



Decomposition of hydrogen peroxide in alkaline cyanide solutions

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Synopsis

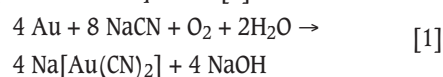
Although oxygen is widely employed as the oxidant of choice in gold leaching by cyanide, its low aqueous solubility presents some drawbacks in practical application; hydrogen peroxide has therefore been considered as a possible alternative. The aim of this investigation was to study the catalytic decomposition of hydrogen peroxide, which generates an oxidizing intermediate species, and to understand its effect on cyanide destruction. Operating conditions that facilitated the effective decomposition of hydrogen peroxide were established by varying the pH and catalyst type and concentration. The oxidizing intermediate, detected using an indirect technique, was found to be the hydroxyl radical (OH[•]). OH[•] is commonly generated in acidic solutions, but this work demonstrated that it is also produced at the alkaline pH values necessary for cyanide gold leaching. The effects of free and complexed iron and copper catalysts on the oxidation and consumption of hydrogen peroxide and cyanide were also investigated. It was shown that the cyano complexes of Fe(II) and Cu(I) are also effective as decomposition catalysts. Hydrogen peroxide concentrations above 0.01 M decreased the free cyanide concentration, which was attributed to the probable formation of the cyanate anion (CNO⁻). Although cyanide consumption increased due to its oxidation in the presence of OH[•], excessive cyanide consumption in the presence of copper was attributed primarily to its complexation by the unstable copper(I) cyanide species. Rate constants for the decompositions of H₂O₂ and cyanide by ferrocyanide and copper cyanide were calculated; the latter was identified as being a better catalyst.

Keywords

hydrogen peroxide, decomposition, Fenton chemistry, cyanide, gold leaching, radical.

Introduction

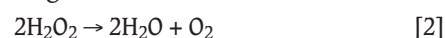
Leaching of gold from its ores using cyanide has been employed for well over a century (Habashi, 2016). Addition of cyanide converts the gold into a cyanide complex (Au(CN)₂⁻) that is soluble in water (Wang and Forsberg, 1990). The leaching reaction can be represented as Equation [1]:



As shown above, leaching also requires the presence of an oxidant, so a source of oxygen (typically air) is introduced into the leach pulp. Leach kinetics are, however, limited by the slow rate at which oxygen transfers from the gaseous to the liquid phase and the resulting low levels of dissolved oxygen. Even with the use of enhanced aeration techniques, such as compressed air or pure oxygen (Adams, 2016;

Loroesch, 1990), the maximum aqueous solubility of dissolved oxygen is about 20 mg/L (Loroesch, 1990). To overcome this limitation of oxygen mass transfer, the application of a liquid oxidant, such as hydrogen peroxide (H₂O₂), has been proposed (Ball *et al.*, 1989; Knorre *et al.*, 1993, 1994). Use of H₂O₂ in the cyanide leaching of gold has the potential to ensure the fast and homogenous distribution of an active oxygen species in the pulp. Peroxide-assisted leaching has been acknowledged to exhibit enhanced kinetics and improved gold recoveries compared with both conventional and improved aeration techniques (Arslan *et al.*, 2003; Guzman *et al.*, 1999; Loroesch, 1990); however, these advantages need to be weighed against the increased cyanide consumption due to its loss by oxidation by H₂O₂.

When H₂O₂ is added to an aqueous system, the resulting decomposition produces dissolved oxygen that is directly available for leaching:



This decomposition is well known to be catalysed by metallic species, specifically iron and copper, in what are termed Fenton and Fenton-like reactions, respectively (Fenton, 1894; Haber and Weiss, 1934; Watts and Teel, 2005). H.J.H. Fenton discovered in 1894 that several metals exhibit a strong catalytic effect that generates highly reactive hydroxyl radicals; these impart oxygen transfer properties that improve the use of hydrogen peroxide. Iron and copper commonly occur as impurities in gold ores (usually as sulphides), so leaching can benefit from the enhanced

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dissolved oxygen content resulting from the catalytic dissociation of H_2O_2 into free oxygen and water. However, if the pH is too high, iron will precipitate as $\text{Fe}(\text{OH})_3$ and H_2O_2 will decompose to oxygen.

