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INFLUENCE OF LEAD NITRATE ON CYANIDE LEACHING OF GOLD AND SILVER FROM TURKISH GOLD ORES

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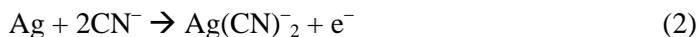
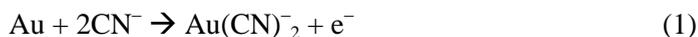
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Abstract: Effect of lead nitrate addition on cyanidation of Havran, Ovacik, Mastra LCu (low copper) and Mastra HCu (high copper) gold ores was investigated by laboratory tests at the Ovacik Gold Mine Metallurgy Laboratory. Leach tests were performed at optimum NaCN additions and pH values while different lead nitrate additions were applied. Ovacik cyanidation plant leaching time, 24 hours for the constant 100 Mg/h ore feed rate was applied as optimal for all lead nitrate tests. Results showed the increase in gold and silver recoveries between 0.4-1.2% for gold and 3.9-11.6% for silver at the end of 24 hours leaching by the addition of lead nitrate as 0.1-0.5 kg/Mg. NaCN consumption decreased or did not change except for the Ovacik ore. In the case of the Ovacik ore it slightly increased.

Keywords: *lead nitrate, gold, silver, cyanide leaching*

Introduction

Extraction of gold from its ores by cyanide leaching has been the preferred method for more than a century because of its simplicity, cost efficiency and the high stability of cyanide. Dissolution of gold and silver in alkaline cyanide solutions can be represented by the half-cell oxidation reactions (Cerovic et al., 2005):



The cathode reaction of dissolved oxygen may be shown as a four-electron transfer reaction (Cerovic et al., 2005):



The anodic dissolution of gold in the aqueous cyanide solution is a complicated process and can be retarded by the formation of intermediate species such as insoluble polymeric Au(CN) film, Au(OH)(CN) and AuS_x on the surface of gold. These species form a passivation layer and may inhibit the diffusion of oxygen and cyanide to the gold surface, causing the inhibition of gold dissolution. The polymerization of the AuCN_{ads} to form ...-Au-CN-Au-CN-.... chain may be the self-poisoning reaction, which blocks the gold surface such that preventing its dissolution (Cerovic et al., 2005; Sandenbergh and Miller, 2001).

It is well known that the presence of heavy metal ions such as lead, bismuth, thallium and mercury exerts the catalytic effect both on gold cyanidation as well as oxygen reduction (Cerovic et al., 2005; Dai and Breuer, 2013; Dai and Jeffrey, 2006; Deschenes et al., 2009; Senanayake, 2008)

The catalytic activity of lead on anodic dissolution of gold consists on the formation of gold-lead alloys such as AuPb₂, AuPb₃ and metallic lead on the surface of gold. These alloys occupy some of the surface sites on gold and prevents the formation of polymerized Au(CN) film and some other passivizing species. However, excessive lead retards the anodic dissolution of gold by formation of Pb(OH)₂ passive layer on gold surface (Deschenes et al., 2000; Sandenbergh and Miller, 2001; Tan et al., 2005).

According to Sandenbergh and Miller (2001) and Cerovic et al. (2005) small amounts of lead nitrate supplying lead up to 2 mg/dm³ increase the anodic dissolution rates of both gold and gold-10% silver alloy. However, dissolution rate started to decrease at lead concentrations above 2 mg/ dm³. Besides, it is shown that oxygen reduction rate on the surface of gold increased and was continuing to increase even above 2 mg/dm³ of lead, up to at least 10 mg/ dm³ lead concentration. Thus, it is stated that maximum dissolution rate is not determined by anodic dissolution reaction, but by the rate of oxygen mass transfer to the metal surface and the catalytic activity of lead in the oxygen reduction reaction. In other words, the dissolution rate of gold was controlled by the mass transfer of oxygen to the gold surface.

