

Destruction of cyanide by hydrogen peroxide in tailings slurries from low bearing sulphidic gold ores

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Abstract

The main objective of this work was to determine the effectiveness and kinetics of hydrogen peroxide in destroying cyanide in the tailings slurry from a gold mine with low sulphide and heavy metal content. The impacts of catalyst (Cu) and hydrogen peroxide concentrations, temperature and pH on the extent and rate of weak acid dissociable (WAD) cyanide destruction were investigated. Experiments were conducted using the variable-dose completely mixed batch reactor bottle-point method. Both the rate and extent of CN_{WAD} destruction generally increased with increasing peroxide doses for either absence or presence of Cu catalyst. Catalyst addition was very effective in terms of not only enhancing the cyanide destruction rate but also significantly reducing the required peroxide dosages to achieve CN_{WAD} concentrations of about 1 mg/l, independent of the temperatures tested (10, 20 and 30 °C). The initial cyanide destruction rates increased between 1.2 and 3 folds with the addition of 30 mg/l of Cu. Kinetic experiments showed that in most cases little CN_{WAD} destruction occurred after a reaction time of 2–4 h. The impact of slurry pH on cyanide destruction varied depending upon the dosages of Cu catalyst. Relatively lower peroxide dose/CN_{WAD} ratios required to achieve less than 1 mg/l of CN_{WAD} may be due to lower heavy metals and sulphide content of the ore, resulting in lower peroxide requirement for metal bound cyanides. During cyanide destruction, nitrate was initially formed as a by-product and then possibly converted to other some volatile nitrogen-containing species, as supported by the mass balance calculations.

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1. Introduction

Gold and silver recovery by cyanidation is widely used in mining operations. Other industrial applications of cyanide include metal processing, electroplating, steel hardening, photographic applications, and synthetic rubber production (Habashi, 1987; Mudder, 2001; Mudder et al., 2001a; Botz and Mudder, 2002; Akcil, 2003a). Although gold mining operations use dilute solutions of sodium cyanide (100–500 ppm), cyanide is used at nearly 90% of the gold mines in relatively high quantities and is potentially toxic.

Several destruction or recovery processes are well proven and can produce treated solutions or slurries with low levels of cyanide and its related compounds

(Botz et al., 1995; Botz, 2001; McNulty, 2001; Akcil, 2002, 2003a; Botz and Mudder, 2002; Akcil et al., 2003). Cyanide treatment processes may be classified as a destruction-based process versus the physical processes of cyanide recovery and activated carbon sorption. Most cyanide destruction processes operate on the principle of converting cyanide into one or more less toxic compounds such as ammonia, cyanate (OCN⁻) and nitrate through an oxidation reaction. Cyanide oxidation can be conducted using chemical, catalytic, electrolytic, biological, ultrasonic, and photolytic methods (Young and Jordan, 1995; Augugliaro et al., 1997, 1999; Saterlay et al., 2000; Botz, 2001; Mudder et al., 2001a,b). Some of the oxidation-based destruction processes include INCO (SO₂/Air), hydrogen peroxide (H₂O₂), Caro's acid (peroxymonosulphuric acid, H₂SO₅), alkaline breakpoint chlorination, and biological treatments (Mudder, 1987; Botz et al., 1995; Barclay et al., 1998; Whitlock and Mudder, 1998; Botz and

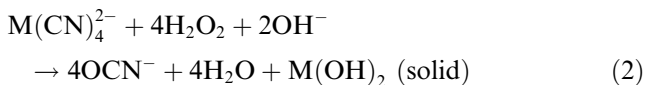
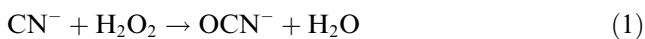
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Mudder, 2000; Mudder et al., 1998, 2001a,b; Adams et al., 2001; Akcil and Mudder, 2003; Gurbuz et al., 2004).

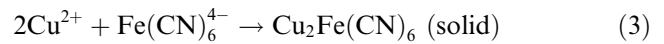
As an oxidation-based process, hydrogen peroxide has been tested and used worldwide for cyanide removal in mining operations (DuPont, 1974; Mathre and DeVries, 1981; Harrison, 1983; Knorre and Griffiths, 1984; Castrantas et al., 1988; Castrantas and Fagan, 1992; Mudder et al., 2001a,b). Hydrogen peroxide was first pilot tested on a continuous scale at the Homestake Mining Company Lead, South Dakota operation in the USA in the early 1980s (Trautman and Ommen, 1981; Mudder et al., 2001a,b). The first full scale hydrogen peroxide treatment facility in the mining industry was built and operated by Degussa at the Ok Tedi Mine in Papua New Guinea. A tailings flow of 1100 m³/h containing 110–300 mg/l of total cyanide was treated to 1–10 mg/l, with the CN_{WAD} level being <0.50 mg/l (Knorre and Griffiths, 1984; Mudder et al., 2001a,b). In many currently operating mining operations, hydrogen peroxide has been used successfully in reducing free and weak acid dissociable (WAD) cyanide concentrations to low levels suitable for discharge. Hydrogen peroxide is effective for the treatment of solutions for the oxidation of free and WAD cyanides, and iron cyanides are removed through precipitation of insoluble copper–iron–cyanide complexes (Botz, 2001). It is a simple process capable of operating over wide pH ranges, while producing environmentally acceptable effluents without increasing total dissolved solids as do other chemical processes. Through a considerable degree of testing conducted in the Homestake Toxicological Testing Facility in Lead, South Dakota utilizing the effluents from a pilot plant facility and a variety of test organisms, the hydrogen peroxide process was found to yield environmentally acceptable effluent (Mudder et al., 2001b). However, it is suggested that the use of hydrogen peroxide to treat slurries is limited due to the high consumption resulting from its reaction with solids in the slurry (Botz, 2001; Mudder et al., 2001a,b; Akcil, 2003a). Furthermore, high concentrations of heavy metals in slurries also may lead to excessive decomposition of hydrogen peroxide (FMC Corp., 2004).

