

Potassium Permanganate as an Alternative for Gold Mining Wastewater Treatment

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The feasibility of using potassium permanganate as a reagent for cyanide oxidation in wastewater was experimentally studied. Both artificial and production wastewater from two different gold mines were tested. The experiments had three goals: determine the optimum reagent concentration and reaction time required to achieve total cyanide removal, obtain knowledge of the reaction kinetics, and improve the management of the amount of reagent. The results indicate that potassium permanganate is an effective and reliable oxidizing agent for the removal of cyanide from gold mining wastewater.

INTRODUCTION

Obtaining gold from complex ores generally requires the use of detrimental agents such as Hg compounds (amalgams) or cyanides. As the use of amalgams is currently decreasing because of the toxicity associated with mercury, cyanide leaching has become the principal system for the chemical processing of complex gold ores. The cyanide–gold interaction was investigated for the first time in 1783 by Scheele.¹ During the 19th century, prestigious scientists such as Faraday, Elsner, and Elkington developed improvements;² however, it was not until 1888 that McArthur and the Forrest brothers established the current metallurgical method of cyanide leaching.³

The cyanide leaching method is feasible because gold can be dissolved into a leaching solution of a cyanide compound while most of the other ore components remain unaltered. After a solid/liquid separation process, the gold is then obtained through cementation or adsorption/electrolysis procedures.⁴ Independent of the recovery method, a refining stage is normally required to ensure the final gold purity. Despite its advantages, the utilization of this technique results in cyanide contamination of the final process water, which needs to be processed because of the presence of compounds with high toxicity. The developed decontamination methods are focused on eliminating weak acid dissociable (WAD) cyanide compounds, which are characterized by their capacity for dissociating under a weak acid pH, normally below

pH 4.5.⁵ The classification of possible treatment processes is shown in Fig. 1.

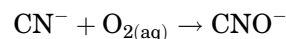
Mitigation processes have high efficiency; hence, they are normally used in industry even though the main problem is still linked to process hazards. These systems are divided into artificial and natural methods depending on the initial presence of the material responsible for decreasing the cyanide concentration in the effluent.

Natural Methods

These methods enable the removal of cyanide compounds using physical and chemical reactions without external reagents. There are three methods of particular importance: dilution, bio-oxidation, and natural removal processes.

Dilution processes are based on decreasing the cyanide concentration by mixing mining wastewater with clear water. An additional recycling method is subsequently required because the process cannot be used as a final effluent treatment.⁶

Bio-oxidation processes transform the cyanide compounds into cyanate using enzyme action and hydrolysis,⁶ according to the following reactions:



Ammonium, a toxic compound, is removed using the nitrification/denitrification process:

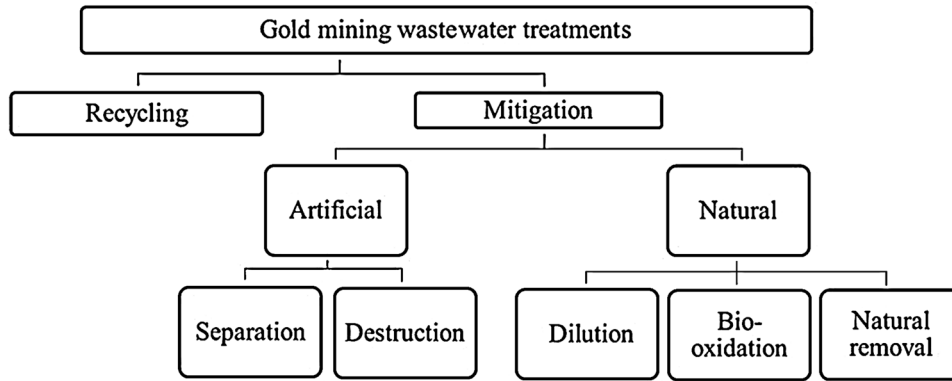
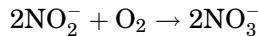


Fig. 1. Classification of wastewater treatment processes.



These processes occur because of the action of aerobic organisms, which decrease the concentrations of not only WAD cyanide compounds but also of strong acid dissociable (SAD) cyanide and thiocyanate compounds. The main disadvantage is that strict control is necessary to reliably achieve low concentration levels of cyanide in the effluent.

Natural removal processes combine volatilization, adsorption, as well as oxidative and hydrolysis reactions for decreasing the effluent cyanide concentration. Because of the large number of control variables, an effective process design is needed; therefore, this process is generally used in combination with other processes (Mudder et al.⁷). There are a large number of variables due to the great number of complex cyanide formation processes (the majority of the elements of the periodic table can combine with cyanide ion) that could exist in the aqueous solutions.

Artificial Methods

The principle of these methods is removing cyanide compounds using an external reagent action. There are two different artificial methods: separation processes and destruction processes.

Separation processes isolate cyanide compounds using physical mechanisms such as membranes, chemical reagents for adsorption/desorption, solvent extraction systems, or any multiple (it depends on the environmental requirements and the physical-chemical characteristics of the contaminated solutions) combinations of these processes.⁶ Two-process combinations are frequently used:

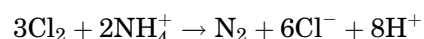
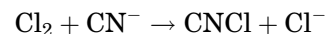
- Free cyanide hydrolysis-distillation: First, the hydrolysis stage occurs, during which cyanide is converted to hydrogen cyanide, followed by the hydrogen cyanide volatilization stage.

