



Behavior and mechanism of cyanide loss in ultrasound-assisted gold leaching process

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Received 8 November 2021; accepted 18 May 2022

Abstract: The potential effect of ultrasound was investigated, which could lead to cyanide loss or decomposition during gold leaching. The variations of cyanide concentration during gold leaching with and without ultrasound were compared. The influence of initial cyanide concentration, pH, temperature, atmosphere, natural loss, hydrolysis, and cavitation effect on the loss of cyanide was examined. The results showed that the loss of cyanide was mainly caused by hydrolysis, oxidation, and reaction with CO₂ in the traditional gold leaching process. With the introduction of ultrasound, the oxidative •OH slightly increased the loss of cyanide. Comparing the concentration variations of total cyanide and free cyanide proved that ultrasound (120 W) exhibited a non-detrimental effect on the loss of cyanide in gold leaching process.

Key words: ultrasound; gold; cyanidation; cyanide loss; •OH radical

1 Introduction

Ultrasound can initiate, promote, and control chemical reactions. Due to its unique mechanical, chemical, thermal, and cavitation properties, it can be applied in solid crushing, degassing, cleaning, and chemical reaction promotion [1–3]. In the past few decades, ultrasound-assisted leaching technology has attracted extensive attention [4,5]. ÖNCEL et al [6] proved that the ultrasound-assisted thiourea leaching could almost entirely leach silver from silver ore. FU et al [7] proposed the method of synergistic extraction of gold by ultrasound and chlorination oxidation from refractory gold ore. Their results showed that ultrasound promoted the shedding of the partial interface layer to create a new reaction interface and reduce the reaction

resistance and thus increased the reaction rate significantly.

Cyanidation is widely used for gold extraction from ores or concentrates because of its low cost and good operational stability [8,9]. However, gold cyanidation usually requires a relatively long reaction time, varying from 24 to 48 h or longer in practice. YU et al [10] reported that ultrasound-assisted cyanide leaching could increase the extraction rate of gold and shorten the leaching time significantly. However, whether and to what extent the extreme condition caused by ultrasound increases cyanide consumption in gold cyanidation remain to be answered. It is known that ultrasound can simultaneously generate oxidizing reagents and extreme local environments with high pressures and temperatures and this property has been used as the sonochemical oxidation process to remediate

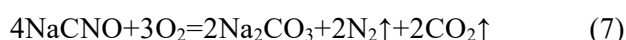
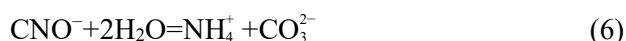
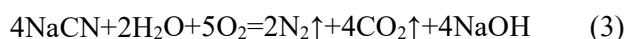
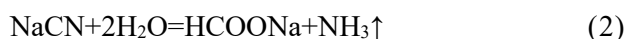
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DOI: 10.1016/S1003-6326(22)66132-6

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wastewater [11,12]. In fact, both ultrasound and radiolysis can split water molecules into strong oxidizing $\bullet\text{OH}$ radicals [13,14]. CN^- could react with $\bullet\text{OH}$ radicals and this can be used in the disposal of cyanide-containing wastewater. Several researchers supposed that the effect of ultrasonic irradiation on the decomposition of cyanide was related to the $\bullet\text{OH}$ radicals generated by cavitation which oxidized CN^- and caused the decrease of cyanide in solution [15–18]. However, NISHIOKA et al [19] believed that cyanide concentration actually gradually decreased due to the reaction of cyanide with CO_2 under natural conditions. The reactions of CN^- loss could be described as follows [19–21]:



Furthermore, the loss of cyanide in tailing ponds was supposed to be due to oxidation, volatilization, hydrolysis, precipitation, complexation, and sorption processes [22–24]. Therefore, whether ultrasound leads to the extra loss of cyanide is controversial.

To illustrate whether there are adverse effects of ultrasound on the cyanide loss in the gold cyanidation process, the behavior of cyanide with and without ultrasonic irradiation was compared in this work. The natural decomposition, hydrolysis of cyanide and the influence of initial cyanide concentration, temperature, atmosphere, and pH on

cyanide loss were investigated with the purpose to explore the mechanism of cyanide loss during the gold leaching process. The potential mechanism of ultrasound on cyanide loss was discussed in combination with the ultrasonic degassing property.

2 Experimental

2.1 Materials

The sample of gold ore was obtained from a local gold company in Yunnan, China. The main chemical composition of the ore sample is shown in Table 1. All the solutions applied in the experiment were prepared with deionized water. Except for sodium cyanide provided by a local gold company, all analytical reagents including silver nitrate, p-dimethylamino benzyl rhodanine, acetone, isonicotinic acid, pyrazolone, chloramine T, potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Company.

