

## Developments of an alternative technology to remove cyanide from mining wastewater

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### ABSTRACT

Public concerns about pit mining using cyanide are unlikely to dissipate in the near future. The combination of inherent negative images of cyanide, coupled with environmental problems associated with precious metals mining will continue disturbing people in the relation with the mining industry. Most new gold mines are required to treat tailings to reduce cyanide levels before they are discharged to storage ponds to meet the stringent environmental management guidelines set by government statutory authorities.

This study deals with an innovative oxidative process, using Potassium Permanganate as oxidant, for the treatment of cyanide-contaminated mine process water. The technology was tested for its ability to detoxify cyanide and immobilize metals in wastewater from cyanide leaching.

A pilot-scale demonstration is described in which a testing was carried out to demonstrate the possibilities of the technology on Río Narcea mine wastewater in Belmonte (Asturias).

### INTRODUCTION

For many years, effective methods for the detoxification of cyanided compounds that appear in wastewaters from mining have been looked for. The procedures that have been developed so far, though they allow a certain control over pollution, show several problems, which make them, little effective for real life. So, procedures widely extended such as those for destruction or regeneration of cyanide are very difficult to optimize in mines because they don't reach the detoxification levels required nowadays by present laws.

Within the most widely used destructive processes we find the oxidative ones. Among them, The Degussa Process and the INCO Process stand out being the ones chosen by the majority of mining plants nowadays due to their great effectiveness. But, anyway, they show several problems of lack of effectivity mainly due to the presence of base metals such as copper, zinc, iron or sulphuric minerals. They make treatments become very expensive because the cyanide products coming from these materials also react with oxidants and this increases the consumption of detoxification agents.

Owing to this, companies are forced to treat contaminated water several times with the same process or to use tandem methods.

A clear example of this problem is Río Narcea Gold Mines, where a new treatment plant for the INCO Process is being built. With it a second treatment for waste water is carried out before it is sent back to the tailing pond.

Besides, recent accidents of breaking of the tailing ponds such as the one in Baia Mare (Romania) or the one in Guayana in 1995 in the Mine Omai were widely followed by the mass media and they became the force that allowed the development of the Environmental Programme by The United Nations (UNEP), developed in Paris in June 2000. In it, several proposals were established to reduce the risks derived from using cyanide and, also, severe restrictions on the water tailing ponds were put.

However, perhaps the main problem faced by the UNEP nowadays in accident prevention nowadays is in underdeveloped countries, where poorer companies don't see to rules very strictly because the necessary technological advances for the design, construction and maintenance of tailing ponds would be very expensive. The safe transport of reactive products and its use would also mean high economic investments that would imply an increase in production and, therefore, would force a closing down.

Taking into consideration all this, we start working in this study. The potassium permanganate is a new alternative for the oxidation of cyanided compounds. The potassium permanganate is a strong oxidant, which is normally delivered in a solid state, being so a safe reactive and easy to deal with one. The scarce information that there is so far about kinetic and the ways the cyanide oxidation reactions work with the permanganate have reduced its uses.

The main advantages that it shows are: a quick and complete decomposition of cyanides, cyanatos and tiocyanatos, a safe and easy transport and use of the reactive; also, that it doesn't give out toxic waste, its costs are low and it is easy to handle.

In the following pages we are going to develop a work based on the experiments carried out with this oxidant in a laboratory, which was used as a pilot plant. We worked with wastewater coming from the gold mine that Río Narcea Gold Mines has in Belmonte - Asturias (Spain).

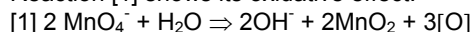
### Experimental Part and Discussion of Results.

The samples studied in this work have been directly taken from waste water coming from the gold treatment plant. Due to the high presence of copper in the ore, most of the cyanide used in the plant is lost in the formation of copper compounds, which are useless later. But, this is necessary to enable the formation of gold cyanided compounds and achieve the recovering of the metal.

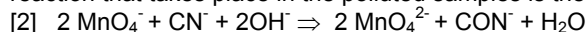
The analyses carried out on the samples through atomic adsorption and colour measurement showed that the most important pollution comes from the presence of copper in a cyanide compound form.