- Acidification-volatilization: The first stage consists of transforming cyanide compounds into hydrogen cyanide using pH reduction; the second stage is hydrogen cyanide volatilization.

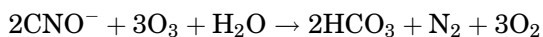
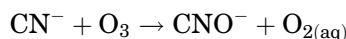
Destruction processes convert cyanide compounds to less toxic ones through chemical precipitation or oxidative treatments.

- Precipitation methods are based on metal cementation properties. Cyanide compounds are transformed into precipitates by reaction with metals such as zinc (Merrill-Crowe process⁸), copper, or iron.⁶ Because of the negative interactions of these metals when thiocyanates are present, these methods must be used as a stage of a more complex overall industrial process.
- Oxidative methods are used because of their simplicity and efficiency with only one treatment stage. They are based on cyanide transformation into cyanate using oxidative reagents. The more common oxidative reagents used are described as follows:

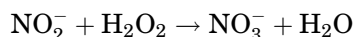
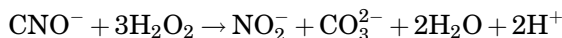
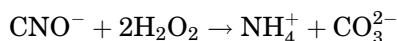
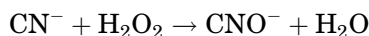
- Chlorine efficiently oxidizes both free and WAD cyanide in a two-stage process that allows their transformation to cyanate.⁹ Although nitrogen is the only final waste product, this method is not economical; the theoretical consumption is 2.73 g Cl₂/1 g CN⁻, but practical values range from approximately 3–8 g Cl₂/1 g CN⁻ (Ref. 10) because of the higher consumption of reagents involved in relation to other competitive methods:



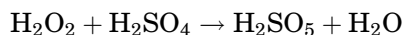
- Ozone efficiently and quickly oxidizes cyanide, cyanate, and thiocyanates. The only final disintegration products are HCO_3^- and nitrogen.¹¹ Recent studies have reported a reagent consumption of 3 g O_3 /1 g CN^- (Ref. 10). However, the absence of detailed studies about the reaction kinetics is a weak point of this process:



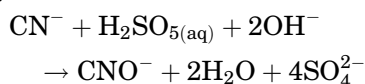
- Hydrogen peroxide removes cyanide and cyanate compounds by hydrolysis, leaving ammonium, carbonate, and nitrate (using excess peroxide)¹² as reaction products; the theoretical consumption is 1.31 g H_2O_2 /1 g CN^- , but practical values range from approximately 2–8 g H_2O_2 /1 g CN^- (Ref. 10).



- Peroxymonosulfuric acid (H_2SO_5), also known as Caro's acid, is an interesting alternative because of its high reaction speed and recycling properties in biological effluent treatment.¹³ Caro's acid is produced from concentrated hydrogen peroxide and sulfuric acid in an exothermic reaction:

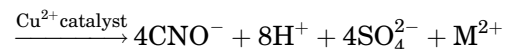
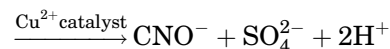
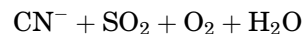


Because of its instability (particularly at elevated temperatures, where it is only stable for several minutes, decomposing into oxygen, water and sulfur trioxide (SO_3)), peroxymonosulfuric acid is produced onsite and is used immediately.¹⁰ The process leaves cyanates as the only final reaction product. However, it is not considered to be a profitable process because of the fairly high price of reagents and safety precautions. The theoretical consumption is 4.39 g H_2SO_5 /1 g CN^- , but practical values range from approximately 5 to 15 g H_2SO_5 /1 g CN^- (Ref. 10).



- Sulfur dioxide (SO_2) is used in the INCO process,¹⁴ which is currently the preferred process in industry because of its efficiency. This process has three stages during which

different reagents are added: first, copper as a catalyst; second, a mixture of SO_2 /air; and finally, sulfur as sodium methabisulfite or sodium sulfite. One disadvantage of the process is the toxicity of the final products for live organisms.



The theoretical consumption of SO_2 in the process is 2.46 g of SO_2 per gram of WAD cyanide oxidized, but the real consumption ranges from approximately 3.0–5.0 g of SO_2 per gram of WAD cyanide oxidized.¹⁵

Generally, among all gold mining wastewater artificial treatment processes, the more profitable ones are those that transform cyanide into other less toxic compounds using an external reagent. Thus, potassium permanganate is an excellent candidate not only because of its oxidative diversity (i.e., it works with both organic and inorganic compounds, as well as under acidic, basic, and neutral conditions) but also because of its simple production and handling.

Potassium Permanganate as an Oxidizing Agent for Cyanide Compounds

Potassium permanganate (KMnO_4) was first used in 1910 for water treatment in London.¹⁵ Studies performed by the University of Florida show the bactericide properties of the potassium permanganate.¹⁶ However, it was not until 1870¹⁷ that KMnO_4 was first used as an oxidizing agent. Currently, KMnO_4 is commonly used in the pharmaceutical industry and for environmental health safety. However, there have been no reports of its use in the industrial treatment of cyanide wastewaters.

The goals of this research are to introduce KMnO_4 as a potential alternative for gold mining cyanide waste treatment and to exploit its advantages. Because KMnO_4 has a high oxidative capacity,¹⁷ it can transform cyanide into cyanate with less toxicity in a simple and efficient manner. The first experiments performed by Sancho et al.¹⁸ showed excellent results with both synthetic and natural gold mining wastewaters.