Table 1 Main chemical composition of gold ore sample (wt.%)

Au*	Fe_2O_3	SiO_2	Al	Ca
1.43	46.61	23.55	5.44	6.41

* g/t

2.2 Sodium cyanide loss

The experimental devices for measuring sodium cyanide loss are presented in Fig. 1. The thermostatic water bath was used to maintain the temperature of the reaction system during the experiment. Except for hydrolysis and natural loss tests, the gas (air, nitrogen, oxygen, or carbon dioxide) was blown into the reactor at the flow rate

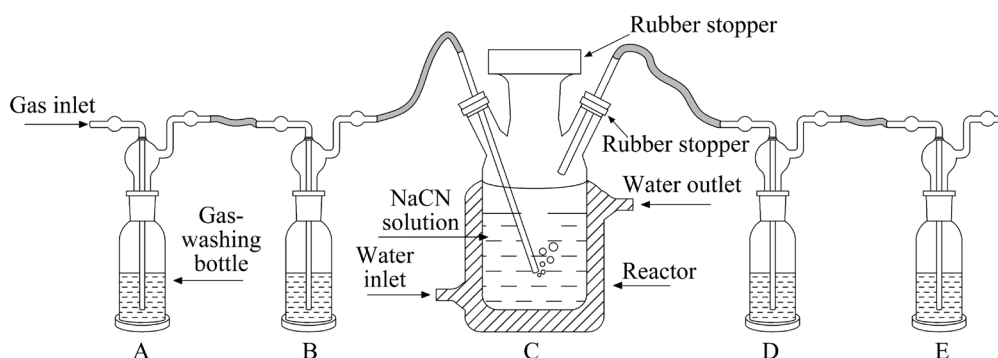


Fig. 1 Experimental setup used for measuring of sodium cyanide loss

of 1 L/min. In the nitrogen and oxygen atmospheres, 60 mL of 0.1 mol/L sodium hydroxide solution was added to the gas scrubbers A, B, D, and E, respectively. In the air atmosphere experiment, 60 mL of deionized water was added to the gas-washing bottles A and B, and 60 mL of 0.1 mol/L sodium hydroxide solution was added to D and E. In the case of carbon dioxide atmosphere, A and B gas-washing bottles were not used, and 1 L of 1 mol/L sodium hydroxide solution was added to D and E.

Ultrasound (20 kHz) was emitted from the top of the reactor through a horn (2 cm diameter) when ultrasound was used for the experimental process. Ultrasonic power was adjustable between 12 and 1200 W. A rubber plug was used to seal the top of the reactor in the case without ultrasonic irradiation (Fig. 1). A three-port glass reactor (300 mL) with 200 mL sodium cyanide solution was used for cyanide loss tests. In the ultrasonic degassing experiment, 500 mL of 0.67 g/L sodium cyanide solution with a pH of 10.81 was added to a 1 L reactor. To investigate the effect of solid particles, 15 g of cullet (100% passing 74 μm sieve) and 750 mL of sodium cyanide solution (0.67 g/L) were added into a 1 L reactor, and mechanical stirring with a rotation speed of 300 r/min was applied.

For comparing the effect of air on cyanide decomposition, 250 mL of 1.32 g/L sodium cyanide solution was poured into two glass reagent bottles. One bottle was sealed, the other was opened to expose sodium cyanide into air, and both were kept in the dark. The natural decomposition of sodium cyanide was investigated by comparing the concentrations of residual sodium cyanide in the two bottles.

The air in the reactor was emptied using nitrogen at a flow rate of 1 L/min for 5 min. Then the reactor was quickly sealed with a rubber stopper, and the reactor was kept at 20 °C for 2 h to investigate the hydrolysis of cyanide.

2.3 Leaching

Ultrasound-assisted and conventional cyanide leaching tests were conducted under the conditions of a liquid/solid ratio of 10:1, 25 °C, an initial NaCN concentration of 0.55 g/L, and a mechanical stirring rotational speed of 350 r/min. NaOH was used as a protective alkali to adjust the pH. According to our preliminary investigations, the

ultrasonic power of ultrasound-assisted leaching was set as 120 W, which could result in a significantly high gold extraction rate. The same three-port reactor was used for ultrasonic-assisted and conventional leaching (Fig. 2).