Debate regarding the reaction pathway for the decomposition of H_2O_2 , specifically concerning the nature of the oxidizing intermediate(s), is ongoing (Barbusiński, 2009). Two main pathways are postulated: one considers hydroxyl radical (OH^\cdot) formation (Barbusiński, 2009; Deguillaume *et al.*, 2005; Haber and Weiss, 1932, 1934); the other is a non-radical pathway that considers ferryl ion (FeO^{2+}) formation (Barbusiński, 2009; Bray and Gorin, 1932). The respective reactions are shown in Equations [3] and [4]:



An aim of this work was to determine the pathway for the decomposition of H_2O_2 , *i.e.*, to identify whether a radical is involved in the reaction, specifically in alkaline cyanide solutions. This could lead to a better understanding of the mechanism by which dissolved oxygen levels are improved by the addition of H_2O_2 and its effects on other possible consumers of cyanide (CN^-) in gold leaching.

The study comprised four main parts: determination of the effects of pH and catalyst type and concentration on the decomposition of H_2O_2 ; the effect of H_2O_2 concentration on the decomposition of cyanide; examination of Fenton and Fenton-like reactions in the presence of cyanide; and detection of the presence of radicals in acidic and alkaline solutions.

Experimental

Reagents

Hydrogen peroxide (30%) was employed as received. Copper and iron, employed as the decomposition catalysts, were added as the respective sulphate salts for experiments in the absence of cyanide and as $\text{K}_4\text{Fe}(\text{CN})_6$ and CuCN for those in the presence of cyanide. Cyanide was also provided as NaCN in some experiments. Concentrated (98%) H_2SO_4 and CaO were employed for pH adjustment. All chemicals were of analytical reagent grade, supplied by Merck and Sigma Aldrich.

Methods

Effect of pH and catalyst concentration on the decomposition of H_2O_2

The experiments for each catalyst were carried out at both acidic (the natural pH of the catalyst, defined as the resulting pH when the metal salt was added to water: pH 2–3 for iron; pH 3–4 for copper) and alkaline conditions (pH 9–10 obtained by addition of CaO). Sixty millilitres (mL) of H_2O_2 (0.6 M) and 0.5 g/L (approx. 0.01 M) of iron or copper, obtained by addition of the respective sulphate salt, were added to deionized water to make up a volume of 1000 mL. The solutions were magnetically stirred at a constant speed of 500 r/min. Individual experiments were carried out at pH values ranging from 4 to 11. After 15 minutes at each pH, a 10 mL aliquot was analysed for residual H_2O_2 concentration.

To study the effect of catalyst concentration, experiments were carried out using an initial metal catalyst concentration of 0.1 g/L (approx. 0.002 M). This was increased stepwise to 3 g/L (approx. 0.06 M) after equilibration for 15 minutes. After equilibration, the dissolved oxygen (DO) content, redox potential (E_h) (reported relative to the Ag/AgCl reference electrode, $E^\circ = 0.222$ V), and H_2O_2 content of each solution were measured.

Effect of H_2O_2 concentration on the decomposition of cyanide

The effect of H_2O_2 concentration on cyanide decomposition in the absence of a metal catalyst was determined using 1000 mL of 0.015 M NaCN and initial H_2O_2 concentrations ranging from 0.005 M to 0.1 M. CaO was added to maintain a pH of 10–11.5 throughout each test. Samples taken after selected reaction times were analysed for pH and cyanide content.