For this research, two different gold mining wastewaters were processed: one of them from Belmonte (Asturias) in the northern Spain and the second one from a large gold mine in the Peruvian Cordillera (Yanacocha). The current research focuses on verifying the oxidative capacity of KMnO_4 for gold mining wastewater independent of its origin (Belmonte mine water and Yanacocha mine water),

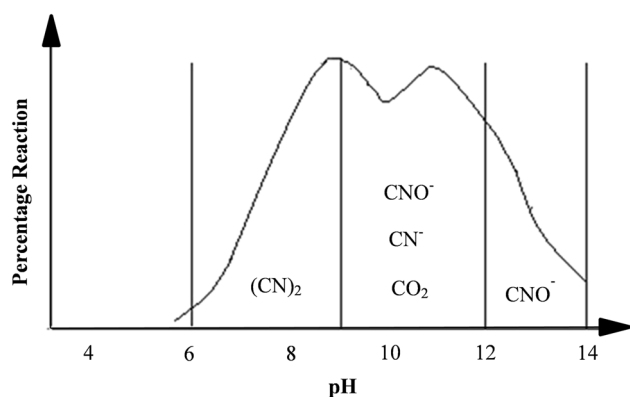


Fig. 2. Cyanide compounds released as a function of pH.

previous treatments (i.e., the SO_2 method in the Belmonte mine and reverse osmosis in the Yanacocha mine), and cyanide concentration, which depends on the water precedence.

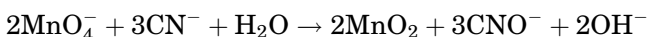
The oxidation of cyanide compounds using KMnO_4 as an oxidizing agent requires strict control of both pH conditions and reagent concentrations to ensure not only efficiency but also safety.¹⁹ The suitable selection of pH conditions is essential, as shown in Fig. 2²⁰:

Four different pH ranges were established:

1. $\text{pH} < 6$: no oxidation reaction
2. $6 < \text{pH} < 9$: release of toxic cyanogen gas
3. $9 < \text{pH} < 12$: wide range of secondary reactions
4. $12 < \text{pH} < 14$: transformation of cyanide to cyanate

Taking these pH ranges into account, the suitable pH range for the desired reactions (and hence, working range) is pH range 4 ($12 < \text{pH} < 14$). The basicity needed for this condition requires the use of a certain amount of lime.

The general oxidation reaction during the oxidation of cyanide with permanganate can be written as:



Studies by the University of Melbourne showed that 4.05 kg of potassium permanganate (KMnO_4) is required to oxidize 1 kg of cyanide (CN^-).²¹ The amount of KMnO_4 required to oxidize a water volume with an initial concentration of cyanide (CN^-) can be written as:

$$\text{Needed g } (\text{KMnO}_4) = \text{Volume (L of water)} \\ \times \text{CN}^- (\text{ppm}) \times 4.05 \times 10^{-3}$$

There are two points to highlight:

1. Alkalinity increases because of free OH^- and the interaction of potassium permanganate-cyanide when there are iron and silver cyanide compounds. The main problem of the cyanide

ion is that it can combine with any metal of the periodic table, and as a consequence, it is possible to find complex cyanides with more or less free energy.

2. The fastest reactions were linked to copper cyanide compounds (such as $\text{K}[\text{Cu}(\text{CN})_2]$), which allowed the presence of Cu^{2+} as a catalyst (because Cu^{2+} can play a catalyzer role). Copper appears in significant amounts in process-mine water, despite precautions to separate it from the plant pulp.

EXPERIMENTAL

The study aims to confirm that KMnO_4 is a cyanide removal reagent not only for artificial waters with added cyanide but also in mining wastewater where different cyanide compounds can be found that could interact during the removal process. These studies were developed for mining water from different origins and different cyanide concentrations to demonstrate the universal validity of the method. In the experiments, pressurized air was used for agitation to improve cyanide removal by increasing the presence of oxygen. Basic conditions, i.e., pH 14, were reached using lime to ensure work safety.

The cyanide concentration was measured using a colorimetric technique that utilizes picric acid as the reagent. This technique is based on how the color of picric acid changes from yellow to orange and even red as the cyanide concentration increases. The first stage focused on obtaining the standard curve (Fig. 3) by using solutions with different cyanide concentrations and measuring the absorbance of each of them. A regression line was obtained and used for measuring the cyanide concentration using spectrophotometry as can be seen in Fig. 3.

Artificial Water Studies

The first study focused on determining the cyanide removal capacity of KMnO_4 in dependence of its concentration. Artificial water with 20 ppm CN^- and $\text{pH} < 12$ were tested, and some lime was added to achieve the pH level of 14. In this test, artificial water was treated using a range of KMnO_4 solution concentrations of 1 mg, 2 mg, 4 mg, 6 mg, 8 mg, and 10 mg of MnO_4^- for each mg of CN^- with a 30-min reaction time.

The second study focused on determining the response effect. In this test, 20 ppm CN^- water was treated with 2 mg of MnO_4^- for each mg of CN^- . Sample extractions were performed after 15 min, 30 min, 45 min, 60 min, 90 min, and 120 min.

The third study investigated the possible interaction between reaction time and reagent concentration during cyanide removal. Contaminated water (20 ppm CN^-) was treated with 2 mg, 4 mg, and 8 mg of MnO_4^- for each mg of CN^- with sample extractions performed after 15 min, 30 min, 45 min, 60 min, 90 min, and 120 min.