Hydrogen peroxide can oxidize free and weakly complexed metal cyanides (i.e., nickel, copper, cadmium, and zinc cyanides) as following (Mudder et al., 2001b):



Soluble copper catalyst may increase the reaction rates. The copper catalyst can be either copper present in solution (from gold/silver cyanidation processes) or can be added as a reagent copper solution. Peroxide is not effective in destroying thiocyanate. Metals complexed

with cyanide are precipitated as metal hydroxides depending on the pH of the solution, with an optimum pH of about 9.0–9.5. However, the oxidation process may operate well over a wide pH range. A pH below about 9.0 is optimal for precipitation of iron cyanides. Generally, higher pH values are employed due to the fact that removal of other metals is preferred over iron cyanide removal. The stable iron cyanide complexes are not converted to cyanate by hydrogen peroxide, but are removed from solution through precipitation as an insoluble copper–iron–cyanide complex (Mudder et al., 2001a,b):



Cyanate produced in the reactions will hydrolyze to form ammonia and bicarbonate, with the rate of hydrolysis being more rapid at lower pH values. Normally, about 10–20% of the cyanide is converted to ammonia during treatment (Mudder et al., 2001b).



Excess hydrogen peroxide added for cyanide oxidation will decompose to yield oxygen and water, an advantage when the concentration of dissolved solids is of concern in the treated water (Mudder et al., 2001b).

Overall, the advantages of the hydrogen peroxide process can be summarized as follows: capital costs are comparable (or less) to other chemical treatments; the process is relatively simple in design and operation; all forms of cyanide can be removed; heavy metals are significantly reduced through precipitation; close pH control is not required; the process is adaptable for batch and continuous flow operations; no production of high quantities of waste sludge and dissolved solids; and the process has been shown effective in bench-, pilot- and full-scale operations. On the other hand, the disadvantages are as follows: the process may not be generally suitable for treatment of tailings slurries; chemical costs may be relatively high; high concentrations of cyanate can be produced, potentially increasing the ammonia concentration in the solution; the process does not remove ammonia or thiocyanate; and cyanide is not recovered (Mudder et al., 2001a,b).

Although it is suggested in the literature that hydrogen peroxide may not be efficient for slurries due to high consumption resulting from auto-catalytic destruction on solid surfaces or from high heavy metals content, there is a need to investigate the efficacy of hydrogen peroxide in destroying cyanide for tailings slurries from ores with relatively low sulphide and heavy metals content. The main objective of this work was to determine the effectiveness and kinetics of hydrogen peroxide in destroying cyanide in the tailings slurry from a gold mine (Ovacik Gold Mine, Turkey) with low sulphide

and heavy metals content compared with other refractory and sulphidic ores. The impacts of catalyst (Cu) and hydrogen peroxide concentrations, temperature and pH on the extent and rate of cyanide destruction were investigated.

2. Materials and methods

2.1. Samples

The tailings slurry samples (after cyanidation process) were taken from the Ovacik Gold Mine. The samples were shipped overnight to the laboratory in the headspace free, high-density polyethylene containers. The pH values of the samples were kept at about 10.5 to minimize the loss of cyanide as HCN gas. The Ovacik gold mine is located near the western coast of Turkey. The ore contains less than 0.02% S²⁻ in the form of pyrite and has high alkalinity value. As sulphide minerals are almost absent (less than 0.15%), there is no risk of acid mine drainage for the ore or waste material (Akcil, 2002, 2003b). Ovacik ore is significantly low in heavy metals contents compared with other typical ores. Table 1 shows the physicochemical characteristics of the tested tailings slurry samples. Average total cyanide and heavy metal concentrations measured during one-year testing period (June 2001–May 2002) were obtained from Akcil (2002). The gold–silver deposit consists of two economically mineable quartz veins epithermally formed in andesite. Gold occurs as free grains as gold–silver combination with an average size of 0.005 mm within the fissures between quartz grains (Akcil, 2003b).

2.2. Experimental procedures

During the experiments, the tailings slurry samples were stored in containers headspace free in the dark at about 8 ± 1 °C to minimize the loss of cyanide. Sample CN_{WAD} concentrations were periodically checked before each experiment to verify the sample integrity, and negligible losses of cyanide (about <2 mg/l) was found during the course of experiments. CN_{WAD} concentrations of the original samples ranged about 57–64 mg/l (Table 1). Furthermore, each experimental matrix was conducted very quickly (i.e., within couple days) so that the samples waited less than of about 10 days in the controlled conditions in the laboratory. Before each experiment, headspace free sample containers were mixed to prevent the settling of solids and homogenize the slurries.