A study by Arslan et al. (2003) on a gold-silver ore resulted in Ag recovery increase from 45.0% to 48.9% as well as Au recovery increase, after 24 hours of cyanide leaching by addition of 300 g/Mg lead nitrate to the leach slurry.

Furthermore, numerous studies have shown that lead nitrate addition reduces the detrimental effect of metallic sulfides, increases gold leaching recovery and/or inhibits the dissolution of metallic sulfides, thus reduces cyanide consumption (Deschenes et al., 2003).

Metallic sulfides such as pyrite, chalcopyrite and pyrrhotite show different reaction mechanisms with lead nitrate. Lead nitrate passivizes the pyrite by forming a hydroxide (Pb(OH)₂) layer on pyrite surface reducing the dissolution of pyrite. Dissolution of pyrite forms a sulfur layer on gold causing inhibition of gold dissolution. Thus, in presence of lead this layer is less important. Pyrrhotite shows the

similar effect inhibiting partially the formation of sulfur layer. However, in the case of chalcopyrite this mechanism is not observed (Deschenes et al., 2000).

On the other hand, in the presence of pyrite and pyrrhotite, formation of lead or lead alloys is not observed on the gold surface, but very thin layer forms in the presence of chalcopyrite. Thus, it is proposed that lead does not deposit on gold because of its high affinity to sulfide minerals. It means that lead nitrate addition should be a function of mineralogical composition of the ore (Deschenes et al., 2000; Deschenes and Prud'homme, 1997).

In this paper, the effect of lead nitrate addition to the cyanidation of the Ovacik, Havran, Mastra Low Copper and Mastra High Copper gold ores was investigated and discussed. The Ovacik and Havran ores are processed in Ovacik Gold CIP Plant in İzmir in Turkey, while Mastra is planned to be processed at a CIP plant which will be built in Gumushane in Turkey. The ores are owned by Kozagold Corporation.

Materials and methods

Mineralogy and metal contents

The Ovacik gold ore consists mainly of quartz (about 90%) with small amount of pyrite and arsenopyrite which are partially oxidized to limonite and to other iron oxides. It is indicated that most of the gold would be free-milling. The small amount contained within pyrite could probably also be liberated fairly readily.

Havran gold ore consists mainly of silicified and carbonate minerals with free gold, pyrite, hematite, magnetite, quartz and calcite. Pyrite is mostly converted to hematite (Güney and Gürkan, 2008).

In the Mastra low copper ore major component is disseminated pyrite while gangue is mainly quartz and fine muscovite and coarse pyrite is present in small quantities veined by galena or rimmed by chalcopyrite. The main gold occurrences were associated with pyrite, chalcopyrite, silica and gold telluride. The gold occurred within the silica and around the sulfide and telluride grains, with grain sizes varying between 1-40 microns (Lycopodium, 1996).

The Mastra high copper ore contains mainly pyrite, chalcopyrite, sphalerite and galena. Gangue is mainly quartz and fine muscovite. Three occurrences of gold were detected optically, which is associated with fine and coarse sulfide mineralization and within gangue minerals (Lycopodium, 1996).

Table 1. Chemical analysis of the ores

Ore	Au, ppm	Ag, ppm	Cu, ppm	Zn, ppm	Pb, ppm	Fe, %	S, %
Ovacik	9.17	15.06	38	42	34	1.69	0.07
Havran	5.19	17.31	65	405	282	0.71	0.02
HCu	14.8	11.56	3192	585	963	1.70	3.15
LCu	17.8	3.11	1686	774	1988	1.55	3.00

Table 1 shows the metal content of the the Ovacik, Havran, Mastra High Copper (HCu) and Mastra Low Copper (LCu) ores.

Equipment and experimental procedure

All experimental works were conducted at the Metallurgy Laboratory of Ovacik Gold Mine. The Havran and Ovacik ore samples were taken from the Fine Ore Bin of the Ovacik cyanide leaching plant, while the Mastra ore was supplied from Gumushane region of Turkey. All samples were dried, crushed by a lab type jaw crusher and divided to about 1 kg samples. The samples were then dry ground to p80: – 59 microns for Ovacik, – 52 microns for Havran, –73 microns for Mastra High Copper (HCu) and –63 microns for Mastra Low Copper (LCu) by lab type disc mill.