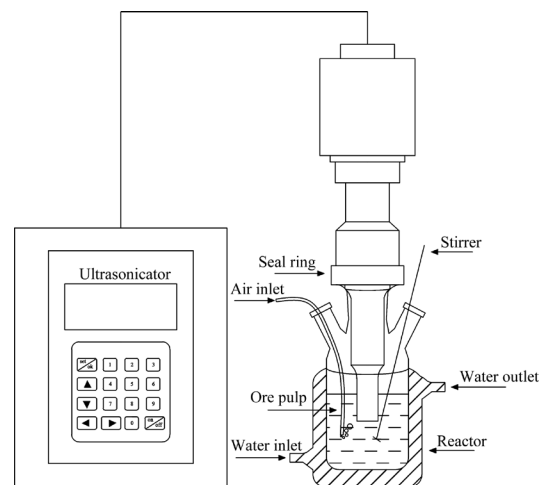


Fig. 2 Experimental setup for ultrasound leaching

2.4 Characterization of samples

The solution pH was measured by a pH meter (PB-10, Sartorius). The gold content in solution samples was determined by an atomic absorption spectrophotometer (Hitachi Z-2300). The concentrations of total cyanide and free cyanide were analyzed by silver nitrate titration. The concentrations of sodium cyanide absorbed in the gas-washing bottles were analyzed by UV-Vis spectrophotometer (UV5, Mettler Toledo) at a wavelength of 638 nm. The dissolved oxygen was measured by a dissolved oxygen meter (HI2004-02, HANNA), and the measurement was performed immediately when the ultrasonic irradiation stopped. Since the temperature of the solution could fluctuate due to ultrasonic irradiation, the dissolved oxygen concentrations measured at different temperatures (around 25 °C) were converted to the corresponding dissolved oxygen concentrations at 25 °C for comparison purposes [25,26].

3 Results and discussion

3.1 Natural loss

The natural loss of cyanide was examined by comparing the variations of cyanide concentration when exposed to air and sealed in bottles. As shown in Fig. 3, at the same initial concentration (1.32 g/L), the cyanide concentration in the open

bottle gradually decreased with increasing time. It decreased by 59.6% (decreased to 0.53 g/L) after exposing to air for 50 h. Comparatively, the concentration of cyanide decreased by only 4.1% (decreased to 1.27 g/L) in the sealed bottle at the same time. Apparently, the natural loss of sodium cyanide in the open bottle was much higher than that in the closed bottle. A further test indicated that the cyanide concentration in the closed reactor under the nitrogen atmosphere was reduced only by 1.5% after 2 h. The loss of cyanide in the closed bottle could be mainly caused by hydrolysis. It is supposed that cyanide is converted to HCN through Reaction (1), but the hydrolysis is weak in an alkaline environment (pH 10.8) and closed reactor. The natural loss of cyanide may mainly be the consumption of CN^- by CO_2 and O_2 in air [19].

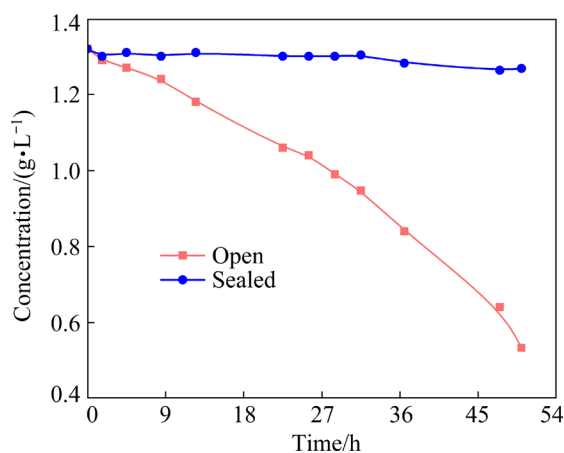


Fig. 3 Natural loss of cyanide under different conditions (10.87 of initial pH, 1.32 g/L of initial NaCN, and room temperature)

3.2 Cyanide loss without ultrasound

3.2.1 Effect of atmosphere

The effect of the atmosphere on the loss of cyanide was investigated (Fig. 4). The cyanide balance indicated that the loss rates of cyanide in the reactor under nitrogen, oxygen, air, and carbon dioxide atmospheres were 3.5%, 3.2%, 7.5%, and 45.5%, respectively. The amounts of sodium cyanide absorbed in gas-washing bottles were 5.12, 3.59, 4.99, and 56.5 mg, respectively. Accordingly, the pH of the solution changed from 10.87 to 11.19, 11.01, 10.59, and 5.94, respectively.

When nitrogen was continuously blown into the reactor, the loss rate of cyanide (3.5%) was higher than that of hydrolysis (1.5%), indicating that the flowing nitrogen promoted volatilization