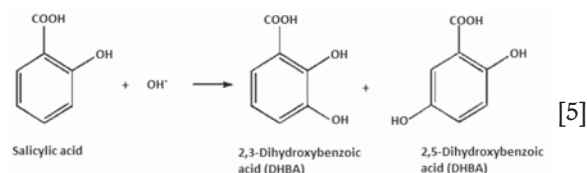
Effect of iron and copper (free and complexed) on the decomposition of H_2O_2 and cyanide

The effects of iron and copper (as both free and complexed ions) on H_2O_2 decomposition were investigated to determine whether H_2O_2 would decompose similarly in both Fenton and Fenton-like reactions. The metals were added both as sulphates ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and as cyanide complexes ($\text{K}_4\text{Fe}(\text{CN})_6$; CuCN) at a concentration of 0.004 M to a solution of 0.01 M H_2O_2 . The pH was maintained in the range 10–11.5.

Determination of the effects of iron and copper cyanide complexes on the aqueous free cyanide concentration followed the same experimental procedure as described above, with 0.01 M free cyanide added as NaCN . The tests were carried out with and without the addition of 0.01 M H_2O_2 . Samples taken at selected reaction times were analysed for pH, H_2O_2 , and cyanide content.

Radical detection studies

An indirect method for identifying the presence of the hydroxyl radical was employed, based on analysis of the products of the reaction between salicylic acid and OH^\cdot . Detection of the 2,3- or 2,5-dihydroxybenzoic acid (DHBA) isomers (Equation [5]) confirms the presence of OH^\cdot (Nguyen *et al.*, 2008). Fenton reactions were carried out in the presence of sufficient salicylic acid to react with the free OH^\cdot generated. To a 1 L solution of specified pH (acidic or alkaline), 0.01 M Fe^{2+} was added, followed by 0.5 M H_2O_2 and 0.12 M salicylic acid (stoichiometric excess of 20% with respect to Fe^{2+}). The solution was allowed to react for 1 hour at 30°C and then cooled to room temperature, after which it was poured into a separating funnel and intimately mixed with diethyl ether to extract only the desired organic products (2,3- and/or 2,5-DHBA). The organic phase was evaporated over low heat, leaving a solid that was collected for identification by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy.



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Analytical methods

H₂O₂ concentrations were titrimetrically determined using 0.025 M KMnO₄ (Klassen *et al.*, 1994). Free cyanide (CN⁻) was determined by titration with 0.1 M AgNO₃, using Rhodamine B as the indicator (Mendham *et al.*, 2000). DO content was measured using a dissolved oxygen meter (model 5100 OUR/SOUR, YSI, USA); pH and E_h were measured using a combination meter (model 704, Metrohm, Switzerland). All tests were repeated twice, giving a total of three replicates to establish the measure of uncertainty, indicated by the error bars on the graphs in Figures 1 to 9.

Results and discussion

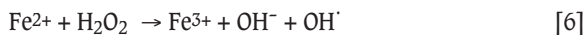
Effect of pH on decomposition of hydrogen peroxide

Figure 1 shows the effect of equilibrium pH on the extent of decomposition of H₂O₂ in the presence of 0.01 M iron or copper. It is evident that, for both metals, an increase in pH increased the extent of decomposition. This result is in agreement with those of Nicoll and Smith (1955), who observed that the decomposition of H₂O₂ in distilled water in the presence of a catalytic impurity increased as the alkalinity of the solution increased. The effective decomposition at high pH values accounts for the reported efficiency of H₂O₂ as an oxidant in alkaline gold leaching (Guzman *et al.*, 1999). It is also evident that copper resulted in more effective decomposition of H₂O₂ above pH 7, indicating that it is a better catalyst than iron in the alkaline pH range.

Effect of catalyst concentration on decomposition of H₂O₂ in acidic and alkaline solutions

Figures 2 and 3 compare the effects of increasing iron or copper catalyst concentration on the E_h and DO due to H₂O₂ decomposition in acidic (natural pH for each catalyst) and alkaline (pH 9–10) ranges.