Leaching tests were conducted by two liters glass beakers and mechanical agitators by sparkling oxygen through the pulp to maintain the 40 ppm dissolved oxygen level which is controlled by dissolved oxygen meter. pH of the slurry was adjusted by lime to be between 10.5–11. Solid/pulp ratio was 43%. Leaching time was 24 hours as at Ovacik CIP plant while pulp temperature was maintained at 20 °C by air conditioning the lab area. NaCN and Pb(NO₃)₂ were added to the pulp as solids at the beginning of the leaching.

After leaching, the final pulp was filtered by pressure filter separating the residual solid and the solution. All samples were analyzed for Au and Ag to determine the metal extraction recovery. Solutions were also analyzed for final NaCN concentrations by silver nitrate titration with rhodamine indicator.

Results and discussion

The cyanide leach tests were applied to the Ovacik, Havran, Mastra Low Copper (LCu) and Mastra High Copper (HCu) ores with different concentrations of lead nitrate additions.

Ovacik ore test results

Three 24 h leaching tests were conducted with 0.4 kg/Mg initial NaCN addition as in the Ovacik plant. The first leaching test was performed without Pb(NO₃)₂, second with 100 g/Mg and third with 300 g/Mg lead nitrate addition. After head and residual solid-solution analysis it is indicated that Ovacik ore showed an increase from 96.72% to 97.35% gold and 73.70% to 77.59% silver leaching efficiency with 0.4 kg/Mg NaCN and 0.1 kg/Mg of lead nitrate. A further increase of lead nitrate to 0.3 kg/Mg resulted in the decrease of Au and Ag leach recovery by comparing with the test of 0.2 kg/Mg lead nitrate, indicating the formation of Pb(OH)₂ passive layer on gold. Besides, NaCN consumption increased from 0.24 kg/Mg without lead nitrate to 0.27 kg/Mg with 0.1 kg/Mg lead nitrate addition. This indicates the precipitation of insoluble lead cyanide. Results are shown in Table 2.

Table 2. Ovacik ore leach results

Initial NaCN addition, kg/Mg ore	Lead Nitrate addition, kg/Mg ore	Au Leach Recovery %	Ag Leach Recovery %	NaCN consumption kg/Mg ore	Initial NaCN in solution, ppm	Final NaCN in solution, ppm
0.4	0.0	96.72	73.70	0.24	302	120
0.4	0.1	97.35	77.59	0.27	302	100
0.4	0.3	97.05	76.11	0.28	302	90

Havran ore test results

Havran ore was investigated in four 24 h leach tests, first without lead nitrate and the others with 0.1, 0.2 and 0.3 kg/Mg lead nitrate. All of the tests were conducted with initial 0.5 kg/Mg NaCN addition corresponding to the plant NaCN consumption for this ore. According to the leach results Au recovery increased from 94.32% to 95.41% with 0.3 kg/Mg lead nitrate while Ag recovery increased from 69.14 % to 74.28%. NaCN consumption decreased up to 0.2 kg/Mg lead nitrate while further increase of lead nitrate to 0.3 kg/Mg resulted in the increased consumption of NaCN. The cause of this phenomenon may be the passivation of the cyanide consuming sulfides by lead nitrate addition up to 0.2 kg/Mg. By further increase of lead nitrate to 0.3 kg/Mg, excessive lead nitrate consumes the NaCN by formation of insoluble lead cyanide. Results are shown in Table 3.