### Description of the Process

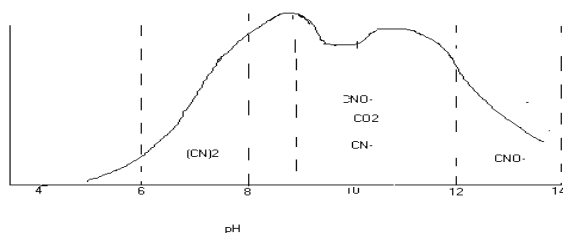
For the tests, Potassium Permanganate at 5% was used. It is a strong oxidant which is usually delivered in a solid state and which has a solubility of 5 gr/l at 20°C for a contact time of 15 minutes; and 30 gr/l at 20°C for a contact time of 1 hour. Besides, it has the advantage that it can be used in a watery solution within a wide pH interval. The oxidation of permanganate can be carried out in alkaline conditions, neuter conditions or acid ones. Reaction [1] shows its oxidative effect.



The tests carried out in the laboratory were made varying the concentration of the reactive. The reduction reaction that takes place in the polluted samples is the following:



As happens in the rest of oxidative reactions in which the permanganate takes part, the degree of oxidation of the cyanide strongly depends on the pH, thus, different by-products are obtained depending on the pH at which the reaction happens.



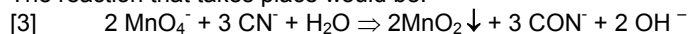
As we can see in the graph, the percentage of reaction between the permanganate and the cyanide is despicable at pH values lower than 6, suggesting that the neuter molecule HCN is resistant to oxidation. The reduction percentage of the permanganate is measurable in the interval of values situated between 6 and 14 with two maximum values for 9 and 12.

It is well known that in every chemical reaction significant variations in any parameter that intervenes in the process implies changes in its estequiometría as in the products obtained. In the case of oxidation with permanganate, the pH comes out to be an important parameter for the reaction products. This way:

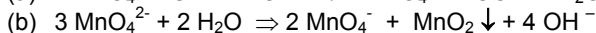
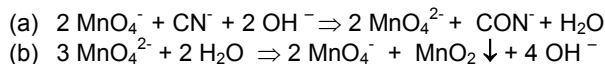
pH < 6	there is no oxidation
pH 6 – 9	oxidation to (CN) <sub>2</sub>
pH 9 – 12	oxidation to CO <sub>2</sub> , CN <sup>-</sup> , CON <sup>-</sup>
pH 12 – 14	oxidation to CON <sup>-</sup>

So, the interval of values between which it would be necessary to carry out the process to be able to work in safe conditions is placed between pH 12 and pH 14. In this range of values the oxidation of CN<sup>-</sup> with the potassium permanganate brings about the formation of the cyanate ion (CON<sup>-</sup>), which is less toxic than the initial cyanides.

The reaction that takes place would be:



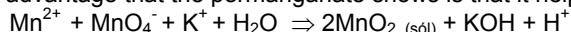
In fact, this equation is the result of two consecutive chain reactions and, so, their estequiometría derives from the addition of both:



To reach the values of pH at which one should work a lime whitewash was used. The use of this lime does not mean a problem, but, it even facilitates the later decanting of the copper hydroxide formed having the Ca<sup>2+</sup> ions an important function, helping in the degree of molecular disgregation of the intermediate permanganate.

Anyway, the consumption of lime comes out to be an important parameter in the process studied because big quantities of reactive are needed to achieve the high levels of alkalinity required; but, at the same time, the lime, when used in excess, forces the appearance of some precipitation problems of the copper hydroxide because we move in the Pourbaix precipitation diagram getting out of its precipitation range.

Another advantage that the permanganate shows is that it helps to precipitate Fe<sup>2+</sup> and Mn<sup>2+</sup> apart from Cu<sup>++</sup>.



### Tests in the laboratory

Below are included the results of the tests carried out. Table 1 presents the results of tests carried out with water with an initial concentration of 15 ppm of CN. The stirring speed for the tests is shown and lime is used to rise the pH to 12. The time taken by the test is 20 minutes.

Table 1: Treatment of water with 15 ppm of initial cyanide

KMnO <sub>4</sub> mg/l	Tiempo Minutos	pH inicial	pH final	CN Cabeza	CN salida	% CN detox	Ratio KMnO <sub>4</sub> /CN K/CN
15	20	8.5	12	15	11.4	24	1
30	20	8.5	12	15	5.8	61.33	2
45	20	8.5	12	15	4.87	67.55	3
60	20	8.5	12	15	1.71	88.60	4
75	20	8.5	12	15	0.85	94.33	5
90	20	8.5	12	15	0.86	94.27	6
105	20	8.5	12	15	0.68	95.45	7

In table 2, the data from the processing of the water from the tank of CIL taken from the treatment plant are included. This water, as it may be seen in the table, has high contents of copper and cyanate.