All hydrogen peroxide oxidation experiments were performed in two phase: kinetic and constant reaction time experiments with variable hydrogen peroxide and catalyst concentrations, pH and temperature. Experiments were conducted using the variable dose completely mixed batch reactor (CMBR) bottle-point method. For each experimental matrix, after dosing hydrogen peroxide and/or Cu catalyst, the slurries in headspace free CMBRs (100-ml pyrex glass bottles sealed with PTFE screw-caps) were kept well mixed (100 rpm) in a temperature-controlled orbital shaker and incubator (Gallenkamp). The bottles were covered with aluminum foil to prevent photodegradation of cyanide during mixing. After the pre-selected reaction time terminated, the bottles were opened in a vacuum hood and quickly dosed with sodium sulfite (Na₂SO₃) to quench the residual peroxide and stop the oxidation reaction.

Table 1
Physicochemical characteristics of the tailings slurry sample from the Ovacik Gold Mine

Parameter ^{a,b}		Total cyanide and heavy metals content ^{c,d} (mg/l)	
CN _{WAD} (mg/l)	57–64	CN _{Total}	144
Cu (mg/l)	1.6	Cd	<0.01
Fe (mg/l)	1.3	Zn	1
Total dissolved solids (mg/l)	2463	Cu	6
Conductivity (mS/cm)	3.99	Pb	<0.05
Turbidity (FTU)	5	As	2
Alkalinity (mg/l as CaCO ₃)	620	Sb	10
Total hardness (mg/l as CaCO ₃)	360	Fe	3
pH	9.5–10.3	Cr	<0.01
Solids (% w/w) ^e	40–43	Hg	<0.01
Nitrite (mg/l)	0.99		
Nitrate (mg/l)	16.5		
Ammonia (NH ₃ -N) (mg/l)	15.3		
Total Kjeldahl Nitrogen (mg/l)	18.5		
Total nitrogen (mg/l)	35.9		

^a The tailings slurry sample taken after cyanidation process was filtered (0.45 μm, cellulose acetate) before all above aqueous-phase analysis.

^b Values represent the average of triplicate measurements. For all the analysis, coefficient of variations between measured values were less than 8%.

^c Data obtained from Akcil, 2002.

^d The tailings slurry samples were taken after cyanidation process. Average values during one-year sampling period (June 2001–May 2002).

^e Unfiltered original slurry samples.

Sulfite was added in slight excess (i.e., 1.2 times) of the stoichiometric requirements to ensure complete quenching. Bottles were then closed and mixed about 3 min at 100 rpm in the shaker for quenching reaction. Then, bottles were opened, and about 5–10 ml of sample was filtered (0.45 μm cellulose acetate sterile syringe filters) very quickly for CN_{WAD} analysis. A total of about 25–30 ml sample was filtered if the sample was to be analyzed for CN_{WAD} , nitrate and heavy metals content. In the preliminary experiments, centrifugation instead of filtration was tested to remove solids before CN_{WAD} analysis. However, it was found that during centrifugation about 3–5% of CN_{WAD} concentration was lost. Therefore, for all experiments, filtration through 0.45 μm was the chosen method to remove solids before aqueous-phase analysis.

For the kinetic experiments, reaction times selected were 0.5, 1, 2, 4, 8, and 24 h. As discussed in the results section, kinetic experiments showed that in most cases, little reduction in cyanide concentration occurred after a reaction time of 4 h; therefore, 4 h of reaction time was selected for the following constant reaction time experiments. Tested hydrogen peroxide doses were 10, 20, 50, 75, 100, 150, 200, 300, 500, and 1000 mg/l. Tested Cu catalyst concentrations were 0, 10 and 30 mg/l. Temperature and pH values investigated in the experimental matrix were 10, 20 and 30 °C and 7.5, 8.5, 9.5, and 10.3 ± 0.2 (original samples), respectively. Sample pH values were adjusted using reagent grade NaOH and/or HCl solutions with different molar concentrations. In an effort to minimize the loss of cyanide in lower pH experiments (i.e., <10.3), the slurries in containers were transferred quickly to smaller containers with quantities necessary for the target experiment, and the pH was adjusted very quickly by adding pre-determined amounts of acid. The small containers (about 1 l) having narrow openings were filled completely with the slurries, and during pH measurement/adjustment, the openings were sealed with parafilm around the pH probe to minimize air–water interface. As with all experiments, the CMBRs used for pH experiments were also filled headspace free. Control experiments (without peroxide dosing) were also periodically conducted to check for the possible losses of cyanide (i.e., via photodegradation, hydrolysis, volatilization, natural degradation) in headspace free CMBRs during mixing. Results even after 24 h of mixing (for different catalyst dosages and pH values) overall suggested that negligible loss of cyanide (± 3 mg/l) occurred with initial CN_{WAD} concentrations of about 57–64 mg/l.

2.3. Analytical methods

Weak acid dissociable (WAD) cyanide parameter was selected to quantify the cyanide concentration in the experiments. It represents the total concentration of free

cyanide (CN^- and HCN) and weak and moderately strong metal–cyanide complexes of Ag, Cd, Cu, Hg, Ni, and Zn. CN_{WAD} is the appropriate selection for most situations since it includes the toxicologically important forms of cyanide (Botz, 2001). Free and complexed cyanide reacts with picric acid reagent to produce orange color that can be measured colorimetrically at a wavelength of 520 nm. A UV–vis spectrophotometer (UV-1601, Shimadzu) was used to measure the absorbances (in triplicate) at this wavelength. Calibration standards were prepared from reagent grade sodium cyanide employing the same CN_{WAD} analysis methodology. Calibration curves were prepared for each test (R^2 values >0.99 for all tests). In all experiments, measured concentrations in triplicates exhibited coefficient of variations less than 3–6%.

