

Technical Note
Cyanidation of Turkish gold-silver ore and the use of hydrogen peroxide

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ABSTRACT

Cyanide leaching of gold-silver ore, obtained from Artvin, Cerattepe region of Turkey, was investigated. The effects of NaCN concentration, solid/liquid ratio, type of pH adjustment reagent, lead nitrate and hydrogen peroxide (H₂O₂) additions in relation to the leaching time on gold and silver leaching efficiencies were examined and the optimum cyanide leaching conditions were determined. Almost all gold and 71% of Ag were extracted with the addition of 15g/l H₂O₂ during the cyanidation carried out for 48h. As a result of this study, it was proven that addition of H₂O₂ as an oxidant during the cyanide leaching had an increasing effect on the leaching recoveries of Au and Ag, a decreasing effect on the leaching period, and thus an accelerating effect on Ag and Au dissolutions. © 2003 SDU. All rights reserved.

Keywords: Gold ores; Cyanidation; Leaching; Hydrometallurgy

1. INTRODUCTION

Gold and silver have been known and processed since the ancient times and are almost as old as the mining history. They never lost human interests and thus, became more valuable over the years. At the beginning, rich gold and silver ores were processed without concentration. But, this type of reserves vanished over the years and recently, poorer and deeper ore bodies needed to be mined. Therefore, gold and silver productions are even more difficult without the application of concentration processes and thus researches on the concentration of gold and silver ores are still continuing. Cyanide leaching has been used over a century to recover gold and silver from the ores. The role of oxygen in cyanide leaching is well understood in the gold industry. Investigations are focused on the use of oxidizing agents, such as O₂ and/or hydrogen peroxide (H₂O₂) and calcium peroxide (CaO₂) addition during the cyanidation in order to enhance the Au and Ag leaching recoveries (Loroesch, 1990; MacMaster and Kenny, 1990).

Gold exploration programs have yielded numerous feasible gold deposits in various parts of Turkey (Karahan and Onal, 1997). These deposits are Kaymaz, Eskisehir (7 tons Au, 3 tons Ag), Efemcukuru, Izmir (34 tons Au), Kucukdere, Balikesir (9 tons Au, 17 tons Ag), Ovacik, Bergama (24 tons Au, 24 tons Ag), Mastra, Gumushane (12 tons Au, 8 tons Ag), Cerattepe, Artvin (37 tons Au, 1050 tons Ag), Kisladag, Usak (245 tons Au) and Cukurdere, Erzincan (131 tons Au). There are also some other ore deposits where precious metals can be recovered as byproducts. Pre-production activities for Ovacik, Bergama mine started and a cyanidation plant (Cyanide/Carbon-In-Pulp/INCO SO₂/Air Process for cyanide destruction) was built in Ovacik-Bergama and is currently operational. Since there are some feasible precious metal deposits explored in Turkey, it is very important to do some investigations on these newly explored ore bodies. Therefore, the aim of this experimental study was to investigate the possibility of extracting gold and silver from Artvin, Cerattepe region ore by using cyanide leaching process and to see the effect of hydrogen peroxide addition during the cyanidation.

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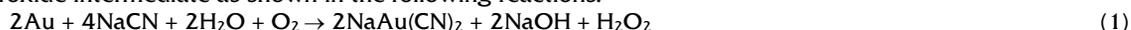
2. PEROXIDE ASSISTED CYANIDE LEACHING

The cyanidation process is based on the conversion of gold and silver to water soluble cyanides. Over a century ago, it was discovered that besides the complexing cyanide ions, an oxidant must be available simultaneously to oxidize the elementary gold. Since that time, oxygen from the air is used by introducing compressed air into the pulp (Loroesch, 1990; MacMaster and Kenny, 1990). Researches and industrial applications over the years showed that the dissolution rates of gold and silver are directly related to the concentration of dissolved oxygen. It was accepted that insufficient transfer of oxygen from gaseous phase into ore pulp was often the reason for low levels of dissolved oxygen and correspondingly slow extraction kinetics and low gold and silver recoveries (Loroesch, 1990).

Considerable effort was put into the improvement of the important oxidant supply, mainly by using advanced techniques for gas dispersion or substituting the compressed air by pure oxygen (Loroesch, 1990). In 1987, the first economically successful application of pure oxygen as an oxidant in the cyanidation of gold ores took place at the South African Fairview Mine. Since the pure oxygen technology is very similar to the aeration with compressed air, in the case of viscous and strong oxygen-consuming pulps, the phase transfer of oxygen gas into the liquid is as difficult as the introduction of air. The idea of controlled addition of an effective liquid oxidant could overcome this problem. Thus, the use of calcium peroxide and hydrogen peroxide were introduced and peroxide assisted cyanide leaching process (PAL) in gold mining industry started to be used (Loroesch, 1990) and seven plants in Australia and South Africa have successfully employed this process.