Table 3. Havran ore leach results

Initial NaCN addition, kg/Mg ore	Lead Nitrate addition, kg/Mg ore	Au Leach recovery %	Ag Leach recovery %	NaCN consumption kg/Mg ore	Initial NaCN in solution, ppm	Final NaCN in solution, ppm
0.5	0.0	94.32	69.14	0.27	378	170
0.5	0.1	95.22	74.01	0.25	378	190
0.5	0.2	95.10	74.36	0.23	378	200
0.5	0.3	95.41	74.28	0.30	378	150

Mastra ore test results

Mastra Low and high copper ore were tested by four leaches one with no lead nitrate and others with 0.1, 0.3, 0.5 kg/Mg lead nitrate all of which were with 0.5 kg/Mg NaCN, to obtain 378 ppm initially as it was found as optimum parameter by the previous tests. The results are shown on Tables 4 and 5.

For LCu ore with 0.3 kg/Mg lead nitrate Au extraction recovery increased from 92.81% to 94.04% while NaCN consumption decreased from 0.30 to 0.20 kg/Mg. Besides, Cu in solution decreased with increased lead nitrate showing that lead nitrate partially passivizes the chalcopyrite surface as well as pyrite surface; thus the decrease in NaCN consumption can depend on passivation of chalcopyrite preventing copper to

react with cyanide (Deschenes et al., 2000). However, increasing the lead nitrate up to 0.5 kg/Mg resulted in slight increase on the consumption of NaCN. Ag recovery increased from 58.19% to 65.58% by 0.3 kg/Mg lead nitrate addition as well. Further increase in lead nitrate up to 0.5 kg/Mg decreased the Au and Ag leach indicating the formation of $Pb(OH)_2$ passive layer on Au and Ag surface (Deschenes et al., 2000; Sandenbergh and Miller, 2001; Tan et al., 2005).

Table 4. Mastra low copper ore (LCu) leach results

Initial NaCN addition, kg/Mg ore	Lead Nitrate addition, kg/Mg ore	Au Leach Recovery %	Ag Leach Recovery %	NaCN consumption kg/Mg ore	Final NaCN in solution, ppm	Cu in solution, ppm
0.5	0.0	92.81	58.19	0.30	150	30.52
0.5	0.1	93.52	59.15	0.29	160	23.06
0.5	0.3	94.04	65.58	0.20	230	14.45
0.5	0.5	93.26	59.84	0.23	200	10.03

Table 5. Mastra high copper ore (HCu) leach results

Initial NaCN addition, kg/Mg ore	Lead Nitrate addition, kg/Mg ore	Au Leach Recovery %	Ag Leach Recovery %	NaCN consumption kg/Mg ore	Final NaCN in solution, ppm	Cu in solution, ppm
0.5	0.0	96.77	38.08	0.41	70	34.84
0.5	0.1	97.14	36.45	0.38	90	31.40
0.5	0.3	96.77	36.25	0.35	110	25.23
0.5	0.5	97.16	49.69	0.34	120	26.78

For high copper ore Au leaching recovery slightly increased from 96.77% to 97.16% while NaCN consumption decreased from 0.41 to 0.34 kg/Mg with 0.5 kg/Mg lead nitrate addition. The aqueous solution analysis indicated that Cu dissolution was prevented with increasing lead nitrate addition. Thus, the reduction of NaCN consumption proportional to the increasing lead nitrate addition can be related to the increased passivation of chalcopyrite by lead nitrate (Deschenes et al., 2000). Besides, Ag leach recovery increased from 38.08% to 49.69% confirming the references indicating the increase of Ag as well as Au recovery (Arslan et al., 2003).

Conclusions

The effect of lead nitrate addition in cyanide leaching of four different gold ores was investigated. All of the ores showed increases in gold and silver leaching recoveries with lead nitrate addition. In the case of the Ovacik ore leach recovery increased from 96.72% to 97.35% in gold and from 73.70% to 77.59% in silver with 0.1 kg/Mg lead nitrate; in the case of the Havran ore 94.32% to 95.41% in gold and 69.14% to 74.28

in silver with 0.3 kg/Mg lead nitrate; in the case of the Mastra LCu ore from 92.81% to 94.04% in gold and 58.19% to 65.58% silver with 0.3 kg/Mg lead nitrate; in the case of the Mastra HCu ore from 96.77% to 97.16% in gold and from 38.08% to 49.69% in silver by 0.5 kg/Mg lead nitrate. NaCN consumption, in general, decreased down to certain lead nitrate concentrations, except the Ovacik ore. In the case of the Ovacik ore it increased proportionally to increasing lead nitrate addition.