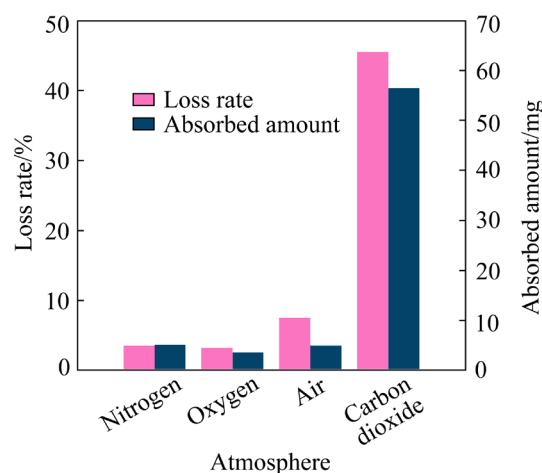


Fig. 4 Effect of atmosphere on cyanide loss rate and absorbed sodium cyanide amount without ultrasound (20 °C, 2 h, 10.87 of initial pH, 0.69 g/L of initial NaCN, and 1 L/min of gas velocity)

of HCN and caused the decrease of cyanide concentration. This result is consistent with those reported in the literature [27,28]. The actual loss rate of cyanide in the oxygenous atmosphere was similar to that in the nitrogenous atmosphere, while the mass of cyanide absorbed in the gas scrubber in the nitrogenous atmosphere was higher than that in the oxygenous one. This is because CN^- only underwent hydrolysis in a nitrogen atmosphere, while part of CN^- was also oxidized to CNO^- in an oxygen atmosphere. CNO^- was unstable and would decompose into N_2 and CO_2 or CO_3^{2-} and NH_4^+ [24,29,30]. At 298 K, the hydrolysis constants K_h of CO_3^{2-} , HCO_3^- , CN^- , and NH_4^+ are 2.12×10^{-4} , 2.27×10^{-8} , 1.61×10^{-5} , and 5.6×10^{-10} , respectively. The increase of pH after 2 h in the oxygen atmosphere was lower than that in the nitrogen atmosphere. CNO^- was mainly decomposed into CO_3^{2-} and NH_4^+ , and the hydrolysis of CO_3^{2-} and NH_4^+ further weakened the hydrolysis of CN^- and the increase of pH. Cyanate would finally transform into ammonia and carbonate [22–24]. Under the air, CO_2 reacted with CN^- and OH^- in the solution, promoting the hydrolysis progress and increasing the consumption of cyanide [22]. Therefore, the synergistic function of hydrolysis, oxidation, and reaction with CO_2 caused a high loss rate of cyanide in the air atmosphere. Cyanide was consumed largely as the acid–base reaction and hydrolysis were promoted by CO_2 . This is consistent with the results obtained by NISHIOKA et al [19].

3.2.2 Effect of initial pH

The effect of initial pH on the cyanide loss is shown in Fig. 5. The cyanide loss decreased from 10.9% to 1% with the increase of initial pH from 9.68 to 11.53, and then remained stable in the pH range from 11.53 to 12.54. For different periods, the pH changed from 9.68 to 10.03, 10.87 to 10.59, 11.53 to 11.38, and 12.54 to 12.51, respectively. The loss rate at pH 9.68 was higher than that at higher pH levels, which was consistent with the results in the literature [22,31].

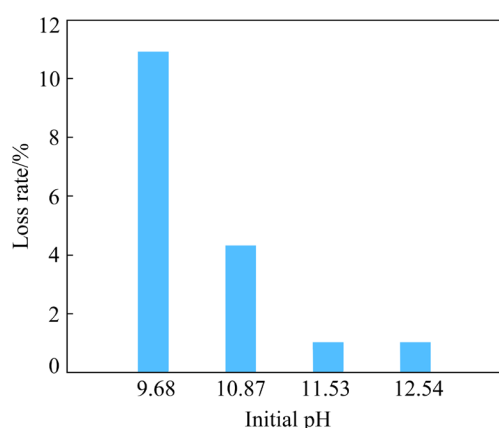


Fig. 5 Effect of initial pH on cyanide loss rate without ultrasound (20 °C, 1 h, 0.69 g/L of initial NaCN, and 1 L/min of air velocity)

3.2.3 Effect of initial concentration of NaCN

The effect of the initial concentration of NaCN on the loss of cyanide in the absence of ultrasound was examined (Fig. 6). When the initial NaCN concentration increased from 0.44 to 1.50 g/L, the loss rate of cyanide decreased from 4.5% to 1.8%, respectively. This is probably because when the

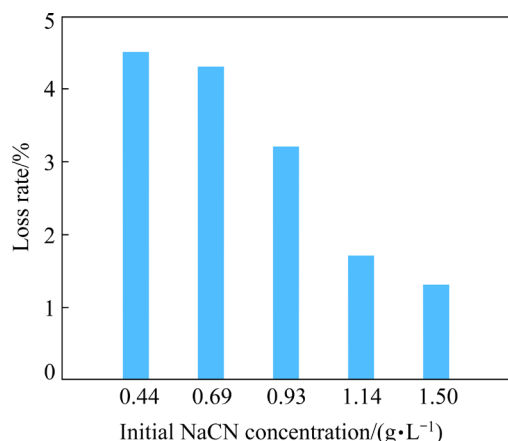


Fig. 6 Effect of initial NaCN concentration on cyanide loss rate without ultrasound (20 °C, 1 h, 10.87 of initial pH, and 1 L/min of air velocity)

concentration of CN^- increased, the hydrolysis of CN^- also decreased, resulting in a decrease in the loss of cyanide. The same trend has been observed in reducing cyanide concentration in gold leaching tailing ponds [22].