Figure 2 shows that the solution potential gradually increased at acidic pH values for increased iron concentrations because the ferrous iron concentration decreased as a result of oxidation to ferric ions in the presence of H₂O₂:



This effect was not evident for Cu²⁺, which is stable in the divalent form under these conditions. In contrast, a decrease in E_h was observed in alkaline solutions for both metals. This is attributed to the formation of stable hydroxide

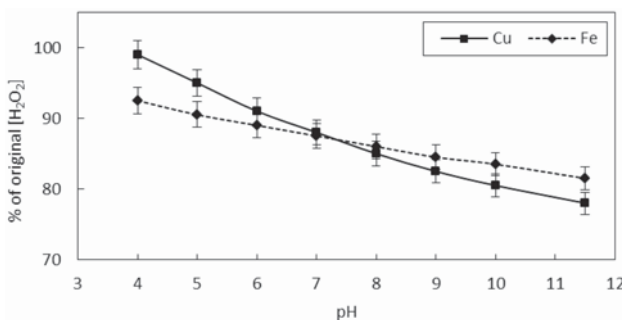


Figure 1—Extent of H₂O₂ decomposition as a function of pH in the presence of iron and copper. (Initial [H₂O₂]: 0.6 M; initial [M²⁺]: 0.01 M; initial pH for Fe test: 2–3; initial pH for Cu test: 3–4)

species of both iron and copper under these conditions. These species are known to be active catalysts in the decomposition of H₂O₂ (Lin and Gurol, 1998). At alkaline pH, heavy metal ions (such as iron or copper) form unstable peroxides, causing decomposition of H₂O₂; in addition, colloidal hydroxides are formed as the pH increases. These metal hydroxides are considered to be more active catalysts for H₂O₂ decomposition than the free or complexed metal ions (Lin and Gurol, 1998; Nicoll and Smith, 1955). It is notable that both catalysts had the most significant effect at a concentration of 0.5 g/L; above this concentration, further improvements in performance were limited.

As shown in Figure 3, the DO content was higher in alkaline solutions for catalyst concentrations above 0.5 g/L, which indicates greater extents of decomposition of H₂O₂ (see Equation [2]). This confirmed that such stable hydroxides tend to be better catalysts than their respective free transition-metal cations (Lin and Gurol, 1998; Nicoll and Smith, 1955). It is also notable that the DO concentrations reached close to 50 mg/L under these conditions, which is considerably higher than the equilibrium oxygen concentration reported when using enhanced aeration with gaseous oxygen (approx. 20 mg/L) (Loroesch, 1990).

Effect of H₂O₂ concentration on rate of decomposition of cyanide

The use of H₂O₂ in treating wastewaters containing cyanide and/or cyanide complexes is common practice (Ozcan *et al.*,

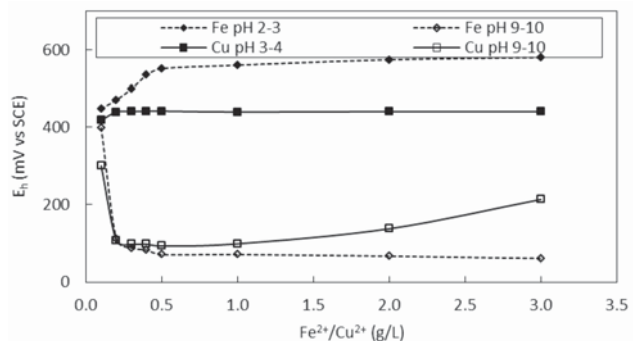


Figure 2—Solution redox potential as a function of Fe²⁺ and Cu²⁺ catalyst concentration in acidic and alkaline solutions. (Initial [H₂O₂]: 0.6 M)