Total dissolved solids, conductivity, turbidity, alkalinity, total hardness, pH, solids content, nitrite, nitrate, ammonia, total Kjeldahl nitrogen, and total nitrogen were measured according to Standard Methods (APHA, 1995). Nitrate was measured employing cadmium reduction method (NitraVer 5 Nitrate Reagent) using a spectrophotometer (DR/2000, Hach). Heavy metal concentrations were measured using atomic absorption spectrometry based on Standard Methods.

A 30% hydrogen peroxide aqueous solution (Merck) was used as the stock solution for all experiments. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (Merck) was used as the copper catalyst. All chemicals used were reagent grade. Distilled and deionized water was used for stock solution preparations and dilutions.

3. Results and discussion

3.1. Kinetic experiments

Kinetic experiments for the destruction of CN_{WAD} were performed with variable hydrogen peroxide and catalyst concentrations (0, 10 and 30 mg/l), and temperature. CMBRs were sampled at reaction times of 0.5, 1, 2, 4, 8, and 24 h. Fig. 1 (A and B) shows the destruction of CN_{WAD} with various peroxide doses in the absence and presence of Cu (30 mg/l) catalyst. Both the rate and extent of cyanide destruction generally increased with increasing peroxide doses for either absence or presence of Cu catalyst cases. Similarly, the initial rate of cyanide destruction (i.e., removal within 30 min) also increased significantly with increasing peroxide dosages (Fig. 2), consistent with the literature in which the rate of catalytic cyanide oxidation with peroxide and Ru/MgO catalyst was determined by $\text{H}_2\text{O}_2/\text{CN}$ ratio (Pak and Chang, 1997). In the absence of catalyst, only peroxide dose of 300 mg/l was able to achieve less than 1 mg/l CN_{WAD} after 4 h of reaction time. Peroxide doses of 150 mg/l or less reduced CN_{WAD}

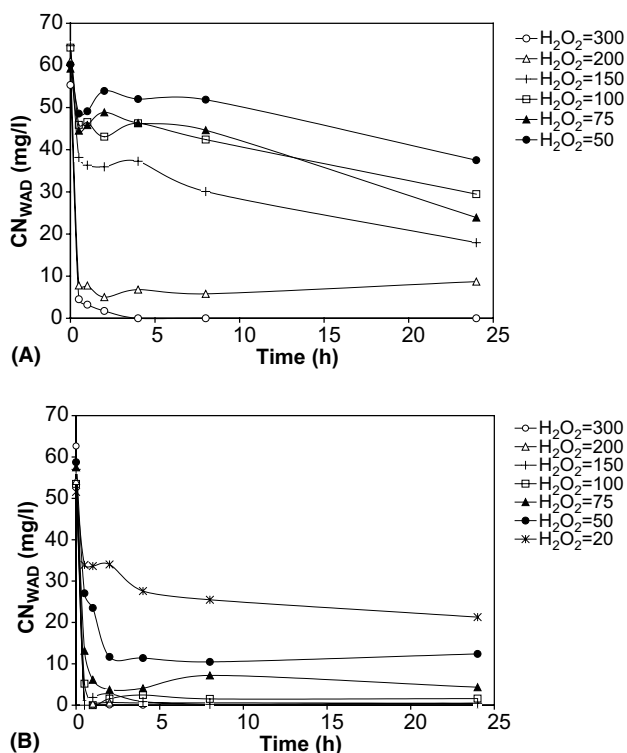


Fig. 1. Destruction of CN_{WAD} with various peroxide dosages in the absence (A) and presence (B) of Cu catalyst ($Cu = 30$ mg/l). Peroxide dosages are in mg/l. $T = 20$ °C, $pH = 10.3$ (original sample).

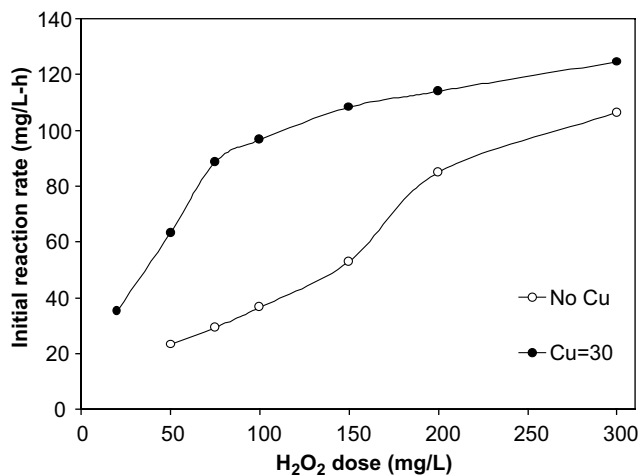


Fig. 2. Impact of initial hydrogen peroxide dosage on the initial destruction rate of CN_{WAD} . $T = 20$ °C, $pH = 10.3$ (original sample). Copper dosages are in mg/l.

concentrations only to about 18–37 mg/l (initial CN_{WAD} concentrations ranged between 57 and 64 mg/l). For the peroxide doses less than 150 mg/l, further reduction in cyanide concentrations were consistently found after 4 h of reaction time in the absence of catalyst (Fig. 1A). However, such a trend was not generally observed with the presence of catalyst (30 mg/l); maximum 2–4 h of

reaction time was sufficient to achieve the ultimate residual cyanide concentrations (Fig. 1B). For peroxide doses less than 150, 30 mg/l of catalyst addition increased percent cyanide removals between 60% and 74% compared with no catalyst case at a reaction time of 4 h. For peroxide doses larger than 150 mg/l, increases in cyanide removals from catalyst addition were about 3–12%. This result suggests that catalyst addition has more positive impact on removals when peroxide doses are relatively smaller (i.e., <150 mg/l).