3.2.4 Effect of temperature

The effect of temperature on the loss of cyanide was examined between 20 and 60 °C (Fig. 7). When the temperature increased from 20 to 30 °C, the loss rate of cyanide increased from 4.5% to 6.0%, respectively. It was reported that when the temperature was higher than the boiling point of HCN (26 °C) [32], the hydrolysis product HCN of CN^- constantly volatilized, promoting the hydrolysis reaction [31]. Therefore, when the temperature was 20 °C, the loss rate of cyanide was lower than that at 30 °C. While the temperature was in the range of 30–60 °C, the loss rate of cyanide was no longer affected by temperature.

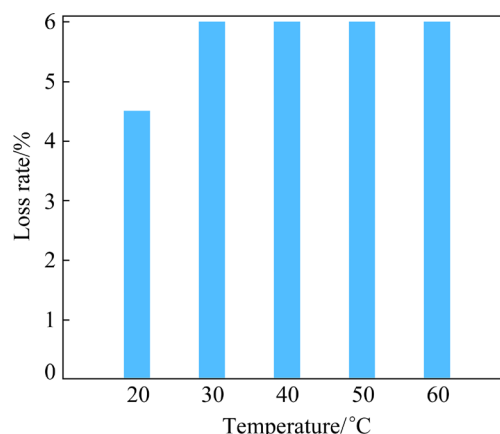


Fig. 7 Effect of temperature on cyanide loss rate without ultrasound (1 h, 10.87 of initial pH, 0.69 g/L of initial NaCN concentration, and 1 L/min of air velocity)

It should be noted that the hydrolysis reaction is endothermic and the volatilization of HCN could be promoted with the increasing temperature. Therefore, increasing the temperature can accelerate the loss of cyanide. However, the increasing temperature also led to the decrease of dissolved oxygen and CO_2 in the solution, reducing cyanide loss. Accordingly, when the reaction temperature was 30–60 °C, the decomposition of cyanide remained virtually unchanged.

3.3 Cyanide loss with ultrasound

The effect of ultrasonic power on the loss of cyanide is shown in Fig. 8. With an increase of the

ultrasonic power, the loss rate of cyanide gradually decreased (6.0% for 24 W, 6.0% for 48 W, 5.9% for 72 W, 4.5% for 96 W, and 3.0% for 120 W, respectively). When the power was low, increasing the ultrasonic power would lead to an increase in the acoustic amplitude, which was conducive to the rupture of more violent cavitation bubbles, and the generation rate of $\bullet\text{OH}$ radicals and the solution degassing rate increased accordingly [33,34]. However, the increased generation rate of $\bullet\text{OH}$ radicals on the oxidation of cyanide may be lower than the increment in the degassing rate on the loss of cyanide, resulting in a gradual decline in the decomposition rate of cyanide. This result is different from the previous work of HARD-CASTLE et al [16] who reported that the destruction rate of cyanide was directly proportional to the increase of ultrasonic power. The discrepancies between these results could be ascribed to the differences in the solution volume and ultrasonic power.

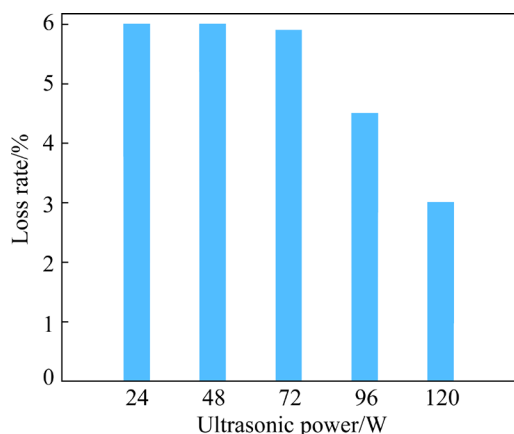


Fig. 8 Effect of ultrasonic power on cyanide loss rate (20 °C, 1 h, 10.87 of initial pH, 0.69 g/L of initial concentration, and 1 L/min of air velocity)

By comparing the loss of cyanide with and without ultrasonic irradiation, the effect of ultrasound on the loss of cyanide was discussed, and the results are shown in Fig. 9. Due to the cavitation effect and energy conversion, the solution temperature in the reactor gradually increased when ultrasound was used. Although a thermostatic water bath was used, the actual temperature of the solution in the reactor was still about 9 °C higher than the set temperature (Fig. 9(b)). Figure 9(a) shows that the cyanide loss rate without ultrasonic irradiation at 30 °C (10.3%) was slightly higher