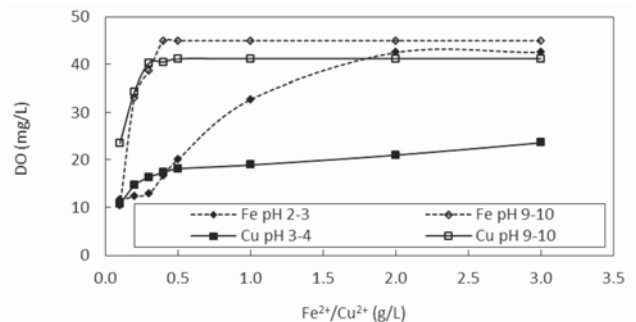


Figure 3—Dissolved oxygen concentration as a function of Fe²⁺ and Cu²⁺ catalyst concentration in acidic and alkaline solutions. (Initial [H₂O₂]: 0.6 M)

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2011). This ability of H₂O₂ to destroy cyanide potentially mitigates against its use in cyanide leaching systems. Figure 4 shows the effect of H₂O₂ concentrations ranging from 0.005 M to 0.10 M on the rate of decomposition of free cyanide. A significant decrease in CN⁻ concentration was observed for H₂O₂ concentrations above 0.01 M. These results agree with those of similar work carried out by Guzman *et al.* (1999), who attributed the decrease in cyanide concentration to the formation of the cyanate anion (CNO⁻), according to Equation [7]:



Effect of iron and copper (free and complexed) on decomposition rate of H₂O₂

Figures 5a and 5b show the effects of iron and copper, respectively, added as sulphate and complexed cyanide salts, on the rate of H₂O₂ decomposition. Both the free and complexed cations affected the stability of H₂O₂. The rate of

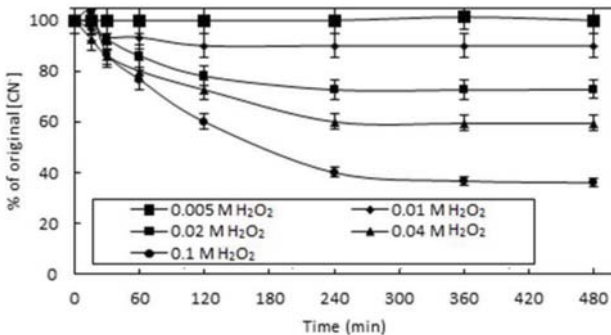


Figure 4—Effect of H₂O₂ concentration on the rate of free cyanide destruction. (Initial NaCN: 0.015 M; pH: 10–11.5)

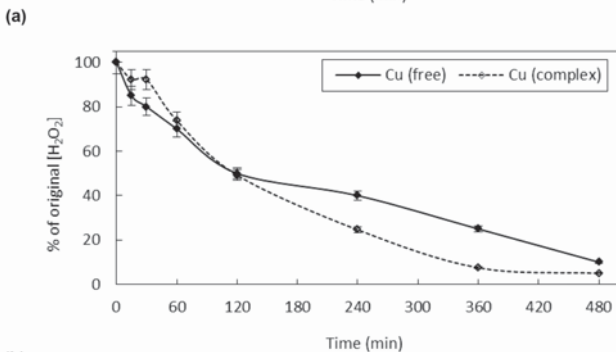
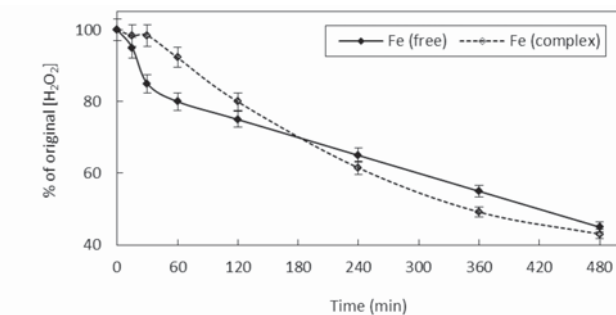