The application of liquid oxidant ensures the fast and homogenous distribution of the active oxygen in the pulp. Furthermore, the oxidant dosage can be controlled automatically according to the oxygen level in the pulp, resulting in very economical oxidant consumption. Consequently, it was shown that the PAL system has the following significant advantages over the conventional aeration technique (Loroesch, 1990): accelerated leaching kinetics, increased gold and silver recoveries by extraction of all cyanide accessible gold and silver, savings in cyanide consumption, and savings in capital investment.

Dissolved oxygen may not be the only effective oxidant used in the cyanidation process. According to Bodlaender's equation described for cyanidation (Bodlaender, 1896), dissolved oxygen is utilized as peroxide intermediate as shown in the following reactions:



The PAL process is a system that may supply the driving forces (dissolved oxygen and hydrogen peroxide) for both of the reactions given above. Therefore, this system may be considered to be the most effective oxidant supplier in the cyanidation.

Calcium peroxide is also used as an oxidant and provides a milder oxidizing environment (Nugent, 1990). It may therefore minimize some reactions, which occur with more reactive hydrogen peroxides. The cyanide oxidation that may occur in the presence of copper and other catalysts is almost negligible.

Although hydrogen peroxide is a strong oxidant used in the detoxification of cyanide, significant cyanide savings have been recorded, in some cases, after the introduction of the PAL system (Loroesch, 1990). For example, Pine Creek Goldfields, a 4000t/d operation in Northern Territory, Australia, reported cyanide savings of 40% by decreasing the NaCN consumption from 1.7kg/t ore to 1.0kg/t ore, as a result of changing the cyanidation technology (Lee *et al.*, 1989).

3. EXPERIMENTAL STUDIES

3.1. Material

The ore samples subjected to the experimental study, taken from the oxidized ore body overlying sulfides, were supplied by Cominco Madencilik A.S. from Artvin, Cerattepe region, which is one of the reserves accepted as economically mineable in Turkey. According to the chemical analysis of the ore sample given in Table 1, it contains 4.6g/t Au and 220g/t Ag. Mineralogical investigations of this ore sample showed that native gold, native silver, cuprite, barite, limonite, hematite, goethite, lepidokrosite, quartz and some sulfide minerals are present in the ore body. Native gold mainly occurs with the grain size of 1µm diameter in the iron oxide minerals and in lesser quantities with the grain size of 1 to 5µm in diameter in the quartz minerals. Native silver grains (1 to 10µm) are mostly dispersed in the quartz minerals and rarely in iron oxides and barite-limonite inclusions.

The ore sample was first crushed below 1 mm and then ground below 0.1mm before being used in the cyanide leaching experiments. Particle size distribution and Ag contents in relation to the particle sizes are determined. Approximately 90% of the sample remained below 0.074mm and most of Ag was accumulated in the size range of below 0.038mm.

Table 1
 Chemical analysis of the ore sample used in the experiments

Element	Content (g/t)	Element	Content (%)
Au	4.6	Mg	0.07
Ag	256	Ca	0.05
Cu	167	Al	1.53
Zn	451	S	18.5
Ni	< 2	As	0.11
Mn	334	SiO ₂	20.1
		Fe	4.23
		Pb	3.69

3.2. Method

Cyanide leaching experiments were carried out in a one liter beaker under continuous stirring at a constant speed of 400rpm. In the experiments, Ca(OH)₂ and NaOH were used for the adjustment of pH whereas hydrogen peroxide (H₂O₂) was utilized as an oxidant. pH was kept constant around 10.5 throughout the tests. In order to determine the NaCN and Ca(OH)₂ consumptions aliquots were taken out at the end of each experiment and analyzed by silver nitrate titration for NaCN and by oxalic acid titration for Ca(OH)₂. Following the leaching, the pulp was filtered and all analyses were made from leach cakes. Silver analyses were made by using AAS and gold analyses by fire assaying.

4. RESULTS AND DISCUSSIONS

In the cyanide leaching tests effects of NaCN and Pb(NO₃)₂ concentrations, type of pH adjustment reagent (Ca(OH)₂ and NaOH), H₂O₂ addition, solid/liquid ratio, and leaching time on Au and Ag leaching recoveries were investigated and the consumptions of NaCN and Ca(OH)₂ were determined.