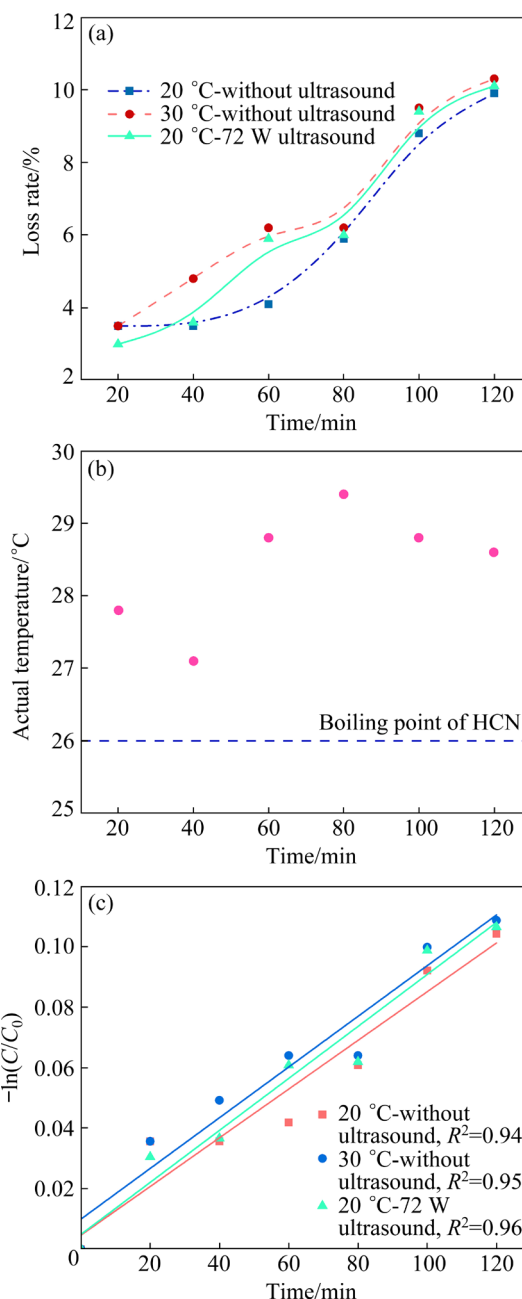


Fig. 9 Comparison of the presence and absence of ultrasound on cyanide loss rate (a), actual temperature of solution during ultrasound irradiation (b), and first-order kinetics plot of cyanide loss (c) (10.87 of initial pH, 0.69 g/L of initial concentration, and 1 L/min of air velocity)

than that without ultrasonic irradiation at 20 °C (9.9%). This phenomenon indicated that the effect of temperature on the decomposition of sodium cyanide may be predominant. Moreover, the loss rate of 20 °C-72 W sample (10.1%) was marginally higher than that at 20 °C without ultrasonic irradiation, as the actual temperature of the solution was higher than 20 °C, which would facilitate the

volatilization of HCN.

In Fig. 9(c), $-\ln(C/C_0)$ is plotted against the reaction time. It could be observed that the loss of cyanide follows the first-order reaction in kinetics ($-\ln(C/C_0)=kt$, where k is the apparent rate constant (min^{-1}), C_0 is the initial concentration, and C is the instant concentration at time t). These results confirmed the loss of cyanide in gold mill effluents [22,28] and the destruction of aqueous sodium cyanide by ultrasound [16–18]. The apparent rate constant k was approximate under different conditions: $8.1 \times 10^{-4} \text{ min}^{-1}$ for 20 °C-without ultrasound, $8.4 \times 10^{-4} \text{ min}^{-1}$ for 30 °C-without ultrasound, and $8.6 \times 10^{-4} \text{ min}^{-1}$ for 20 °C-72 W ultrasound. These results indicated that ultrasound contributed little additional damage to cyanide in the solution.

3.4 Potential role of ultrasound

The potential role of ultrasound on the loss of cyanide can be discussed from two aspects: the $\bullet\text{OH}$ radicals are produced by the cavitation oxidizing CN^- , thereby increasing the damage of sodium cyanide [35]; owing to the collapse of cavitation bubbles, the solubilities of O_2 and CO_2 in the solution decrease, thus reducing the loss of cyanide. The $\bullet\text{OH}$ has an extremely short life span and is particularly unstable in alkaline solutions [36,37]. The $\bullet\text{OH}$ dissociates rapidly in the alkaline medium through Reaction (8) and the dissociation product $\bullet\text{O}^-$ has weaker activity and oxidizing properties [38–40]. Furthermore, $\bullet\text{OH}$ can be removed by carbonate in solution, weakening its oxidative effect on cyanide [41].