In terms of achieving CN_{WAD} concentrations of 1 mg/l or less, a peroxide dose of 100 mg/l was sufficient after 2 h of reaction time with the 30 mg/l catalyst. However, the concentration of the Cu catalyst also had significant impact on cyanide removals (Fig. 3A). Although a catalyst dose of 10 mg/l improved the removals compared with no catalyst addition, the achieved CN_{WAD} concentration even after 24 h of reaction time was around 5 mg/l. The optimum copper to initial cyanide concentration (Cu/CN_{WAD}) ratio was found to be about 50%, based on the 100 mg/l of peroxide dose (with 30 mg/l of

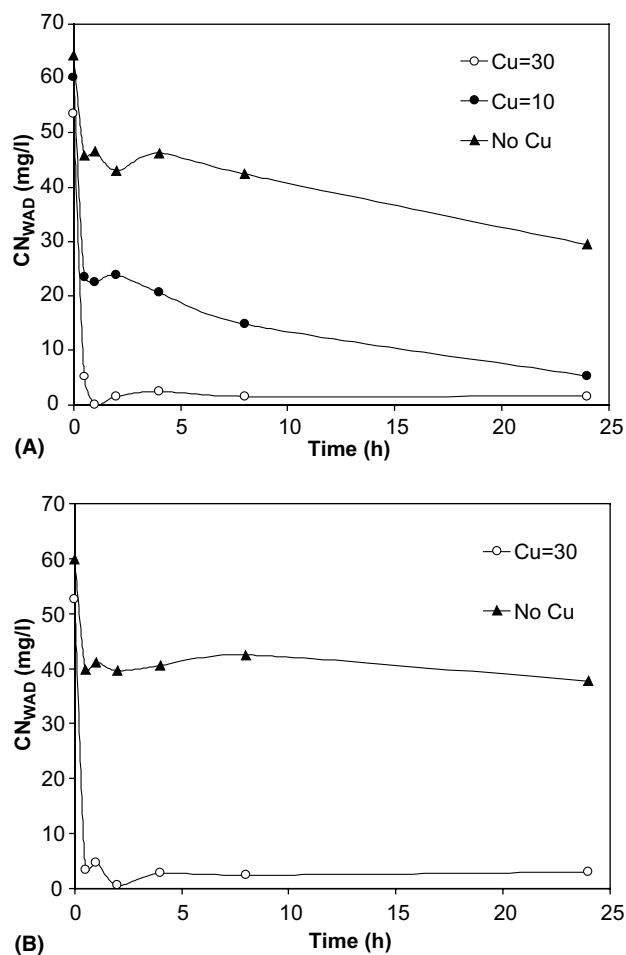


Fig. 3. Impact of copper catalyst concentration on the destruction of CN_{WAD} (A: $T = 20$ °C; B: $T = 30$ °C). For both figures: $H_2O_2 = 100$ mg/l, $pH = 10.3$ (original sample), copper dosages are in mg/l.

Cu) to achieve CN_{WAD} concentrations less than 1 mg/l after 2 h of reaction time. This ratio is larger than the ratios (10–20%) reported by Mudder et al. (2001a,b). However, as can be noted in Fig. 3A, although not tested copper doses between 10 and 30 mg/l may also reduce cyanide concentrations to low levels, resulting in reduced Cu/CN_{WAD} ratios. Furthermore, it should be noted this ratio is obtained for a slurry with a solids content of about 40%. In addition, the original slurry samples contained about 1.5 mg/l of copper in the background. The dosed copper concentrations (10 and 30 mg/l) did not include this background level. In a series of laboratory experiments examining the treatment of a cyanidation water with hydrogen peroxide, the initial copper concentrations ranged from 6 to 40 mg/l (Mudder et al., 2001b).

Consistent with the literature for tailings slurries from typical ores (Knorre and Griffiths, 1984; Botz, 2001; Mudder et al., 2001a,b), all these results overall indicate that Cu catalyst also significantly increases both the rate and extent of cyanide destruction in slurries from ores with low sulphide and heavy metals content. The initial cyanide destruction rates increased between 1.2 and 3 folds (for the range of peroxide doses tested) with the addition of 30 mg/l of Cu compared with no Cu addition (Fig. 2). Similarly, the addition of 10 mg/l of Cu was suggested to increase cyanide destruction rate 2–3 folds (FMC Corp., 2003). However, increasing the copper concentration may also increase downstream problems associated with metals removal.

Addition of Cu catalyst significantly increased cyanide removals independent of temperature (Fig. 3A and B). Tested temperature values were 10, 20 and 30 °C. For all temperatures (data for $T = 10$ °C not shown), similar trends were observed in that Cu catalyst was effective in enhancing both the rate and extent of cyanide destruction. Fig. 4 shows the impact of temperature