4.1. Effect of NaCN concentration

In order to determine the optimum cyanide concentration, a set of experiments were carried out at the following conditions: 1/10 solid/liquid ratio, -0.1mm of particle size, room temperature, 0.4g/l Ca(OH)₂, 0.5-3g/l NaCN, 0-24 hours of leaching time and the results are summarized in Table 2. Increasing NaCN concentration had a remarkable effect on Ag leaching recovery up to 8h of leaching, but had no effects after that point and 46% Ag extraction was observed at the end of 24h cyanide leaching. Au extraction efficiencies increased from 93.5 to 95.5% by increasing NaCN concentration from 0.5 to 3g/t while NaCN consumption increased from 1.96kg/t to 8.31kg/t ore in the mean time. Therefore 1g/l NaCN concentration was used in the following tests by considering the economical and environmental facts.

Table 2
 Experimental results carried out at different NaCN concentrations

NaCN (g/l)	0.5	1	2	3
Time (h)	%Ag Recovery	%Ag Recovery	%Ag Recovery	%Ag Recovery
1	24.9	33.1	32.5	38.6
2	-	34.2	33.5	39.9
3	-	35.7	-	40.2
4	32.1	-	-	-
5	-	36.8	34.4	40.6
8	41.0	41.2	40.9	41.3
24	45.7	45.0	45.4	45.5
%Au Recovery (24h)	93.5	94.7	95.0	95.5
NaCN Consumption (kg/t)	1.96	4.40	6.36	8.31

4.2. Effect of solid/liquid ratio

Experimental conditions were: 1/10, 2/10, 3/10 solid/liquid ratio, -0.1mm of particle size, room temperature, 0.4g/l Ca(OH)₂, 1.0g/l NaCN, 0-24 hours of leaching time and the results are shown in Table 3.

Increasing solid/liquid ratio caused a small decrease in Ag leaching efficiencies and lesser extent reduced Au leaching efficiencies. It was also found that NaCN consumption was decreased from 4.4kg/t to 2.3kg/t ore with increasing solid/liquid ratio. At the constant NaCN concentration, the amount of NaCN concentration per unit surface area in contact with the solution decreases when the amount of solid in the solution increases.

Table 3
 Experimental results carried out at different solid/liquid ratios

S/L Ratio (%)	10	20	30
Time (h)	%Ag Recovery	%Ag Recovery	%Ag Recovery
1	33.1	24.95	22.8
2	34.2	25.85	24.7
3	35.7	-	-
4	-	28.5	27.8
5	36.8	-	-
8	41.2	28.5	27.8
24	45.0	42.8	38.7
% Au Recovery (24h)	94.7	92.3	92.3
NaCN Consumption (kg/t)	4.40	2.20	2.28

4.3. Effect of reagent type used in pH adjustment

It is well known that the solution pH should not be lower than 10 during the cyanide leaching applications. The decrease in solution pH causes a decrease in the free cyanide ion (CN⁻) concentration resulting in an increase of NaCN consumption and in the production of poisonous HCN gas. In order to prevent this unwanted situation two types of reagents, namely Ca(OH)₂ and NaOH, are used and the experimental conditions were: 1/10 solid/liquid ratio, 0.1mm particle size, room temperature, 0.4g/l reagent used in pH adjustment, 1.0g/l NaCN, and 0-24 hours of leaching time. According to the results shown in Table 4 it was observed that using Ca(OH)₂ resulted in a 35 percent improvement in Ag leaching efficiencies than the ones found in the case of using NaOH. However, using NaOH instead of Ca(OH)₂ increased Au leaching recovery from 94.7 to 96.6% while NaCN consumption decreased from 4.4kg/t to 1.96kg/t ore. During the experiments with NaOH, some difficulties were observed in filtration due to the formation of gel type leach cake. Because of this reason, Ca(OH)₂ was chosen as a pH adjustment reagent for the following tests. In the literature, it was found that Ca²⁺ ions have decreasing effect on gold dissolution and are advantageous in the cyanidation of silver ores, in preventing the detrimental effects of ions containing sulfur and complexes, which hinder silver dissolution and consume CN⁻ ions (Acarkan *et al.*, 1994). The protective alkalinity has a two-fold action and when the protective alkali is introduced to the pulp, it first dissociates to Ca²⁺ and (OH)⁻ ions. The alkalinity of the medium is determined by the (OH)⁻ ions formed and thus the hydrolysis of the free CN⁻ ions is hindered. Ca²⁺ ions react with various elements in the solution and form compounds with the elements dissolving from the sulfide minerals. Since Ca²⁺ ions preferably form compounds with S²⁻ and (SH)⁻ ions, their harmful effect on cyanidation is eliminated (Hedley and Tabachnick, 1958). Thus, Ca²⁺ ions are helpful in the extraction of silver.