Figure 5—Effect of free and cyanide complexes of (a) iron and (b) copper on the rate of decomposition of H₂O₂ under alkaline conditions. (Initial H₂O₂: 0.01 M; pH 10–11.5; initial [M²⁺], CuCN or K₄Fe(CN)₆: 0.004 M)

decomposition in the presence of Fe was essentially unaffected by the nature of the ion; copper, however, had a more pronounced effect when present as the cyanide complex. Although copper(II)-cyano complexes have been characterized, they are unstable and decompose rapidly, forming copper(I)-cyano complexes and cyanate, CNO⁻, in the presence of H₂O₂ (Sceresini and Breuer, 2016): the presence of cupric copper (the free Cu²⁺ ion) therefore causes loss of cyanide as cyanate. These results indicated that H₂O₂ decomposed in the presence of iron and copper as both free and complexed species in Fenton and Fenton-like reactions, respectively.

Figure 6 shows the corresponding first-order plots based on the data of Figure 5. The rate constants, *k*, for the decomposition of H₂O₂ by these catalysts were calculated from the slope of a linear least-squares fit:

$$\text{Slope} = (\Delta \ln[\text{H}_2\text{O}_2]) / \Delta t = -k \quad [8]$$

where the concentration of H₂O₂ is given in M.

The equations, rate constants and correlation coefficients (R²) for the linear plots are summarized in Table I. The relative values of the rate constants confirm that the rate of decomposition of H₂O₂ in the presence of copper was faster than that of iron and that the rates were slightly faster when the metal ions were present in the form of the respective cyanide complexes. The free copper ion reduced the initial H₂O₂ concentration by 90% in 480 minutes, compared with only 55% in the presence of the free iron species. Similarly, the presence of copper cyanide reduced the H₂O₂ concentration by 95% in 480 minutes, compared with only 50% for ferrocyanide (Figure 6).

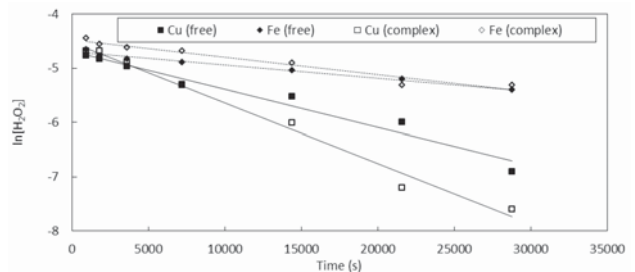


Figure 6—First-order plots for the decomposition of H₂O₂ in the presence of FeSO₄ and CuSO₄ (free cations) and K₄Fe(CN)₆ and CuCN (complexed cations)

Table I
Equations of best linear fit, correlation coefficients and rate constants for the first-order decomposition of H₂O₂ in the presence of iron and copper, present as free (sulphate media) or complexed (cyanide media) cations, based on the data in Figure 6

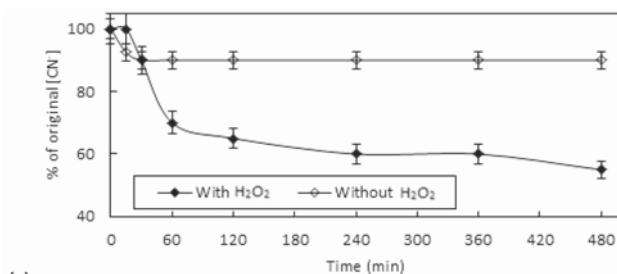
Catalyst	Regression equation	Rate constant (s ⁻¹)	R ² value
Fe (free)	$y = -2.0\text{E}-05x - 4.7$	2.0×10^{-5}	0.98
Fe (complex)	$y = -3.0\text{E}-05x - 4.48$	3.0×10^{-5}	0.95
Cu (free)	$y = -7.0\text{E}-05x - 4.69$	7.0×10^{-5}	0.96
Cu (complex)	$y = -0.0001x - 4.53$	1.0×10^{-4}	0.99