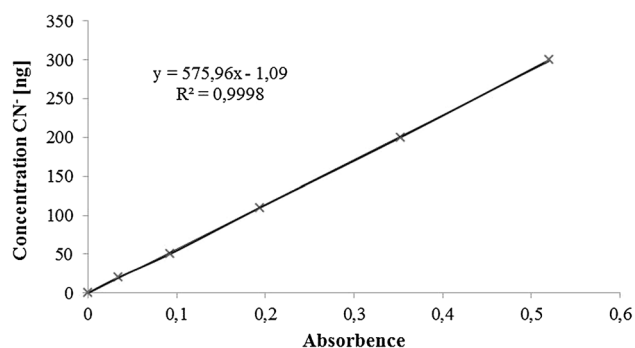


Fig. 3. Standard curve for cyanide concentration measurement.

Mining Wastewater from a Spanish Plant

Gold ores from Belmonte Mine were treated using cyanide leaching. These gold ores contained silver and copper because of the mine's geological characteristics. Even though the effluents were treated using the INCO process,²² a waste effluent with 0.4 ppm of CN^- was obtained because of the low efficiency of the process. To verify the KMnO_4 oxidative capacity, other samples were taken from the main stream (0.8 ppm CN^-) and from the already closed mud pond drainage water (7.9 ppm CN^- concentration). Moreover, copper and cyanide kinetics studies were performed to determine the removal rate.

Increasing the reagent concentration from 1 mg to 10 mg of MnO_4^- for each mg of CN^- reduced the reaction time to 20 min when operative pond water (OW) (0.4 ppm CN^-) was used because of the low CN^- concentration. In the second set of tests with the INCO-treated main stream (PW) (0.8 ppm CN^-), tests were performed following the same procedure as with the pond effluent, using a 30-min reaction time and increasing the reagent concentration from 1 mg to 8 mg of MnO_4^- for each mg of CN^- . The third set of tests was performed with wastewater from the nonoperative pond water (NOW). The main feature of this wastewater is the high cyanide concentration (7.9 ppm CN^-). The tests were performed with a 30-min reaction time and increasing the concentration of reagent from 1 mg to 10 mg of MnO_4^- for each mg of CN^- .

Kinetics studies were conducted by performing water extractions (taking samples to know the amount of cyanides in a period of time) during treatment after 5 min, 10 min, 20 min, and 30 min for both OW and NOW and after 5 min, 10 min, and 20 min for PW.

In addition, kinetics studies were repeated using pressurized air agitation to improve the oxidation yield. The objective was to reduce the required reagent concentration to maximize cyanide removal.

First, the OW was treated for 30-min reaction time (required time to remove cyanides; longer times would not be adequate for the plant effectiveness)

and reducing the reagent concentration to 2 mg of MnO_4^- for each mg of CN^- . Extractions were performed at 5 min, 10 min, 20 min, 25 min, and 30 min. Second, a test was performed for the PW using a 20-min response time. The reagent concentration was reduced to 1.5 mg of MnO_4^- for each mg of CN^- . Extractions were performed at 5 min, 10 min, and 20 min. Finally, kinetics studies were repeated for the NOW, keeping the 30-min reaction time and reducing the amount of reagent to 2 mg of MnO_4^- for each mg of CN^- .

Mining Wastewater from Yanacocha Mine

Gold ores from the Yanacocha Mine were treated using osmosis. These gold ores were originally associated with iron oxides, sulfides, and quartz because of the mine's geological characteristics. The cyanide concentration in the final wastewater was approximately 23 ppm CN^- because of the low efficiency of the decontamination process (i.e., osmosis).

The first set of studies was performed with increasing reagent concentrations from 1 mg to 12 mg of MnO_4^- for each mg of CN^- and a 30-min reaction time. Both the copper and cyanide removal rates were studied, similar to the Spanish plant. In addition, studies with pressurized air were performed with a 30-min reaction time and 3 mg of MnO_4^- for each mg of CN^- reagent concentration.

RESULTS AND DISCUSSION

Artificial Water Studies

The initial studies with artificial water show that increasing the reagent concentration will improve cyanide removal from the water (Fig. 4).

However, reaction time does not have a direct relationship with cyanide removal. The test results show that most of the cyanide is removed during the first 45 min, and then the removal stagnates (Fig. 5).

Combining both the reagent concentration and the reaction time reduces the required reaction time (Fig. 6). Artificial water studies establish a reaction time of less than 45 min and an optimum reagent concentration of 4 mg of MnO_4^- for each mg of CN^- .

Mining Wastewater from a Spanish Plant

As described above, three water sources, OW, PW, and NOW, were tested (i.e., OW from the operative pond with 0.4 ppm of CN^- , PW from the INCO main stream with 0.8 ppm CN^- , and NOW from the already closed operative pond with 7.9 ppm CN^-). For each water source, two experimental blocks were performed: First, increasing volumes of reagent were added for a given reaction time, and then, extractions were performed at different periods of time from the treated water to establish the cyanide removal kinetics.