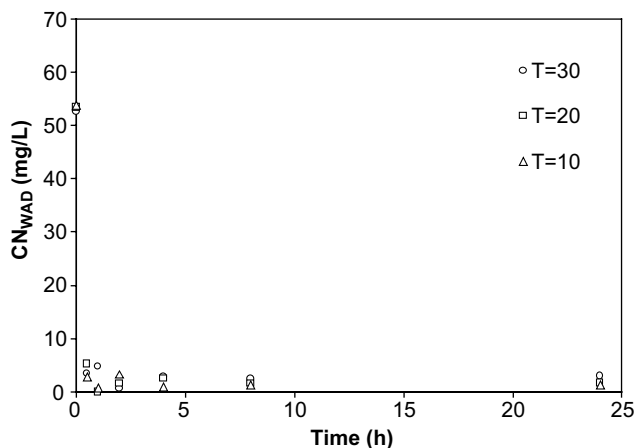


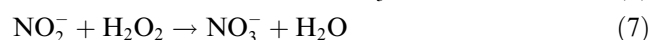
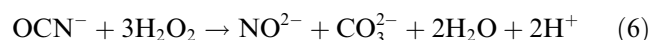
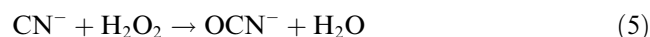
Fig. 4. Impact of temperature on the destruction of CN_{WAD} . $H_2O_2 = 100$ mg/l, $Cu = 30$ mg/l, $pH = 10.3$ (original sample).

on cyanide removals at a constant Cu dose of 30 mg/l. There was no statistical difference (at the significance level of $p < 0.001$) between removals achieved by temperatures of 10, 20 and 30 °C. Similar result was also found for the case of no copper addition (data not shown). These results overall suggest that removal of CN_{WAD} by hydrogen peroxide seems to be not affected by slurry temperatures between 10 and 30 °C whether Cu catalyst is present or not. This observation may be especially important for mines treating cyanide in their tailings slurries with seasonal variations in process water temperatures.

The required hydrogen peroxide doses per amount of CN_{WAD} oxidized were approximately 1.7 and 5 (gr H_2O_2 /gr CN_{WAD}) in the presence (30 mg/l) and absence of Cu catalyst, respectively, based on the target CN_{WAD} concentration less than 1 mg/l ($T = 20$ °C). The theoretical usage of hydrogen peroxide is 1.31 g H_2O_2 per gram of free cyanide oxidized, however, the actual usage in practice may range from about 2.0–8.0 g H_2O_2 per gram of cyanide oxidized. Teck-Corona facility in Canada treating 2400–3600 m^3 /day of decant solution used a hydrogen peroxide-to-cyanide weight ratio of 4.6:1 (Botz, 2001; Mudder et al., 2001a,b). The values obtained in this work agree well with these in the literature. It should also be noted that somewhat lower peroxide dose (1.7 g H_2O_2 /gr CN_{WAD} in the presence of 30 mg/l Cu) found in this work to achieve CN_{WAD} concentration less than 1 mg/l may be due to the fact that Ovacik ore is low in metals content, resulting in lower peroxide dose requirement for metal bound cyanides.

Reaction times necessary to achieve CN_{WAD} concentrations approximately 1 mg/l were found about 1–2 h for the optimum peroxide and copper concentrations determined (i.e., 100 and 300 mg/l of peroxide in the presence (30 mg/l) and absence of copper catalyst, respectively, at $T = 20$ °C). Similarly, it is suggested in the literature that reaction periods typically range from about 30 min to 3 h depending upon the copper to cyanide ratio, the untreated and treated cyanide levels, and hydrogen peroxide dosage (Mudder et al., 2001a,b).

Hydrogen peroxide reacts with cyanide to produce cyanate and, when added in excess, nitrite and carbonate and, eventually, nitrate form (Monteagudo et al., 2004):



Nitrate concentrations were measured during the kinetic experiments. Consistent with the literature, it was found that for all of the peroxide doses nitrate concentrations initially increased (in 1–2 h of reaction time), and then decreased significantly after 24 h of reaction time,

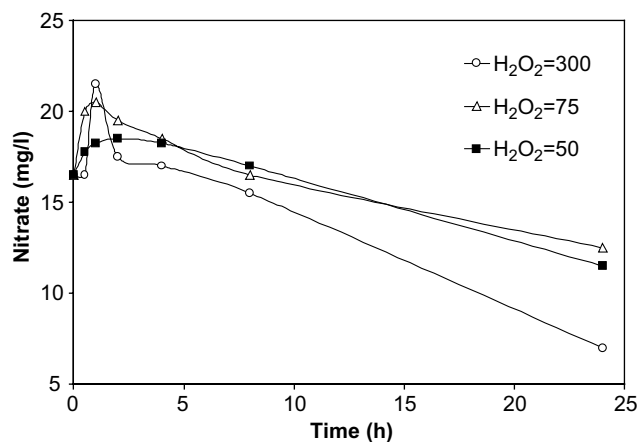


Fig. 5. Occurrence of nitrate during destruction of CN_{WAD} (No Cu, $T = 20$ °C, $pH = 10.3$ (original sample)). H_2O_2 dosages are in mg/l.

suggesting that nitrate was initially formed as a by-product from cyanide destruction, and then possibly converted to other some volatile nitrogen-containing species which may escape the solution (Fig. 5). Furthermore, the extent of initial increase in nitrate concentration increased with peroxide dose applied. The largest peroxide dose applied (300 mg/l) also provided the lowest nitrate concentration after 24 h of reaction time. Mass balance calculations on nitrogen supported these findings since total percent nitrogen remaining in solution after 24 h of reaction time decreased significantly with increasing peroxide dosages. It was reported that cyanate, nitrite, nitrate and carbonate were the main oxidation products of free cyanide ions that were photocatalytically oxidized in aqueous suspensions containing various catalysts (e.g., polycrystalline TiO_2) (Mihaylov and Hendrix, 1993; Augugliaro et al., 1997, 1999). Similar to our work, the mass balance of nitrogen in these studies suggested that some volatile nitrogen-containing species were formed at mild oxidation conditions (Augugliaro et al., 1997, 1999). Furthermore, an industrial wastewater containing cyanide was efficiently treated photocatalytically in aqueous TiO_2 semiconductor dispersions, with ultimate mineralization to CO_2 and N_2 gases (Hidaka et al., 1992).