Table 4
 Experimental results carried out at by using different pH adjustment reagent

Reagent Type (0.4g/l)	Ca(OH) ₂	NaOH
Time (h)	%Ag Recovery	%Ag Recovery
1	33.1	23.6
2	34.2	-
3	35.7	-
4	-	25.4
5	36.8	-
8	41.2	34.6
24	45.0	36.3
%Au Recovery (24h)	94.7	96.6
NaCN Consumption (kg/t)	4.40	1.96

4.4. Effect of lead nitrate addition

It is well known that the addition of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) in suitable quantities increases the extraction of gold and silver, especially from their refractory ores. However $\text{Pb}(\text{NO}_3)_2$ may hinder the extractions if it is added in very high quantities. The required amount of $\text{Pb}(\text{NO}_3)_2$ for increasing extractions depends on the mineral composition of ores and NaCN consumption may be lowered with the optimum amount of $\text{Pb}(\text{NO}_3)_2$ addition during the cyanide leaching process.

In order to see the effect of $\text{Pb}(\text{NO}_3)_2$ on Ag and Au leaching efficiencies and to find the optimum amount of $\text{Pb}(\text{NO}_3)_2$ addition, a set of experiments were conducted at the following conditions: $\text{Pb}(\text{NO}_3)_2$ addition of 0-300g/t ore, 1/10 solid/liquid ratio, -0.1mm of particle size, room temperature, 0.4g/l reagent used in pH adjustment, 1.0g/l NaCN, and 0-24 hours of leaching time. As it can be seen from the results given in Table 5 that increasing the amount of $\text{Pb}(\text{NO}_3)_2$ addition increased both Ag and Au extractions, and by adding 300g $\text{Pb}(\text{NO}_3)_2$ /t ore, 48.9% Ag and 100% Au leaching efficiencies were achieved. NaCN consumption decreased from 4.4g/t to 3.9g/t ore by adding $\text{Pb}(\text{NO}_3)_2$. In the literature, similar behavior of lead nitrate (200g/t ore) was observed during the cyanide leaching of gold ores containing pyrite and small amounts of pyrrhotite and chalcopyrite and the results showed the reduction in cyanide consumption and an enhancement of gold leaching kinetics (Descenes and Wallingford, 1995).

Table 5
 Experimental results carried out by adding different amounts of lead nitrate.

Pb(NO ₃) ₂ addition (g/t ore)	none	150	300
Time (h)	%Ag Recovery	%Ag Recovery	%Ag Recovery
1	33.1	35.0	36.9
2	34.2	35.1	38.7
3	35.7	-	-
4	-	36.9	39.8
5	36.8	-	-
7	-	38.8	41.0
8	41.2	-	-
24	45.0	43.2	48.9
%Au Recovery (24h)	94.7	98.6	100.0
NaCN Consumption (kg/t) (24h)	4.40	3.91	3.91

4.5. Effect of hydrogen peroxide addition

The constant experimental conditions were: $\text{Pb}(\text{NO}_3)_2$ addition of 300g/t ore, 1/10 solid/liquid ratio, -0.1mm of particle size, room temperature, 0.4g/l reagent used in pH adjustment, 1.0g/l NaCN, 0-48 hours of leaching time and 0-15g/l H_2O_2 addition. Figure 1 shows the change of silver recovery with time at different H_2O_2 concentrations used in the cyanidation. In the experiments without H_2O_2 addition, Ag leaching recovery increased gradually with time and reached about 61.5% at the end of 24h of leaching and leveled off after that point. When H_2O_2 was added, Ag leaching recovery increased rapidly up to 2h of leaching and thereafter continued to increase slowly with increasing time. Similar curves were also observed with different amounts of H_2O_2 addition, with increasing H_2O_2 concentrations shifting the Ag leaching recovery-time curves to higher values. Thus, increasing H_2O_2 concentrations resulted in increasing Ag leaching recoveries.

