V_{abs}) was also held constant at 1/1.5. The operation temperature of acidification–volatilization column was adjusted by using a thermostat-controlled water bath with a sensitivity of $\pm 1\,°C$.

The experiments for conversion of the cyanides in the waste solution samples in the acidification–volatilization column and removing them by air flow for absorption of the cyanides in the absorption columns were carried out simultaneously. The mixing in the columns was provided by the flow of air. In order to prevent the escape of HCN gas during sulfuric acid addition on the waste samples in the acidification–volatilization column in the beginning of the experiments, the absorption columns were filled with sodium hydroxide solution and air flow was provided by using a vacuum pump and then the acid was added on the samples of waste solution in the acidification–volatilization column. The required acid amounts were determined according to the results of pH–acid consumption experiments and all of the acid was introduced at the beginning of the experiment.

Since the results are dependent upon the kind and amount of the simple cyanide compounds and metal cyanide complexes in the waste solution, free and total cyanides were determined and the complex cyanide amount was found as the difference between the amounts of total and free cyanides. Recovery efficiencies were computed according to these three kinds of cyanide amount values. Because the amount of complexated cyanides was determined from mass balance according to the analyses of the free and total cyanides, it was not analyzed directly and recovery efficiency was also calculated with respect to complexated cyanides in order to be able to explain the excessive amount of cyanides obtained in the absorption columns. Otherwise, this amount would be higher than the amount of free cyanides in the sample of waste charged into the acidification–volatilization column, and in this case, it would be higher than the 100% of the initial amount of free cyanides.

The cyanide recovery efficiencies were calculated on the basis of the initial cyanide amounts in the waste solution in the acidification–volatilization column and the cyanide amounts reabsorbed in the absorption columns by using the formulas given below:

$$\%R\,(\text{total cyanide}) = \frac{V_{abs} \times C_{abs}}{V_{samp} \times C_{To}} \times 100 \qquad (8)$$

$$\%R\,(\text{free cyanide}) = \frac{V_{abs} \times C_{abs}}{V_{samp} \times C_{Fo}} \times 100 \qquad (9)$$

$$\%R\,(\text{complex cyanide})$$
$$= \frac{V_{abs} \times C_{abs} - V_{samp} \times C_{Fo}}{V_{samp} \times (C_{To} - C_{Fo})} \times 100 \qquad (10)$$

where V_{abs}: volume of NaOH solution in the absorption column (ml), C_{abs}: CN^- concentration in absorption solution (mg/ml), V_{samp}: amount of sample in acidification and volatilization column (ml), C_{To} and C_{Fo}: total and free cyanide concentrations in the sample, respectively.

Free cyanide analyses were performed by titration of the samples taken from the waste solution with silver nitrate solution. Total cyanide was determined by using the combination of distillation and colorimetric methods. For this purpose, the distillates of the samples were colorated by pyridine–barbituric acid and then the colorimetric measurements were performed at 578 nm wavelength by using the Spectronic Model 20 spectrophotometer [9].

The pH values were determined by using glass–calomel electrodes.

3. Results and discussion

3.1. Acid consumption and pH variation

Different amounts of H_2SO_4 were added on the samples taken from waste stock solution, with pH value of 10.8, including 156 mg/l free cyanide and 358 mg/l total cyanide. As can be seen in Fig. 2, there is a critical point at about pH = 3 and acid consumption increases dramatically below this point. This can be explained by the fact that the cyanides in the complexes also begin consuming the acid towards low pH values while only free cyanides were consuming acid according to Eq. (2) in acid–base titration at higher pH values.

