Cyanide and Metal Removal from Gold Cyanidation Effluents

Linda A. Figueroa[1], Inge Delius[2], Christopher Bellona[3]

[1]*Department of Civil and Environmental Engineering, Center for Mining Sustainability, Colorado School of Mines, Golden, Colorado, 80401 lfiguero@mines.edu, ORCID 0000-0003-3588-6705*

[2]*Department of Civil and Environmental Engineering, Center for Mining Sustainability, Colorado School of Mines, Golden, Colorado, 80401 ideliuscordova@mines.edu, ORCID 0000-0002-8185-3712*

[3]*Department of Civil and Environmental Engineering, Center for Mining Sustainability, Colorado School of Mines, Golden, Colorado, 80401 cbellona@mines.edu, ORCID 0000-0003-3366-3559*

Abstract

Gold cyanidation effluent often contains high levels of cyanide and metals. While removal in synthetic water is well demonstrated, real process water introduces complexities that need further study. Batch tests with process waters from three Peruvian sites evaluated an electrochemical approach for contaminant removal. Cyanide destruction was two orders of magnitude slower in real water, and copper removal varied with water composition. The results underscore the need to understand process water chemistry to create a reliable treatment design framework. Additional research is essential for optimizing cyanide and metal removal in practical applications.

Keywords: Copper, metal cyanide complex, electrochemical treatment, process water chemistry

Introduction

Cyanide is commonly used in the mining industry to extract gold from gold-bearing ores, particularly low-grade ores where gold cannot be extracted through processes such as crushing and gravity separation. Cyanidation is the most common lixiviant for gold extraction and is added in excess. At alkaline pH, the cyanide ion (CN^-) dissolved the gold contained in the ground ore under mildly oxidizing conditions by forming water soluble gold-cyanide complexes such as $NaAu(CN)_2$. After recovery of the gold cyanide complex, the remaining process water (barren solution) contains the excess cyanide and metals extracted from the gold ore.

Cyanide discharge standards vary with the receiving environment. The International Cyanide Management Code has designated a limit of 50 mg/L in process water storage facilities. In the US, pretreatment standards for discharge into a publicly owned treatment works is 1.2 mg/L. Additional, drinking water and aquatic limits are 200 ppb and 50ppb, respectively. Copper and Zinc are the major metals observed in cyanidation process waters. Drinking water limits for copper and zinc are relatively high, 1 mg/L and 5 mg/L, respectively. Aquatic limits on copper and zinc are the primary drivers of treatment. Specific values depend on the discharge and receiving water chemistry. Copper limits are on the order of 10 of mg/L with zinc limits on the order of 100 mg/L. The release or reuse of barren solutions from gold cyanidation processing requires reduction of the cyanide and metals to discharge standards.

Electrochemical oxidation of cyanide along with the formation of copper and zinc solid phases has the potential to meet the treatment goals without chemical addition. Investigations with synthetic waters have demonstrate the ability to concurrently removal both contaminants. However, real process waters introduce complexities that require further investigation (Sierra-

Alvarado *et al.* 2022). Batch tests with process waters from three Peruvian sites evaluated an electrochemical approach for contaminant removal.

Methods

Real process wastewater samples came as barren solutions from three different small gold processing facilities in the Arequipa region of Peru. These waters were transported to the lab facility in Arequipa for electrochemical experiments. The initial pH of real wastewater solutions was adjusted and throughout the experiments maintained at approximately 11.5 by addition of 1M NaOH to avoid release of HCN gas. Each experimental condition was implements over a 2-day period. Ten experimental conditions in all were evaluated, only experiments where pH 11.3–11.5 was maintained were assessed, Tab. 1.

Experiments were carried out in a 1L beaker which worked as the electrolytic cell. The pH and temperature of the water were measured using a pH meter equipped with a temperature probe (Thermo Scientific Orion model 520A and 420A+) which was suspended by a swing arm electrode holder. Electrical power was supplied using a DC Power Supply made by EXTECH (model 382202, 0 to 18V, 0 to 3A). The beaker was placed on a magnetic stirring plate to keep the solution well mixed throughout the experiment. The anode was composed of pure graphite plate sheets while the cathode was composed of pure copper sheets. All experiments were carried out at ambient temperature, 20 ± 2°C. The electrode cross sectional area was approximately 15×3 cm with a 3mm width for graphite sheets and 1mm width for copper sheets. The electrodes were held at about 3cm from each other. The submerged area of the electrodes in the solution was 19.5 cm^2.