In the case of lead nitrate addition to cyanide leaching of these Turkish ores increase in production of gold and silver is predicted as 2704 troy oz Au and 26362 troy oz Ag per year, when plant ore feed tonnage is estimated as 100 Mg/h with 24 h leaching time and when the average recovery increases are calculated as 0.8% for gold and 7.8% for silver with average tenors of 12 ppm gold and 12 ppm silver. Thus, the annual increase of revenue has been expected as \$4.3 million for gold and \$0.8 million for silver when metal prices are predicted as \$1600/troy oz for gold and \$30/troy oz for silver.

References

- ARSLAN F., OZDAMAR D.Y., MUDUROGLU M., 2003, *Cyanidation of Turkish gold-silver ore and the use of hydrogen peroxide*, The European Journal of Mineral Processing and Environmental Protection, vol 3, No 3, 309–315.
- CEROVIC K., HUTCHISON H., SANDENBERGH R.F., 2005, *Kinetics of gold and a gold – 10% silver alloy dissolution in aqueous cyanide in the presence of lead*, Minerals Engineering 18, 585–590.
- DAI X., BREUER P.L. 2013, *Leaching and electrochemistry of gold, silver and gold–silver alloys in cyanide solutions: Effect of oxidant and lead(II) ions*, Hydrometallurgy, Vol. 133, 139–148.
- DAI X., JEFFREY M.I. 2006 *The effect of sulfide minerals on the leaching of gold in aerated cyanide solutions*, Hydrometallurgy, Vol. 82, Iss. 3–4, 118–125.
- DESCHENES, G., LACASSE, S., FULTON, M., 2003, *Improvement of cyanidation practice at Goldcorp Red Lake Mine*, Minerals Engineering 16, 503–509.
- DESCHENES G., LASTRA R., BROWN J.R., JIN S., MAY O., GHALI E., 2000, *Effect of lead nitrate on cyanidation of gold ores: Progress on the study of the mechanisms*, Minerals Engineering, 13, 1263–1279.
- DESCHENES G., PRUD'HOMME P.J.H., 1997, *Cyanidation of a copper-gold ore*, Int. J. Mineral Processing, 50, 127–141.
- DESCHENES G., XIA C., FULTON M., CABRI LOUIS J., PRICE J. 2009, *Evaluation of leaching parameters for a refractory gold ore containing aurostibite and antimony minerals: Part I – Central zone*, Minerals Engineering, Vol. 22, Iss. 9–10, 799–808.
- GUNEY A., GURKAN V., 2008, *Cesitli Kayac Orneklerinin Mineral Ozellikleri ve Altin Faz boyutlarının Belirlenmesi*, ITU Maden Fakultesi Vakfi Iktisadi Isletmeleri, Technical Report.
- LYCOPODIUM PTY. LTD., 1996, *Prefeasibility study*, volume 3 (1996).
- SANDENBERGH R.F., MILLER J.D., 2001, *Catalysis of the leaching of gold in cyanide solutions by lead, Bismuth and Thallium*, Minerals Engineering 14, 1379–1386.
- SENANAYAKE G., 2008 *A review of effects of silver, lead, sulfide and carbonaceous matter on gold cyanidation and mechanistic interpretation*, Hydrometallurgy, Vol. 90, Iss. 1, 46–73.
- TAN H., FENG D., LUKEY G.C., VAN DEVENTER J.S.J., 2005, *Effect of carbon coatings on gold dissolution in the presence of sulfide and lead*, Minerals Engineering 18, 1361–1372.