3.2. Effect of pH and time

Four experiments were performed with initial pH values of 5.5, 3.5, 3.0 and 2.7 (corresponding kg H_2SO_4 consumption/kg CN^- values are 1.2, 1.6, 2.0 and 2.4, respectively). The temperature was held constant at $25 \pm 1\,°C$ and recovery values calculated in terms of free and total cyanide are shown in Figs. 3 and 4. When the pH level of liquid waste lowered from 5.5 to 2.7, higher recovery values could be reached faster for both free and total cyanide amounts. This effect is more
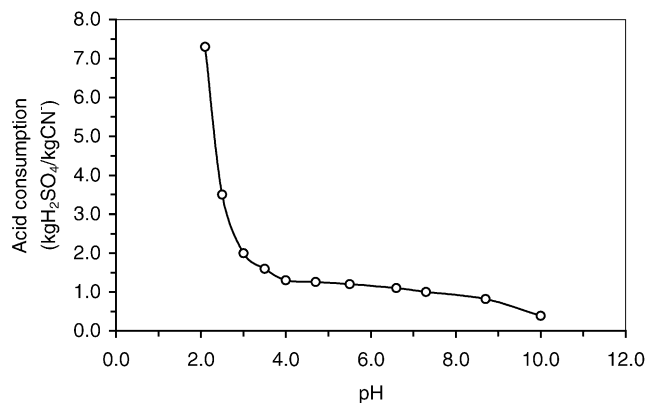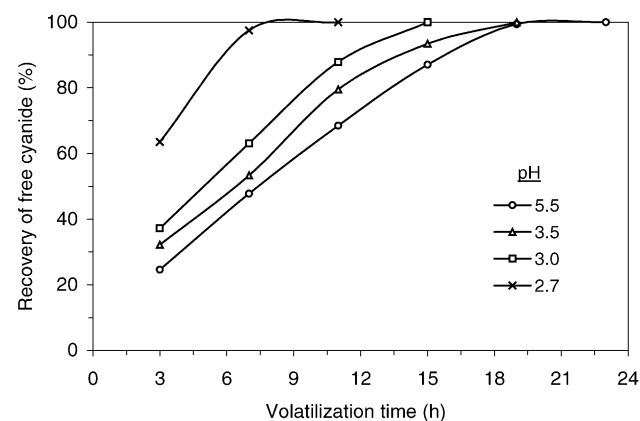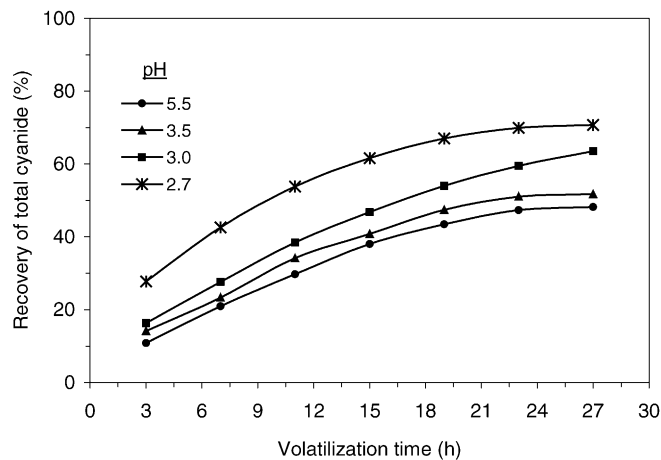

Fig. 2. Acid consumption versus pH change curve.

Fig. 4. Recovery of total cyanide vs. time for various pH values.

clearly seen at pH = 2.7 and this can be explained by the fact that the critical point was at pH < 3 in Fig. 2. Since the acid consumption will increase markedly at lower pH levels, the pH = 2.7 (the acid consumption value of 2.4 kg H_2SO_4/kg CN^-) and 23 h volatilization time conditions, under which 70% total cyanide recovery was reached, were chosen as optimal conditions. This is because stable cyanide complexes cyanides cannot be converted to HCN readily. Only 48% of the complex cyanides could be regenerated whereas 100% of free cyanide was recovered in a shorter period of time.

3.3. Effect of temperature and time

The same conditions as for $25\,°C$ (pH: 2.7; NaOH concentration in absorption columns: 1 g/l; air flow rate: 10 l/h; waste solution volume in volatilization column/NaOH solution volume in absorption column: 1/1.5) were repeated for 35 and $15\,°C$ in order to investigate the effect of temperature on regeneration. It was found that the $10\,°C$ raise in temperature does not bring any advantage in terms of recovery (Figs. 5 and 6). However, in the case of $10\,°C$ lowering in temperature, especially total cyanide recovery became very low and about 40% decrease was observed in it with respect

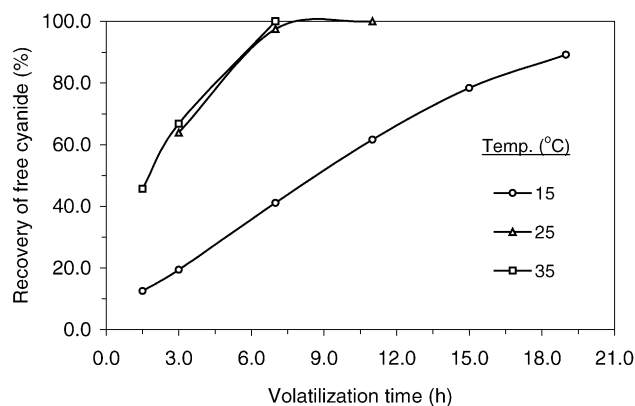Fig. 3. . Recovery of free cyanide vs. time for various pH values.