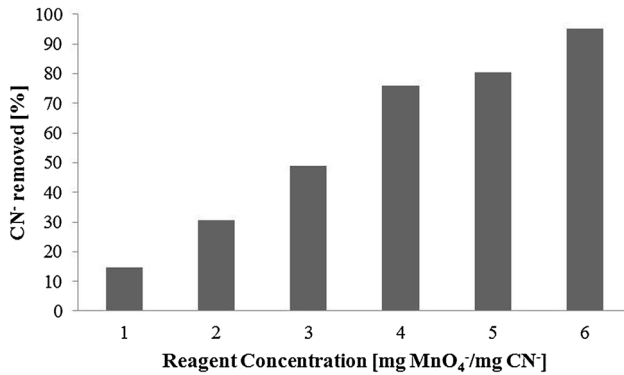


Fig. 4. Cyanide removal versus reagent concentration.

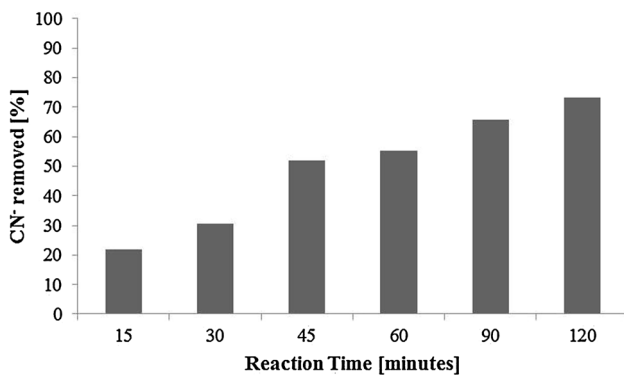


Fig. 5. Cyanide removal versus reaction time.

Mining Wastewater From a Spanish Plant: OW Treatment

The reagent concentration was increased from 1 mg to 10 mg of MnO_4^- for each mg of CN^- , and the reaction time was reduced to 20 min in the OW treatment (0.4 ppm CN^-) because of the low concentration of CN^- . Using 4 mg of KMnO_4 , a progressive cyanide removal was observed, followed by an increasing presence of CN^- . This occurs because of the presence of thiocyanates, which break the S-CN bond once the complete removal of WAD cyanide has been achieved. To avoid this interaction, two improvements were introduced: The reagent concentration was decreased to 3 mg of MnO_4^- for each mg of CN^- and the reaction time was increased to 30 min. These two parameters resulted in total cyanide removal (0.01 ppm detection limit, CN^- concentration lower than 0.01 ppm is supposed to be completely removed), as reported in Fig. 7.

Kinetics studies confirmed the conclusions obtained for artificial waters. Cyanide is completely removed after a 30-min treatment (Table I). The Cu^{2+} amount was determined using atomic absorption spectroscopy,²³ whereas CN^- was determined using calorimetry of picric acid.²⁴

Mining Wastewater from a Spanish Plant: PW Treatment

The strong presence of thiocyanates can be observed in the results from the second set of

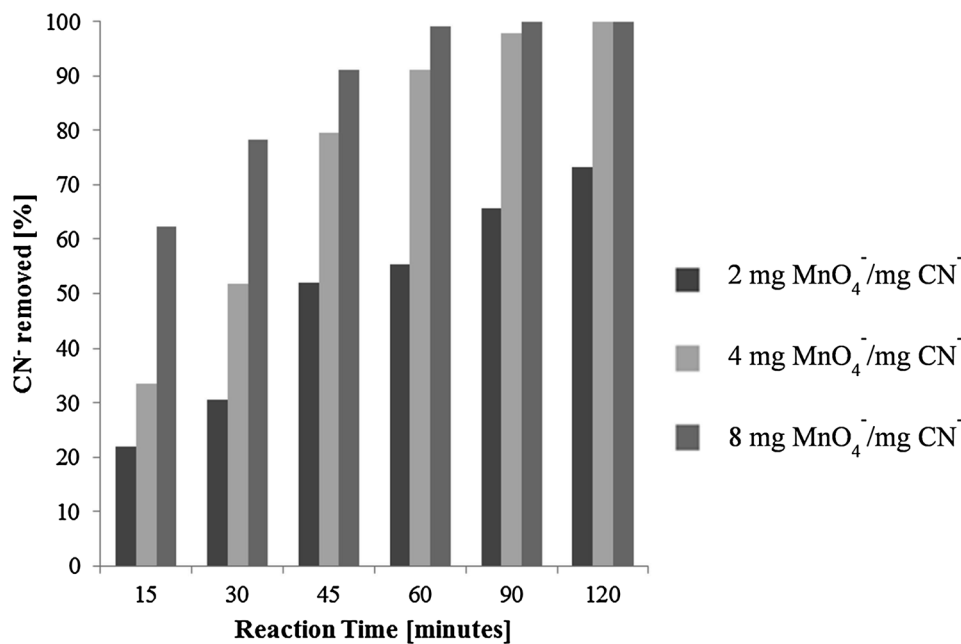


Fig. 6. Cyanide removal for different combinations of reaction time and reagent concentration.

experiments performed with PW (0.8 ppm CN^-). Potassium permanganate eliminates all cyanide from the water. Nevertheless, the excess of reactive particles leads to interactions with the thiocyanates, and new cyanide compounds are created (Fig. 8). Reducing the reagent optimum concentration to 2 mg of MnO_4^- for each mg of CN^- in solution is necessary to avoid this thiocyanate-permanganate interaction.

The dilution of the sample was necessary to achieve total cyanide removal. The required dilution ratio was two parts of clear water to one part of wastewater (Table II).

Using 2 mg of MnO_4^- for each mg of CN^- and a dilution of two parts of clear water to each part of wastewater, the reaction time needed to eliminate cyanide was 15 min (Fig. 9).