3.2. Constant reaction time experiments

Kinetics experiments showed that in most cases little reduction in cyanide concentration occurred after a reaction time of 4 h; therefore, 4 h of reaction time was selected for the constant reaction time experiments to investigate the impacts of peroxide and Cu doses, temperature and pH on the extent of cyanide destruction. Fig. 6(A and B) shows the impacts of Cu catalyst and peroxide dosages on CN_{WAD} removals at temperatures of 20 and 30 °C, respectively. Similar to kinetic experiments, increasing the peroxide and Cu catalysts dosages

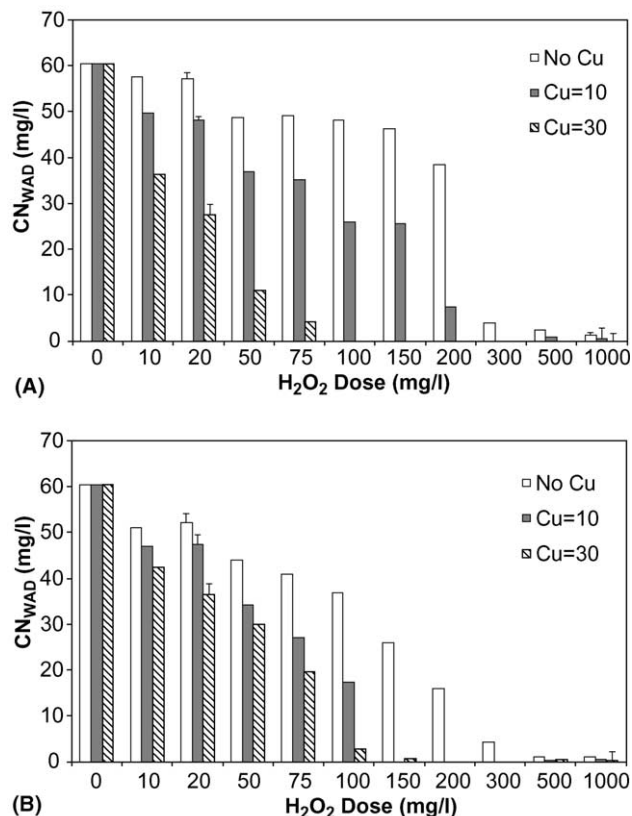


Fig. 6. Impacts of Cu catalyst and peroxide dosages on the destruction of CN_{WAD} (A: $T = 20$; B: $T = 30$ °C). Reaction time = 4 h, $pH = 9.5$. Error bars indicate the 95% confidence intervals.

significantly increased the destruction of CN_{WAD} , independent of all the three temperatures tested (data for $T = 10$ °C not shown).

A peroxide dose of 100 mg/l with 30 mg/l Cu concentration resulted in CN_{WAD} concentrations about 1 mg/l. On the other hand, CN_{WAD} concentrations achieved without catalyst were about 40–45 mg/l at the same above conditions. Without the Cu catalyst, peroxide doses of about 300–500 mg/l were required to reduce CN_{WAD} concentrations down to 1–3 mg/l range for all temperatures. With Cu catalyst concentration of 10 mg/l, about 200 mg/l of peroxide dose was sufficient to obtain above levels of CN_{WAD} . These results again highlight the importance of catalyst addition in terms of not only enhancing the cyanide destruction rate but also significantly reducing the required peroxide dosages to achieve cyanide concentrations of about 1 mg/l, values typical of discharge standards for mining operations. While providing advantages associated with cyanide removal, however, addition of copper in concentrations as high as 30 mg/l may result in downstream problems in terms of metal removal in the treatment system and complying with stringent metal discharge standards.

Similar with results of pH 9.5 (Fig. 6), increasing peroxide and Cu catalyst concentrations also increased

the destruction of CN_{WAD} at pH of 8.5 and 7.5 (Fig. 7) (data for pH = 7.5 not shown). Fig. 8 shows the impact of pH on the destruction of CN_{WAD} . Although not consistent for all peroxide doses, generally a higher degree of cyanide destruction was observed at pH of 7.5 and 8.5 compared with pH of 9.5 in the absence of Cu catalyst. Removals at pH 7.5 and 8.5 were generally comparable. On the other hand, in the presence of 30 mg/l of Cu catalyst, the extent of cyanide destruction was greatest at a pH of 9.5. These results indicate that the impact of slurry pH on cyanide destruction may vary depending upon the dosages of Cu catalyst. With relatively high Cu dosages (i.e., 30 mg/l), it seems that the rate and extent of cyanide destruction is significantly increased to a point that the negative impacts of higher pHs can be overcome with the positive impacts of high Cu presence. Similarly, the optimum pH for the catalytic cyanide oxidation with hydrogen peroxide and Ru/MgO catalyst was found between 6 and 8 (Pak and Chang, 1997).