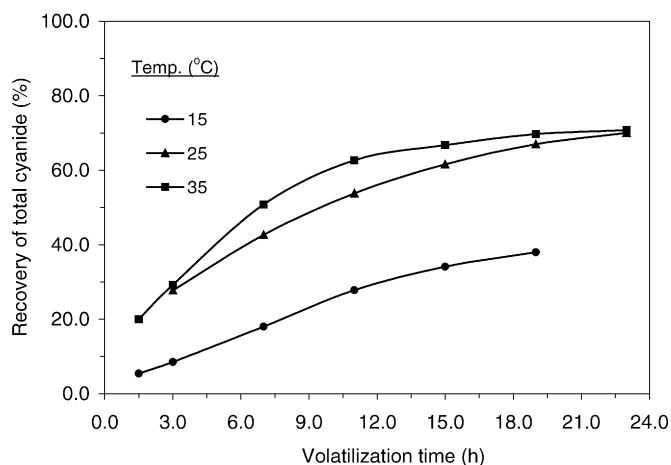Fig. 5. Recovery of free cyanide vs. time for various temperatures.

Fig. 6. Recovery of total cyanide vs. time for various temperatures.

to that of 25 °C. This is because of the fact that the solubility of HCN gas in water, formed during acidification, decreases with increasing temperature. In this case, the solubility of the gas is exceeded. This result is in accordance with literature [8,12].

3.4. NaOH consumption and loading capacity

A synthetic solution of pH = 10.8 and concentration of 2 g NaCN/l was prepared. The acid consumption was 2.4 kg H_2SO_4/kg CN^- for the first column, and a volume ratio of volatilization/absorption = 1/1.5 was obtained. Acidification and volatilization of cyanide were performed at 25 °C. Due to the 10 l/h air flow rate, approximately 10 h was enough for reaching saturation in the first absorption column with 0.025 M NaOH concentration. During this process, in the second column, added in order to trap the HCN gas that may escape from the first column, about 2.5% of the total cyanide retained in the first column was absorbed and the cyanide loading capacity of the sodium hydroxide solution in the first column was determined as 1.4 kg NaCN/kg NaOH (1.65 kg NaOH/kg CN^- consumption) (Fig. 7).
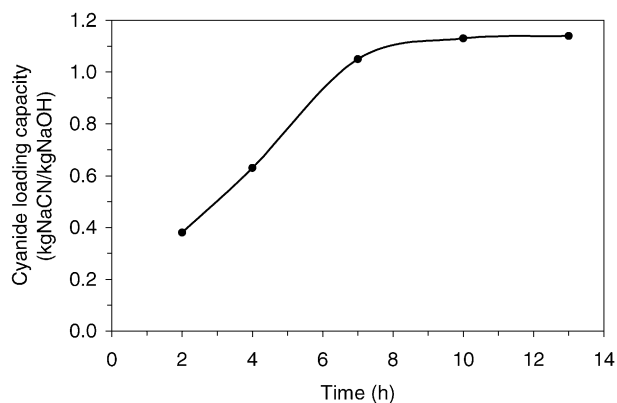

Fig. 7. The change in cyanide loading capacity with time.

4. Conclusions

At low pH values, the recovery efficiencies of both the free and complex cyanides increased and volatilization times necessary for the same cyanide recovery values decreased. However, at pH < 3, the H_2SO_4 consumption increases markedly and this must be taken into consideration in determination of the optimal pH value. On the other hand, the increase in temperature decreased the solubility of HCN gas, formed during acidification, in water. This improved the regeneration of especially free cyanides and the recovery reached the optimal value at 25 °C. The optimum conditions for regeneration were obtained as pH 2.7, 2.40 kg H_2SO_4/kg CN^- and 1.65 kg NaOH/kg CN^- consumption, 25 °C temperature and 23 h volatilization time. Under these conditions, 100% of free cyanide and 48% of complex cyanide and consequently 70% of the total cyanide in the waste solution are recovered.

The optimal total cyanide recovery obtained in this study on the leaching wastes of the finely disseminated epithermally formed Gümüşhane–Mastra gold ore was on a low level. However, since this recovery consists of mainly very toxic free cyanides and weak cyanide complexes giving free cyanides readily, it will be very useful in prevention of the harmful environmental effects of cyanide wastes and this method will be more advantageous in the case of gold leach wastes with higher free cyanides or easily decomposing weak cyanide complexes content.

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