Kinetics studies with PW demonstrated that although total cyanide removal was only achieved after 15 min, most of the cyanide was eliminated during the first 10 min (Table III).

Mining Wastewater From a Spanish Plant: NOW Treatment

The results from the third set of experiments performed with NOW (7.9 ppm CN^-) show that cyanide removal with 4 mg MnO_4^- for each mg of CN^- achieves 1.8 ppm CN^- . This situation seems to be similar to the ones analyzed before and described above; in this case, this result is because of the presence of sulfides that interact with the picric acid and hence provide false results that indicate

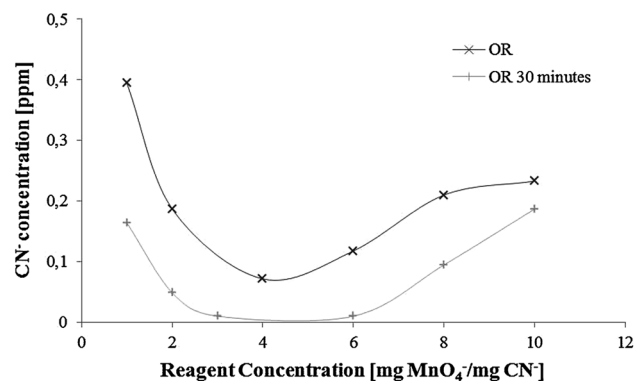


Fig. 7. Cyanide removal versus reagent concentration before and after the reagent concentration decreasing and the reaction time increasing.

incomplete removal of the cyanide. Picric acid helps to potassium permanganate to the cyanide removal. The presence of metallic sulfides supposes a block in the mechanism of cyanide removal by means of the potassium permanganate. This mechanism is known as false positive. In this way, a new reagent was added to the effluent sample (CuCO_3). This new reagent eliminates the sulfides and makes easier the cyanides completely removal. After reaction, the color of the solution changed from light to dark blue because of the appearance of precipitated copper sulfide. The sample was filtered and all tests repeated with the same parameters in the clear solution. The amount of CuCO_3 needed to eliminate the false positive result was 500 mg of CuCO_3 for 100 mL of NOW (Table IV). Is known false cyanide positive as the incomplete cyanide removal due to the oxidizing action of the potassium permanganate as a consequence of the presence of sulfide anions (S^{2-}) in the aqueous solution.

Figure 10 shows the results with and without using copper carbonate. In this case, the optimum reagent concentration is found to be 4 mg of MnO_4^- for each mg CN^- using CuCO_3 to eliminate interactions and a reaction time of 30 min. A kinetics study shows the same effect even though the cyanide concentrations are higher for this sample. Cyanide and copper are completely removed after a treatment for 30 min (Table V).

In summary, the studies performed using gold mining wastewaters from the Spanish plant confirmed that KMnO_4 is an efficient oxidizing agent. To improve the kinetic yield, the studies were

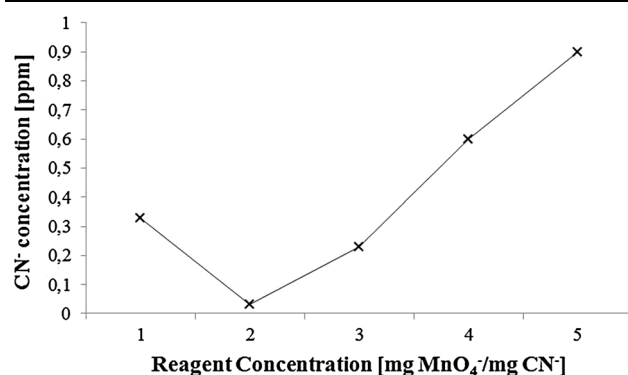


Fig. 8. INCO main stream cyanide removal versus reagent concentration.

Table I. Removal of Cu^{2+} and CN^- from artificial water as a function of time

Extraction time	ppm Cu^{2+}	Percentage Cu^{2+} removed	ppm CN^-	Percentage CN^- removed
5 min	0.2	25	0.3	17
10 min	0.1	62	0.2	46
20 min	<0.1	92	<0.1	88
30 min	0.0	100	0.0	100

repeated using pressurized air for agitation to reduce the reagent concentration consumption necessary to achieve total cyanide removal.

Mining Wastewater From a Spanish Plant Using Pressurized Air

The time needed to remove cyanide from the wastewater from OW was 30 min. The reagent concentration was reduced from 3 mg to 2 mg of MnO_4^- for each mg of CN^- and air agitation was used. Extractions were performed at 5 min, 10 min, 20 min, 25 min, and 30 min. Testing revealed positive results (the potassium permanganate amount was reduced) when the amount of reagent needed to achieve cyanide total removal was decreased to 2 mg MnO_4^- for each mg of CN^- (Table VI).

PW wastewater was treated for 15 min and the same dilution used as in the first test (i.e., two parts of clear water for each of wastewater), but additional pressurized air agitation was used. The reagent concentration was reduced from 2 mg to 1.5 mg of MnO_4^- for each mg of CN^- . Extractions

were performed at 5 min, 10 min, and 15 min. The use of pressurized air allowed the reagent concentration consumption (potassium permanganate concentration was reduced from 4 mg to 2 mg of MnO_4^- , due to the oxygen solution in the water as a consequence of the partial pressure of the oxygen in the air) to be reduced without reducing efficiency (Table VII).