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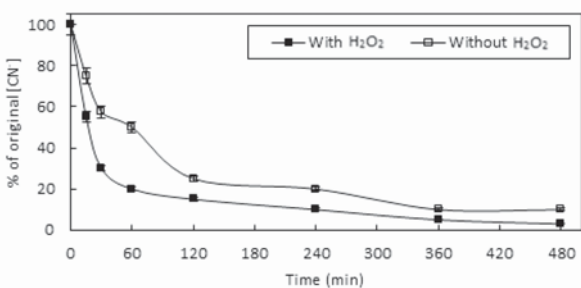
Effect of iron and copper cyanide complexes on rate of decomposition of free cyanide in the absence and presence of H₂O₂

Using a H₂O₂ concentration of 0.01 M, which was shown to have negligible effect on the degradation of free cyanide (supplied as NaCN) (Figure 4), it was of interest to monitor whether cyanide would be similarly destroyed when the catalysts were introduced as the cyano complex ions. Figures 7a and 7b show the decrease in free cyanide with time in the presence and absence of H₂O₂ when using iron and copper as the catalysts, respectively. Ferrocyanide is regarded as a strongly bound complex and is therefore not easily dissociated (Adams, 2016; Sharpe, 1976), which is why it tends to remain stable during detoxification of free cyanide and cyanide complexes by H₂O₂ (Griffiths *et al.*, 1987; Ozcan *et al.*, 2011). A small decrease in the initial free cyanide concentration was, however, still observed (Figure 7a) This was attributed to a Fenton-like reaction between H₂O₂ and ferrocyanide, which produces the hydroxyl radical intermediate (OH[•]) that, in turn, reacts with free CN⁻. In the absence of H₂O₂, no decrease in the free cyanide concentration occurred for the case of ferrocyanide, confirming the stability of the complex.

For the case of CuCN, the free cyanide concentration dropped markedly both in the presence and absence of H₂O₂. It is well-known, however, that copper forms a series of strong cyanide complexes (Ringbom, 1963), of which the tri- and tetracyanide species predominate at alkaline pH values (Sceresini and Breuer, 2016):



(a)



(b)

Figure 7—Effect of (a) iron and (b) copper cyanide complexes on the rate of degradation of free cyanide in the presence and absence of hydrogen peroxide. (Initial H₂O₂: 0.01 M; pH: 10–11.5; initial NaCN: 0.01 M; initial K₄Fe(CN)₆ or CuCN: 0.004 M)

Only a slightly greater extent of cyanide destruction occurred in the presence of H₂O₂, indicating that this phenomenon is primarily due to complexation, rather than to reaction with the hydroxyl radical due to Fenton-like reactions.

The degradation of free cyanide both with and without H₂O₂ occurred according to second-order kinetics in the presence of iron and copper cyanides, as shown in Figure 8, derived from the data presented in Figure 7. The relative values of the rate constants (Table II), calculated by the equation:

$$1/[\text{CN}^-]_t = kt + 1/[\text{CN}^-]_0 \quad [10]$$

where the concentration of CN⁻ was calculated in g/L, confirmed that copper(I) cyanide caused faster decomposition of CN⁻ than ferrocyanide, both with and without H₂O₂.

Radical detection studies

Salem *et al.*, (2000) proposed OH[•] as an intermediate product in reactions where the catalyst is a transition-metal complex. In this work, evidence for the existence of the OH[•] radical in the decomposition of H₂O₂ was assumed based on an indirect method (Nguyen *et al.*, 2008). Aromatic hydroxylation of salicylic acid to specifically yield the 2,3- and/or 2,5-DBHA isomers can only occur via the OH[•] radical (see Equation [5]). The hydroxylation reaction was carried out in the presence of H₂O₂ and an iron catalyst under acidic pH (2–3) and alkaline pH (10–11) conditions and the reaction products were analyzed.