The current efficiency describes the efficiency in which electrons are transferred in an electrochemical system to facilitate a reaction. To calculate current efficiency (E_C), the number of Coulombs used by the reaction of interest is divided by the total number of Coulombs available in the electrochemical system.

$$E_C = \frac{Coulombs\ used\ by\ reaction\ of\ interest}{Available\ Coulombs} \times 100$$

The current efficiency for cyanide, copper and zinc reactors were based on the stoichiometries shown below (Marsden 2006).

$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^-$

$Cu^+ + e^- \rightarrow Cu$

$Zn^{2+} + 2e^- \rightarrow Zn$

Results and Discussion

Samples were collected at the beginning and end of each experiment. The initial measured concentrations varied some with each experiment conducted. The average values for each site are presented in Tab. 2. Cyanide, copper and zinc removal are shown along with the current efficiency in Tab. 3. Initial and final molar concentrations of the different forms of cyanide along with copper and zinc are shown in Fig. 3.

Reduction of all cyanide forms and metals was higher at 5V applied compared to the application of 2V. In experiments with synthetic water, copper removal is higher at lower voltages (Felix-Navarro 2003). Lower removal of cyanide and metals were observed at 2V for Site 1 relative to Site 2. The metal-cyanide complex concentrations were double the values at Site 1. Concurrent destruction of free and WAD cyanides was observed at 5V for all sites and at 2V for Site 1. However, only free cyanide destruction was observed

***Table 1** Experiments conditions for real process water samples.*

Experimental Condition	Site	Voltage	pH	Conductivity (mS/cm)
1	1	2	11.5	13.3
2	1	5	11.5	
3	1	5	11.5	
4	2	2	11.3	5.0
5	2	5	11.4	
6	3	5	11.5	24.5

Table 2 *Average values for real process water samples.*

Component	Site 1	Site 2	Site 3
Initial pH	10.8	11.3	9.7
WAD+Free Cyanide	1180	2390	2290
Total Cyanide	1440	2670	2780
Free Cyanide	790	1530	1510
Cl^-	820	680	20500
NO^{3-}	130	60	540
NO^{2-}	220	100	120
SO_4^{2-}	6000	4500	13800
PO_4^{3-}	90	190	0
Ca	1030	1610	1920
Na	4950	3190	15200
Sr	10	10	120
K	170	290	360
Si	210	230	220
Zn	130	620	150
Mg	240	240	470
Fe	10	20	2
Cu	230	180	580
As	12	1	4

Table 3 *EPercent of cyanide and metal removal and current efficiency.*

	% removal				% current efficiency		
ID	Free CN	WAD CN	Copper	Zinc	Free CN	Cu	Zn
Site 1@5V	90	92	96	73	14	1	1
Site 1@ 2V	45	60	69	69	71	4	4
Site 2@5V	59	58	67	45	32	1	4
Site 2@2V	11	0	0	0	82	0	0
Site 3@5V	86	79	94	0	98	9	0

for Site 2 at 2V. Additional investigation is needed on the impact of metal cyanide complexes concentrations at low and high applied voltages.

Current efficiency results are consistent with the hierarchy of electro potential of the reactions: Cyanide > Copper > Zinc. Site 3 process water current efficiency was 100% for the observed removals. A longer reaction time may have resulted in subsequent zinc removal when additional electrons (current) are provided. Copper and zinc removals greater than 65% and 40%, respectively were observed when current efficiency was 20–80%. Higher removal of the cyanide and metals at current efficiencies < 100% may still require longer reaction times if the limitation is kinetic.