For the tests with NOW, a 30-min reaction time and reduction of the reagent to 2 mg of MnO_4^- for each mg of CN^- were used. During these tests, it was discovered that a treatment using copper carbonate is needed to avoid sulfide interactions. Extractions were performed after 5 min, 10 min, 20 min, 25 min, and 30 min (Table VIII).

In conclusion, independent of the initial cyanide concentration of the mine solution, using pressurized air agitation results in a 50% reduction in the amount of permanganate needed to remove all the cyanide.

Mining Wastewater from a Peruvian Plant

As stated above, the initial set of studies with wastewater from this mine was performed by increasing the reagent concentration from 1 mg to 12 mg of MnO_4^- for each mg of CN^- with a 30-min reaction time.

As shown in Fig. 11, certain stagnation occurs for a reagent concentration greater than 4 mg of MnO_4^- for each mg of CN^- , followed by a small increase in the cyanide concentration because of the presence of thiocyanates. The first test revealed a need for optimization not only to reduce the concentration of the reagent but also to achieve total cyanide removal from the wastewater. Two sets of studies were performed: one using dilution and another using pressurized air.

Table II. Dilution ratio (wastewater:clear water)

Dilution relation	Absorbance	ppm CN^-
1:1	0.015	0.5
1:2	0	0
1:3	0	0

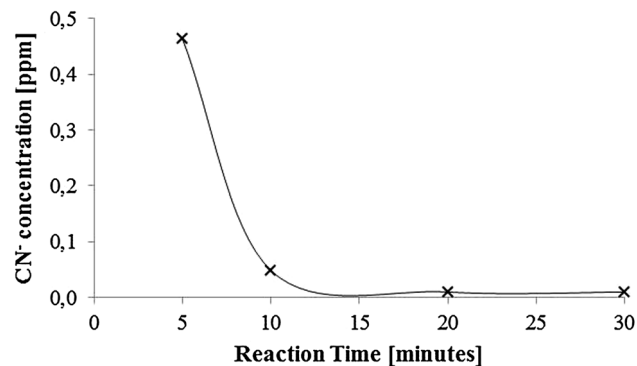


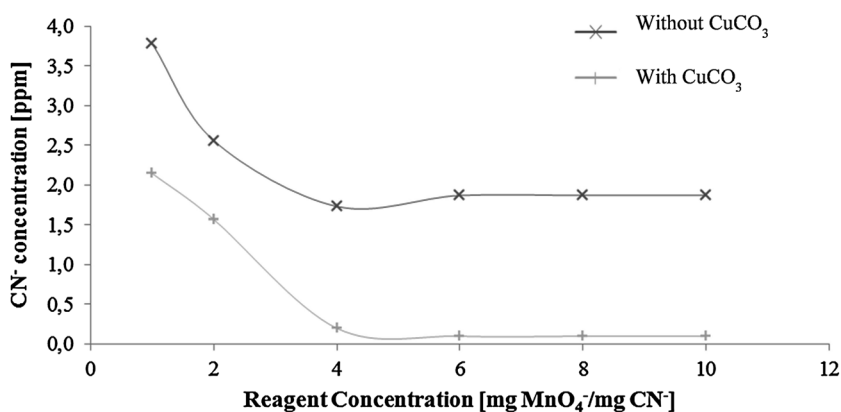
Fig. 9. INCO main stream cyanide removal versus reaction time after dilution.

Table IV. CuCO_3 needed to eliminate a false cyanide positive

CuCO_3 (mg)	Absorbance	ppm CN^-
200	0.02	0.6
300	0.01	0.3
400	0.005	0.1
500	0.0	0.0

Table III. Removal of Cu^{2+} and CN^- from the INCO main effluent (kinetics studies)

Extraction time	ppm Cu^{2+}	Percentage Cu^{2+} removed	ppm CN^-	Percentage CN^- removed
5 min	0.1	50	0.2	58
10 min	0	100	0.1	83
15 min	0	100	0	100

Fig. 10. Cyanide removal from (NOW) with and without CuCO₃.**Table V. Removal of Cu²⁺ and CN⁻ from the NOW studies**

<u>Extraction time</u>	<u>ppm Cu²⁺</u>	<u>Percentage Cu²⁺ removed</u>	<u>ppm CN⁻</u>	<u>Percentage CN⁻ removed</u>
5	6.3	10	7.3	8.8
10	4.2	40	5.2	35
20	1.1	85	1.6	80
30	0.0	100	0.0	100

Table VI. Removal of Cu²⁺ and CN⁻ from the OW studies with pressurized air agitation

<u>Extraction time</u>	<u>ppm Cu²⁺</u>	<u>Percentage Cu²⁺ removed</u>	<u>ppm CN⁻</u>	<u>Percentage CN⁻ removed</u>
5 min	0.2	30	0.3	21
10 min	0.1	65	0.2	57
20 min	<0.1	97	<0.1	92
25 min	<0.1	99	<0.1	97.5
30 min	0.0	100	0.0	100

Table VII. Removal of Cu²⁺ and CN⁻ from the PW kinetic studies with pressured air agitation and dilution

<u>Extraction time</u>	<u>ppm Cu²⁺</u>	<u>Percentage Cu²⁺ removed</u>	<u>ppm CN⁻</u>	<u>Percentage CN⁻ removed</u>
5 min	0.1	50	0.2	42
10 min	0.0	100	0.1	76
15 min	0.0	100	0.0	100

Dilution studies were performed with a 20-min reaction time, 4 mg of MnO₄⁻ for each mg of CN⁻ reagent concentration and dilution ratios of six clear water to each of wastewater (six clear water: one wastewater). Dilution after the first mix seems to be an excellent procedure to reduce the final cyanide concentration. In addition, the testing verifies that more dilution implies a lower final cyanide concentration using the same reagent concentration (Fig. 12).