Table 2: Treatment of the water from the tank CIL

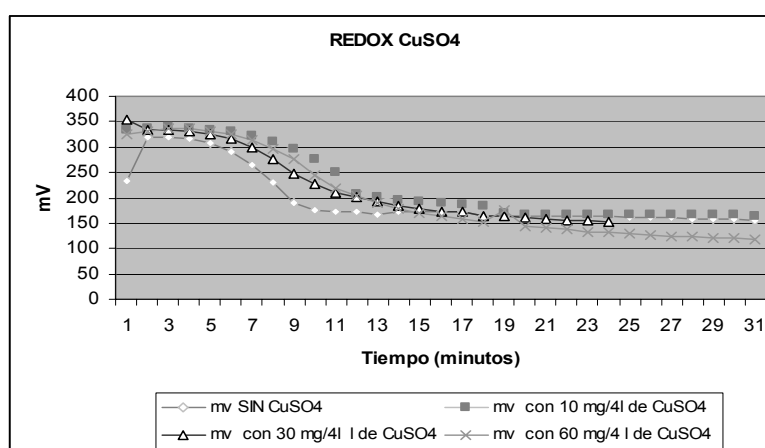
KMnO <sub>4</sub> mg/l	Tiempo Minutos	pH final	CN Cab	CN sal	% CN detox	Cu Cab	Cu sal	% Cu detox	Ratio KMnO <sub>4</sub> /CN
312	20	12	312	90.75	70.91	160	98.5	38.43	1
624	20	12	312	30.25	90.30	160	35.5	77.81	2
936	20	12	312	4.27	98.63	160	0.1	99.93	3
1248	20	12	312	2.3	99.26	160	4.8	97	4
1560	20	12	312	4.078	98.69	160	0.1	99.93	5
1872	20	12	312	4.452	98.57	160	0.1	99.93	6

### Tests with catalyst

One of the worries that the method of destruction of cyanide and copper with potassium permanganate presents is the time of reaction because, in a process in continuum this is an economic parameter of great importance.

In the previous studies carried out and in the bibliographic references, it is shown that copper comes out to be an excellent catalyst for the reaction of destruction, helping, besides, to the flocculation and later decanting of the deposit formed.

In the samples analyzed there is already copper in solution but tests were made using different quantities of copper sulphate to test its influence over the speed of reaction when acting as a catalyst. Four tests were carried out in parallel using samples of 4 litres with 10, 30, 60 mg of copper sulphate and without a catalyst, measuring in each minute the Redox potential that the process showed.



In Table 3 we can see the results of the tests carried out .

**Table 3: Analysis of mine water treated with copper sulphat as catalyst**

KMnO <sub>4</sub> mg/l	Tiempo Minutos	CuSO <sub>4</sub> mg	pH final	CN Cab	CN sal	% CN detox
152	15	62.5	12.4	26	0.088	<b>99.66</b>
152	30	62.5	12.4	26	0.071	<b>99.73</b>
152	60	62.5	12.4	26	0.07	<b>99.73</b>
176	15	1000	12.4	44.9	3.12	<b>93.05</b>
176	45	1000	12.4	44.9	2.59	<b>94.23</b>
176	60	1000	12.4	44.9	3	<b>93.32</b>
176	15	100	12.4	44.9	2.6	<b>94.21</b>
176	30	100	12.4	44.9	1.98	<b>95.59</b>
176	45	100	12.4	44.9	1.96	<b>95.63</b>
176	60	100	12.4	44.9	1.71	<b>96.19</b>

**Tests in pilot plant.**

Below are the results of the tests carried out in the pilot plant. The installation was built in the plant that Río Narcea Gold mines has in Belmonte. The plant consists of a tank of 5 m<sup>3</sup> of capacity with an inside stirring rod made of two blades placed at different levels. The tank's feeding is through an upper hopper wagon that unloads in the middle of the tank. Finally, the tank has a brim in the upper part through which the water, once treated, overflows and from where the samples are taken for their analysis.

Inside the tank, a pH-measurer has been placed, which, thanks to a pLC, enables the control of the dosage of the lime whitewash to be able to keep the pH in the required alkaline levels.

The potassium permanganate has been delivered in a solid state in 25 Kg tanks by the Company Carus Nalón dissolving in mixtures at 2,5% that allows its use without having the problem of a possible crystallization of the reactive. Stuck to the permanganate tank a dosaging bomb, with Teflon membranes was placed, which allows the dosage of the permanganate into the mixing tank.

In the Table 4 the results obtained are included.