Tert-butanol is a typical $\bullet\text{OH}$ scavenger, and the removal mechanism is presented in Reaction (9) [33,42]. The effect of $\bullet\text{OH}$ radicals on cyanide loss under different conditions was examined and the results are shown in Fig. 10. When the solution was not irradiated by ultrasound, the loss rate of sodium cyanide was 3.5% after 2 h of nitrogen blowing. After blowing nitrogen and adding ultrasonic irradiation simultaneously, the loss rate was 4.5%, slightly higher than that blown nitrogen without ultrasonic irradiation. Moreover, under the conditions of the presence of tert-butanol, nitrogen gas, and ultrasonic irradiation for 2 h, the loss rate was 3.0%, similar to the loss rate when nitrogen was blown but without ultrasonic irradiation. This means only about 1.5% of cyanide

was actually oxidized by $\bullet\text{OH}$ radicals.

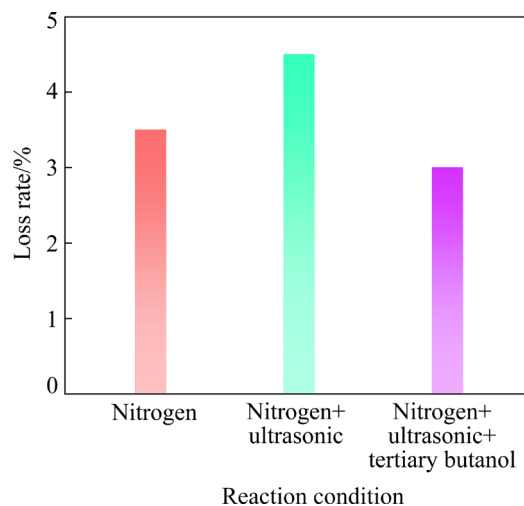
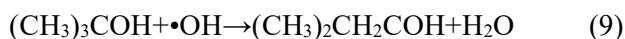


Fig. 10 Effect of $\bullet\text{OH}$ radicals on cyanide loss rate (20 °C, 2 h, 10.81 of initial pH, 0.67 g/L of initial concentration, 20 mL of tert-butanol, and 1 L/min of nitrogen velocity)

The dissolved oxygen in the solution with and without ultrasound irradiation was also measured (Fig. 11). The saturated concentration of dissolved oxygen at 25 °C was $\sim 8.08 \text{ mg/L}$ under the condition of blowing air continuously. After the introduction of ultrasonic irradiation, the dissolved oxygen content gradually descended and kept at 7.72 mg/L ultimately. Thus, in the sodium cyanide solutions, the dissolved oxygen was decreased by

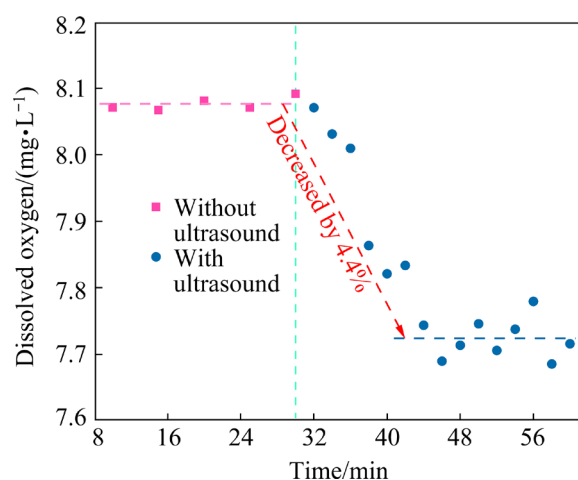


Fig. 11 Variations of dissolved oxygen in sodium cyanide solution before and after degassing by ultrasound (72 W, 10.81 of initial pH, 0.67 g/L of initial concentration, and 1 L/min of air velocity)

4.4% via ultrasonic irradiation. Previous results proved that the continuous collapse of cavitation bubbles is the main reason for decreasing gas solubility in the solution [38,43]. Consequently, the degassing property of ultrasound is beneficial to reducing the loss rate of cyanide.

It should be noted that when cavitation bubbles collapse in a homogeneous solution, the shape of the bubbles remains spherical and symmetrical before collapsing. However, bubbles will collapse near the solid surface when solid particles are present, which promotes the cavitation effect [44,45]. Hence, the presence of mineral particles in the ultrasound-assisted cyanide leaching process strengthens the cavitation process. In a separate test, cullet was used to replace ore to avoid the reaction between ore and sodium cyanide. Coincidentally, when solid particles were present and air was blown for 2 h, the loss rate of cyanide was both 4.5% in the presence and absence of ultrasound. Since solid particles intensified cavitation, the generation of $\bullet\text{OH}$ radicals and the degassing property were strengthened and the loss of sodium cyanide was not affected by ultrasound.