Studies with pressurized air were performed with a 30-min reaction time and 3 mg of MnO₄⁻

for each mg of CN⁻ reagent concentration. In addition, dilution was added in 2 mL, 3 mL, and 4 mL clear water to each mL of wastewater to achieve total removal of the cyanide from the sample. Both copper and cyanide removal were studied, similar to the tests with the wastewaters from Spanish plant (Table IX). The combination of pressurized air and dilution provides high process efficiency and achieves 99.2% cyanide removal using 3 mg of MnO₄⁻ for each mg of CN⁻ instead of 4 mg.

Table VIII. Removal of Cu^{2+} and CN^- from NOW kinetic studies, with pressurized air agitation and CuCO_3

<u>Extraction time</u>	<u>ppm Cu^{2+}</u>	<u>Percentage Cu^{2+} removed</u>	<u>ppm CN^-</u>	<u>Percentage CN^- removed</u>
5 min	5.5	22.0	6.4	20.0
10 min	2.9	58.0	4.1	48.8
20 min	0.8	88.5	1.2	85.0
25 min	0.1	98.5	0.1	98.8
30 min	0.0	100	0.0	100

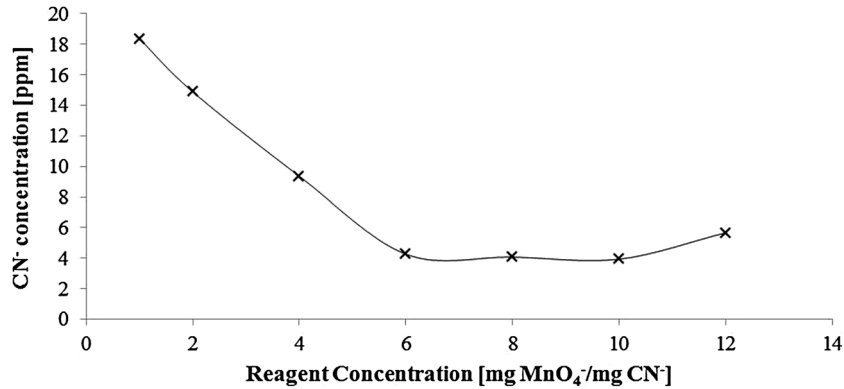
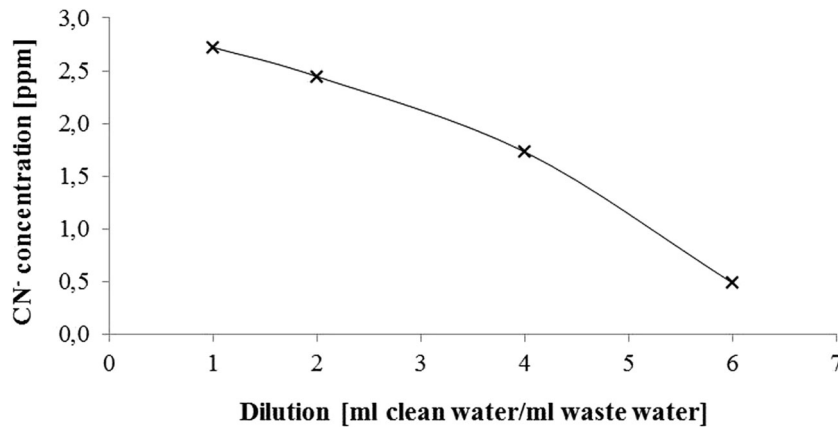


Fig. 11. Cyanide removal evolution versus reagent concentration.

Fig. 12. Cyanide removal evolution versus dilution using 4 mg of MnO_4^- for each mg of CN^- .**Table IX. Removal of Cu^{2+} and CN^- after dilution using pressurized air**

<u>Dilution relation</u>	<u>ppm CN^-</u>	<u>Percentage CN^- removed</u>	<u>ppm Cu^{2+}</u>	<u>Percentage Cu^{2+} removed</u>
2	2.0	91.2	1.0	97.8
3	1.1	95.2	0.3	99.3
4	0.2	99.2	0.1	99.8

CONCLUSION

The study demonstrated the oxidative properties of potassium permanganate for wastewater treatment of cyanide, namely its ability to transform the cyanide into less toxic species, such as cyanate, both in artificial and mining wastewater and achieves total cyanide removal. Three important points of this process are:

1. It is absolutely safe because the final waste products are MnO_2 and $\text{Cu}(\text{OH})_2$ and the reaction occurs in alkaline conditions; hence, there is no release of hydrocyanic acid.
2. The process enables a high yield of cyanide elimination. The required reagent concentration is 4 mg of MnO_4^- for each mg of CN^- for both synthetic water and mine water without using pressurized air agitation. This consumption can be reduced by the presence of thiocyanates and pressurized air agitation.
3. Optimization tests demonstrate that the results can be further improved by combining dilution and pressurized air, which results in total cyanide removal while reducing the reagent concentration by 50%.

This study demonstrates that KMnO_4 is a suitable oxidizing agent for cyanide wastewater because of its efficiency, safety, and high yield. Due to the sample handling and distribution of potassium permanganate, it is a safe and efficient method for new decontamination technologies.

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