As seen from Figure 1, leaching time was decreased with the addition of H_2O_2 in the cyanidation. For instance, 62% of Ag recovery was achieved in 2h of cyanidation with 15g/l H_2O_2 addition and this value was higher than the one observed at the end of 24h cyanidation without H_2O_2 addition. Ag recovery was increased from about 38.7% to 62% with 15g/l H_2O_2 addition in 2h cyanide leaching resulting in 60% increase in Ag recovery. The change in Ag recovery with the increase of time from 24h to 48h was not very remarkable. Figure 1 also indicates that the effect of H_2O_2 addition on Ag leaching recovery in the cyanidation carried out for 48h was almost negligible among the experiments with H_2O_2 addition. Almost all gold was leached in all cases. In the earlier studies conducted on the peroxide assisted cyanide leaching of cyanidation plant tailings, up to 50% of silver leaching recoveries were achieved by using 12g/l H_2O_2 addition during the cyanidation (Dincer *et al.*, 1998). As a result of microscopic examinations of leached particles with an electron microscope, a porous structure that was observed, permitted the cyanide solutions to contact easily with the silver and silver minerals locked in the silicate matrix. In another study on gold cyanidation using hydrogen peroxide, it was found that small amounts of H_2O_2 addition actually reduced the cyanidation rate, while higher H_2O_2 dosage rates the cyanidation rate doubled when compared with that of conventional treatment (Guzman *et al.*, 1999).

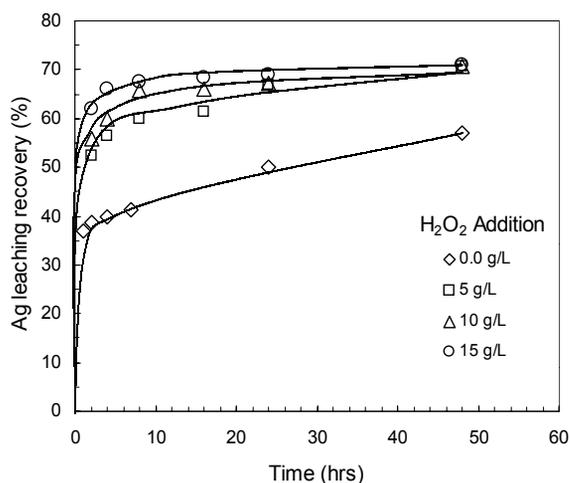


Figure 1. Effect of H₂O₂ addition on Ag leaching recovery with time

In the cyanidation of Au and Ag ores, maximum leaching recoveries with the least reagent consumption are desired. The changes of NaCN and Ca(OH)₂ consumptions with time for different concentrations of H₂O₂ additions are given in Table 6. As observed from the table, increasing H₂O₂ concentration resulted in increasing NaCN consumption along with increasing Au and Ag recoveries. The consumption of NaCN at the end of the 48h leaching period was found to be as 9-9.5kg/t ore. As also seen from the table is that cyanide consumption increases with time even though Au and Ag leaching rates decreases after certain time and starts to stabilize. It is assumed that the high NaCN consumptions are due to the possible decomposition of cyanide with time, since H₂O₂ is used commercially in the decomposition of cyanide tailings (Knoore *et al.*, 1984). There is a noticeable increase in the consumption of Ca(OH)₂ with a small amount of H₂O₂ addition, but the effect decreased with increasing H₂O₂ concentration so that at the end of 48h leaching the consumption of Ca(OH)₂ reached to relatively constant value at around 7-8kg/t ore.

Table 6
 Effect of H₂O₂ addition on NaCN and Ca(OH)₂ consumptions

H ₂ O ₂ Addition	Reagent Consumption (kg/t ore)							
	0.0g/l		5g/l		10g/l		15g/l	
Leaching Time (h)	NaCN	Ca(OH) ₂	NaCN	Ca(OH) ₂	NaCN	Ca(OH) ₂	NaCN	Ca(OH) ₂
2	1.67	0.22	2.65	3.05	2.65	1.39	3.13	1.39
4	2.65	1.39	3.13	3.38	3.63	3.96	3.63	3.71
8	3.40	1.55	3.63	4.37	4.12	4.20	4.12	3.96
16	3.63	1.62	4.61	5.03	4.61	4.37	5.10	4.20
24	3.91	1.73	5.10	6.02	5.10	5.03	5.11	4.70
48	9.02	-	9.26	7.90	9.41	7.67	9.51	7.34

5. CONCLUSIONS

As a result of cyanide leaching tests carried out with a gold-silver ore obtained from Artvin-Cerattepe region of Turkey, the addition of H₂O₂ provided remarkable increases on the leaching recoveries of Au and Ag. With 15g/l H₂O₂ addition during the cyanidation, almost all Au and 71% of Ag were leached. The use of H₂O₂ also diminished the time required for leaching. This fact represents an advantage from the economical point of view. Ag leaching recovery obtained at the end of 24h leaching was lower than the one obtained in 2h with H₂O₂ addition. In this experimental study, it was proven that the use of H₂O₂ as an oxidant in cyanide leaching resulted in increasing of Au and Ag recoveries and in decreasing of leaching period.

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