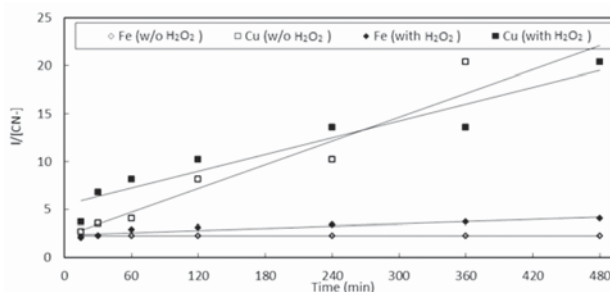


Figure 8—Second-order degradation of free cyanide in the presence of K₄Fe(CN)₆ and CuCN in the presence (closed symbols) and absence (open symbols) of H₂O₂. (Initial H₂O₂: 0.01 M; pH: 10–11.5; initial NaCN: 0.01 M; initial K₄Fe(CN)₆ or CuCN: 0.004 M)

Table II

Equations of best linear fit, correlation coefficients and rate constants for the second-order destruction of free cyanide in the presence of iron and copper, present as complexed cyanide cations, based on the data in Figure 8

Catalyst	Regression equation	Rate constant (g ⁻¹ min ⁻¹)	R ² value
Fe (without H ₂ O ₂)	y = 5E-05x + 2.25	0.00005	N/A
Fe (with H ₂ O ₂)	y = 0.0038x + 2.36	0.0038	0.87
Cu (without H ₂ O ₂)	y = 0.042x + 2.22	0.042	0.95
Cu (with H ₂ O ₂)	y = 0.029x + 5.46	0.029	0.92

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NMR spectra of the hydroxylation products compared well with that of the standard 2,3-DHBA isomer (National Institute of Advanced Industrial Science and Technology, 2013): peaks characteristic of the hydrogen atoms of this isomer were observed at chemical shifts of 6.5 to 8.5 ppm. IR spectra indicated the presence of carboxylic acid, alcohol, and carbonyl groups, which are the functional groups present in this isomer. Identification of the hydroxylation product of salicylic acid as 2,3-DHBA by NMR and IR spectroscopy, irrespective of whether the reaction was carried out in acidic or alkaline media, indirectly confirmed the presence of OH⁻ and showed that H₂O₂ decomposed to this radical under both pH conditions. It was important to confirm the presence of this intermediate because it is highly reactive (standard reduction potential of 1.4 V) compared with the ferryl ion (0.9 V) (Petri *et al.*, 2011) and could possibly react with contaminants in a gold leach pulp, leading to further losses in such application. This high reduction potential of OH⁻ may also improve Au leaching kinetics.

Conclusions

The aim of this work was to study how the addition of H₂O₂ affects the cyanide concentration, the E_h, and the DO concentration in cyanide gold leaching. The effects of transition-metal cation catalysts, such as iron and copper (free and complexed), and pH on the stability of H₂O₂ were established. It was found that the cyano complexes of Fe(II) and Cu(I) effectively act as hydrogen peroxide decomposition catalysts in alkaline media. Increasing pH and catalyst concentration increased the rate of decomposition of H₂O₂. Copper (free and complexed) cyanide was found to be more effective in decomposing H₂O₂ than the corresponding iron(II) species.

It was established that a H₂O₂ concentration greater than 0.01 M caused loss of free cyanide. In the presence of copper, loss of free cyanide by complexation was attributed to the formation of stable higher copper(I) cyanide complexes. No loss of cyanide by complexation was observed in the presence of ferrocyanide, in accordance with the known relatively high stability of this complex. Additional losses of cyanide in the presence of hydrogen peroxide were attributed to the presence of the hydroxyl radical in Fenton-like reactions for both iron and copper.

An oxidizing intermediate in the Fenton and Fenton-like reactions, assumed on the basis of detection and identification by an indirect technique to be the hydroxyl radical, was found to be present in both acidic and alkaline solutions. This radical was responsible for the increased oxidation potential observed in alkaline solutions. Proving the presence of this species in alkaline solutions (in the presence of transition metal ion complexes) and understanding its effect on free cyanide degradation could aid in minimizing cyanide losses and establishing economical H₂O₂ dosages for industrial applications in gold leaching.

Acknowledgements

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