**Table 4:**

KMnO <sub>4</sub> mg/l	Tiempo Min	Agit r.p.m.	QAP m <sup>3</sup> /h	pH final	CN Cab	CN sal	% CN detox	Cu Cab	Cu sal	% Cu detox	Ratio KMnO <sub>4</sub> /CN
222.42	12:15	1500	8	12	40.4			60			5.50
222.42	13:0	1500	8	12	38.39	4.06	<b>89.41</b>	63.8	3	<b>95.30</b>	5.79
222.42	15:30	1500	8	12	37.72	3.16	<b>91.61</b>	60.7	2.30	<b>96.21</b>	5.90
222.42	17:00	1500	8	12	38.18	2.25	<b>94.11</b>	60.2	2.60	<b>95.68</b>	5.83
222.42	18:00	1500	8	12	35.66	2.21	<b>93.80</b>	59.3	1.90	<b>96.80</b>	6.24

The results of the following table were obtained with the same conditions than the previous ones and the use of pressurized air to improve the mixture. The air pipe was adapted to a valve placed in the lower part of the mixing tank.

**Table 5:**

KMnO <sub>4</sub> mg/l	Tiempo Min	Agit r.p.m.	QAP m <sup>3</sup> /h	pH final	CN Cab	CN sal	% CN detox	Cu Cab	Cu sal	% Cu detox	Ratio KMnO <sub>4</sub> /CN
192.50	13:00	1500	8	12	35.00			63.90			
192.50	13:15	1500	8	12	33.47	2.14	<b>93.61</b>	63.90	0.80	<b>98.75</b>	51.12
192.50	16:55	1500	8	12	32.55	2.06	<b>93.66</b>	65.20	1.10	<b>98.31</b>	52.16
192.50	17:15	1500	8	12	34.41	2.52	<b>92.68</b>	62.80	1.00	<b>98.41</b>	50.24
192.50	17:30	1500	8	12	32.37	1.84	<b>94.32</b>	61.50	1.30	<b>97.89</b>	49.2
192.50	18:05	1500	8	12	32.37	2.04	<b>93.70</b>	62.70	1.30	<b>97.93</b>	50.16

**Discussion of the results and conclusions**

The experimentation part that includes the tests carried out in laboratory to eliminate the cyanided compounds from mine effluents with potassium permanganate as an oxidant agent allows us to establish some results and parameters which are key for a good functioning of the process and which were used for the later setting up of the pilot plant.

First, and as we can see in tables 1 and 2, the fact that stands out is that when the concentration of permanganate is increased, the percentage of detoxified cyanide also rises. The same for high concentrations as for small quantities of cyanide in solution, the data given come to corroborate the results found in the bibliographic references, which confirm that the best ratio of permanganate to cyanide is of 4,05 and the best ratio of permanganate to copper is of 0,8.

Thinking of a future stirring up of the process at an industrial scale, the time of permanence of the effluent inside the oxidation tanks is key for its economic viability. So, the possibility of using a catalyst in the reaction, as the case of the copper, appears as a necessary experimentation way.

In table 3, and through the study and observation of the Redox graph, the improvement of the process using the catalysts becomes quite evident.

Once the water had been treated, it was analysed to determine the possible presence of free cyanide and of residual manganese as unwanted by-products in the process that might be generated as oxidation residue. As the results of the analyses were negative, the method can be considered as harmless for the environment.

The experimentation phase in the pilot plant is necessary to validate a method as the one being explained in this work. The tests carried out after the pilot plant was functioning were made following the guidelines obtained in the laboratory and they fulfilled the expectations that wished. In the first results in continuum, as it can be seen in table 4, drastic destructions of the compounds to treat are obtained. In spite of the inconveniences that these type of tests involve due to the variables added to them. This is the case of the variation in the concentration of the compounds present throughout the whole process and which make it impossible to control strictly the dosage of permanganate.

Applying pressurized air as a help to the mixture, (table 5), allows a slight fall of the consumption of permanganate to obtain the same detoxification degree. In the same way, including an intermediate stirring rod allows better results thanks to the strong stirring that the mixture undergoes. So, the process in continuum shows great effectivity, though specific characteristics for each type of mine exploitation should be included.

Finally, it can be concluded that after the studies made, and due to the great simplicity and effectivity of the process, it comes out to be an ideal method for its use in continuum, as it does not present problems for using it, apart from the purely mechanic ones. Besides, with this method, high levels of destruction of the cyanide present in the water are achieved regardless its initial concentration, getting even to total destruction. Whatsoever, the copper present in the water can also be eliminated precipitating it as hydroxide, and thus, this way the water of the tailing pond can be used again as water of process even in extreme situations, this is as much for waters with low concentrations as for waters with high concentrations.

To conclude, we must emphasize that the technical developed is easy to fit in a productive process already working, being able to be put at the end of the production line, so that it does not interfere neither in the balance of the currents nor in the balance of the process.