3.5 Cyanidation process

The cyanide loss rate in the conventional gold cyanide leaching and the ultrasound-assisted process was examined. Figure 12(a) shows that the gold extraction rate increased along with the escalation of leaching time (0.5–4.0 h). The gold extraction rate reached 93.9% after leaching 4.0 h under the ultrasonic irradiation. In the conventional gold leaching process, the gold extraction rate was only 82.5% at the same leaching time. Obviously, the gold extraction was improved in the presence of ultrasound. The variation of cyanide concentration during leaching is shown in Fig. 12(b). The variations of free cyanide concentration in conventional and ultrasound-assisted leaching solutions were quite similar. However, the total cyanide concentration during the ultrasound-assisted leaching was slightly higher than that in the conventional leaching. In both cases, both total cyanide and free cyanide concentrations decreased gradually with an increase of leaching time. After leaching, the total cyanide concentration in the slurry was much lower than the initial cyanide concentration.

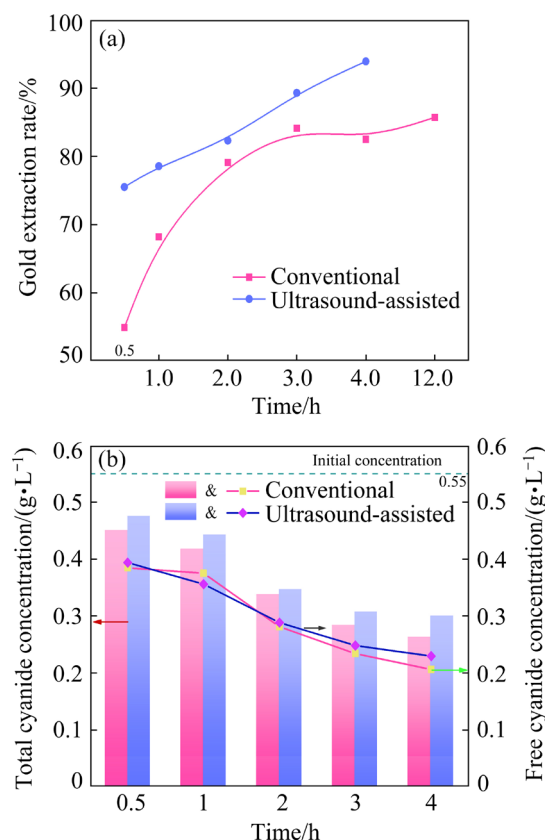


Fig. 12 Comparison of gold extraction rate in the absence and presence of ultrasound (a), and variations of concentrations of total cyanide and free cyanide during leaching (b)

4 Conclusions

(1) Under experimental conditions of initial pH of 10.87, initial cyanide concentration of 0.67 g/L, air velocity of 1 L/min, and reaction time for 2 h at 20 °C, the loss rate of cyanide with ultrasound was similar to that without ultrasound. The loss of cyanide followed the first-order kinetics with the kinetic constants k of $8.1 \times 10^{-4} \text{ min}^{-1}$ for 20 °C-without ultrasound and $8.6 \times 10^{-4} \text{ min}^{-1}$ for 20 °C-72 W ultrasound.

(2) The loss of cyanide could be mainly ascribed to hydrolysis, oxidation, and reaction with CO_2 . Continuous aeration promoted the volatilization of HCN. Only about 1.5% of cyanide was oxidized by $\bullet\text{OH}$ radicals when the ultrasonic irradiation time was 2 h. Ultrasound exhibited an obvious degassing property, which would be beneficial to reducing cyanide loss.

(3) The concentration of total cyanide in the ultrasound-assisted gold leaching was quite close to that in conventional gold cyanidation, indicating

that ultrasound exhibited only a slight impact on cyanide loss under the experimental conditions.

Acknowledgments

The authors are grateful for the financial supports from the National Natural Science Foundation of China (No. U1702252).

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超声波辅助氰化浸金过程中氰化物的损失行为和机理

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摘 要: 研究超声波对金浸出过程中氰化物损失或分解的影响。比较引入和不引入超声波时浸金过程中氰化物浓度的变化。探讨氰化物初始浓度、pH、温度、气氛、自然损失、水解和空化效应对氰化物损失的影响。结果表明, 在传统氰化浸金工艺中, 氰化物的损失主要是由水解、氧化和与 CO₂ 反应造成的。随着超声波的引入, 具有氧化性的 $\cdot\text{OH}$ 自由基使氰化物的损失略微增加。对总氰化物和游离氰化物浓度变化的比较证明, 在实际浸出中引入 120 W 超声波对氰化物损失影响较小。

关键词: 超声波; 金; 氰化法; 氰化物损失; $\cdot\text{OH}$ 自由基

(Edited by Wei-ping CHEN)