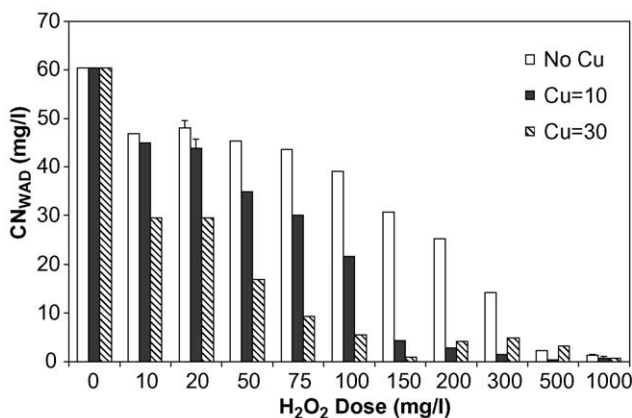


Fig. 7. Impacts of Cu catalyst and peroxide dosages on the destruction of CN_{WAD} at pH of 8.5. Reaction time = 4 h, $T = 20^\circ C$. Error bars indicate the 95% confidence intervals.

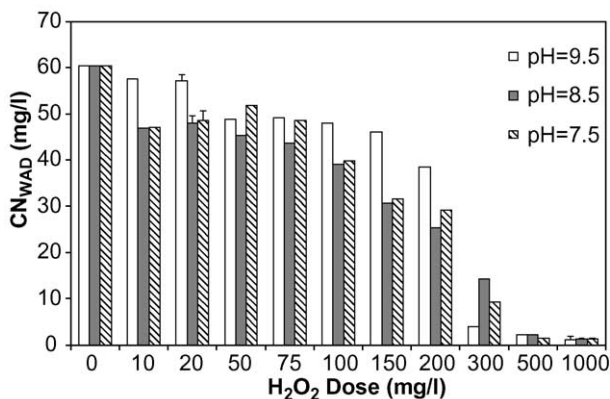


Fig. 8. Impact of pH on the destruction of CN_{WAD} . Reaction time = 4 h, $T = 20^\circ C$, no Cu present. Error bars indicate the 95% confidence intervals.

The pH of slurries is important in terms of two main aspects: effects on cyanide destruction and precipitation of released metals after destruction. With hydrogen peroxide, metals complexed with cyanide are precipitated as metal hydroxides depending on the pH of the solution, with an optimum pH of about 9.0–9.5. However, a pH below about 9.0 is optimal for precipitation of iron cyanides. In addition, cyanate produced in the reactions hydrolyzes to form ammonia and bicarbonate, with the rate of hydrolysis being more rapid at lower pH values. Furthermore, final effluents to be discharged should be in the pH range of 7.5–8.5 to minimize the toxic effects of ammonia (Mudder et al., 2001a,b). Therefore, the selection of optimum pH for the treatment of tailings slurries using hydrogen peroxide should consider the following issues all together for each specific case: cyanide destruction, removal of target heavy metals, effluent toxicity, formed by-products, and the impacts of catalyst dosages.

4. Conclusions

Both the rate and extent of CN_{WAD} destruction generally increased with increasing peroxide doses for either absence or presence of Cu catalyst. Catalyst addition was very effective in terms of not only enhancing the cyanide destruction rate but also significantly reducing the required peroxide dosages to achieve CN_{WAD} concentrations of about 1 mg/l, values typical of discharge standards for mining operations. However, increasing the copper concentration may also increase downstream problems associated with metals removal. Catalyst addition had more positive impact on removals when peroxide doses were relatively smaller (i.e., <150 mg/l). Destruction of CN_{WAD} with hydrogen peroxide was not significantly impacted by slurry temperatures between 10 and 30 °C whether Cu catalyst was present or not. This observation may be especially important for mines treating cyanide in their tailings slurries with seasonal variations in process water temperatures. The impact of slurry pH on cyanide destruction varied depending upon the dosages of Cu catalyst. This impact should be considered when employing cyanide destruction with peroxide in tailings slurries.

The initial cyanide destruction rates increased between 1.2 and 3 folds with the addition of 30 mg/l of Cu. Reaction times necessary to achieve CN_{WAD} concentrations approximately 1 mg/l were found about 1–2 h for the optimum peroxide and copper concentrations determined (i.e., 100 and 300 mg/l of peroxide in the presence (30 mg/l) and absence of copper catalyst, respectively, at $T = 20^\circ C$). Furthermore, in most cases, little CN_{WAD} destruction occurred after a reaction time of 2–4 h. During cyanide destruction, nitrate was initially formed as a by-product and then possibly

converted to other some volatile nitrogen-containing species, as supported by the mass balance calculations.

In the absence of catalyst, only peroxide dose of 300 mg/l was able to achieve less than 1 mg/l CN_{WAD} after 4 h of reaction time. However, a peroxide dose of 100 mg/l was sufficient for this target CN_{WAD} concentration after 2 h of reaction time with the 30 mg/l catalyst. The required hydrogen peroxide doses per amount of CN_{WAD} oxidized were approximately 1.7 and 5 (gr H_2O_2 /gr CN_{WAD}) in the presence (30 mg/l) and absence of Cu catalyst, respectively, based on the target CN_{WAD} concentration of less than 1 mg/l ($T = 20\text{ }^\circ\text{C}$). Somewhat lower peroxide doses found in this work may be due to the fact that Ovacik ore is low in sulphide and metals content, resulting in lower peroxide dose requirement for metal bound cyanides. This result suggests that the efficiency of peroxide in destroying cyanide from tailings slurries with or without catalyst may vary depending on the characteristics of the ore, and the efficiency should be evaluated on a specific case.

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