Conclusions

The effects of applied voltage, initial cyanide and copper concentrations and composition of the electrolyte on the degradation rates of cyanide and removal of metals from real gold cyanidation wastewater were studied. In general, cyanide degradation rates

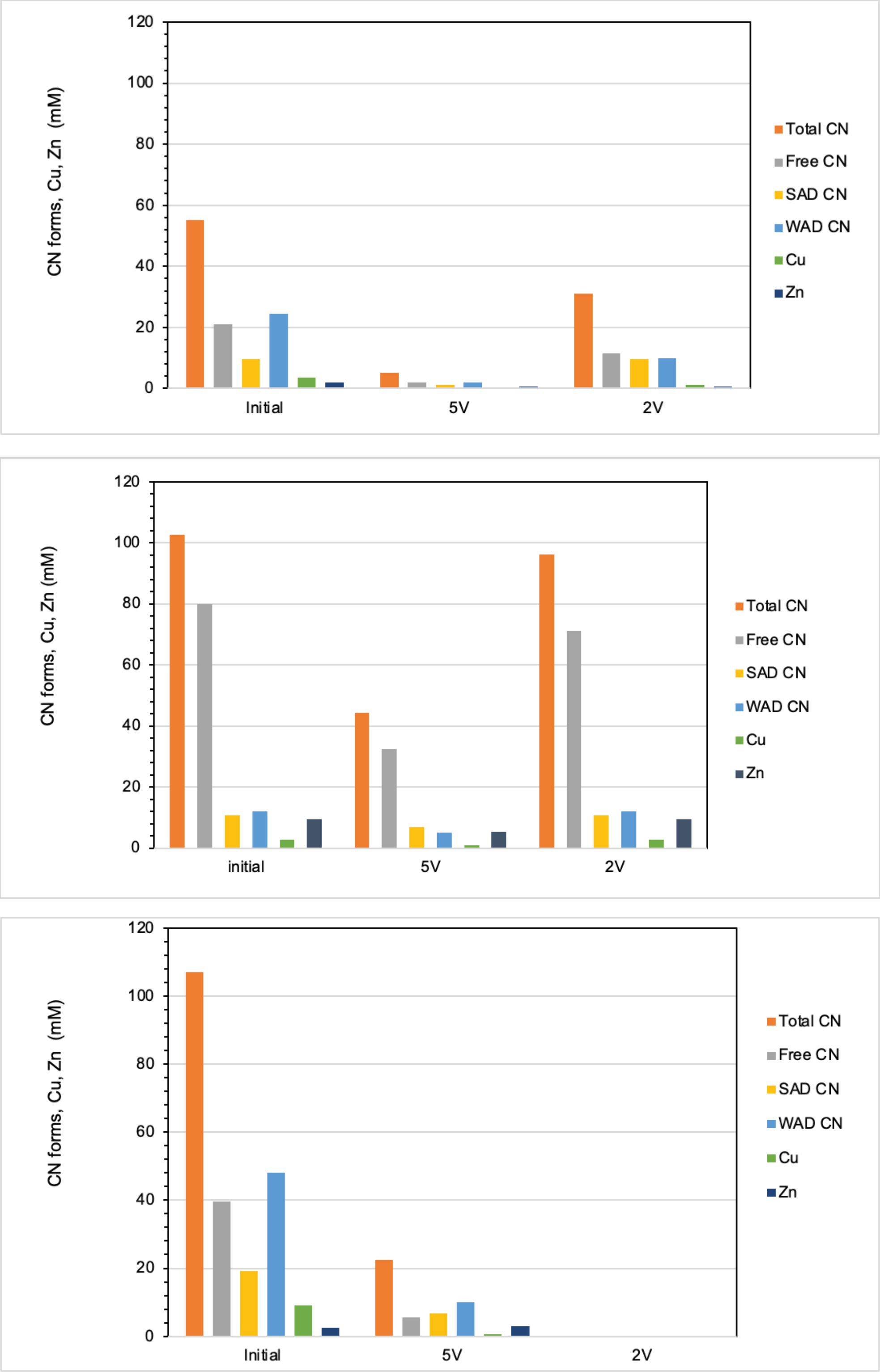

Figure 1 *Initial and final concentrations of cyanide and metals from the field sites: (a) Site 1, (b) Site 2 and (c) Site 3 (no data at 2V).*

increased with conductivity and higher applied voltages. Real wastewater contained additional constituents and higher the rate of cyanide degradation had more complex relationships with voltage and conductivity than observed in studies with synthetic waters. In process wastewater, more metal removal occurred at higher applied voltage which is opposite compared to synthetic waters. Zinc and copper were the only metals removed from process wastewater during the electrochemical experiments. Real wastewater with the highest measured conductivity removed over 90% copper and 80% cyanide at 5 V. Additional work is needed with real gold cyanidation process wastewater to determine optimal conditions based on water composition.

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