Passive treatment for the removal of residual cyanide in drainage from closed gold mine tailing ponds

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Abstract

In the gold mining industry, tailings from the cyanide leaching process contain variable quantities of a number of cyanide compounds; as tailings are transferred to a pond for sedimentation and consolidation of the solid fraction, the supernatant water contains residual cyanide. A natural degradation of cyanide in tailings ponds is reported in the specialised bibliography, but in most cases, this is not sufficient to reduce the residual cyanide concentration to levels which would allow these waters to be directly discharged into the existing receiving water courses. In order to develop low cost and environmental friendly long-term methods for treating leachates from tailing ponds, wetland-based passive systems have been tested at the site of a gold mine in Spain. In this case study, most cyanide compounds are in the 'weak acid dissociable' (WAD) form and, almost all of them as copper-cyanide. In order to obtain relevant information concerning the performance, effectiveness and suitability of engineered wetland systems for the treatment of wastewaters containing cyanides (and metals), several experiments at laboratory and field scale were undertaken. At the laboratory scale, tests included static aerobic cells, anaerobic dynamic columns, oxidation cascades and a laboratory wetland. An average CNwad removal rate of 90.36% was found in the lab wetland, achieving residual CNwad concentrations below 2 mg/l. Removal rates of Cu and other metals reached values in the range of 90-99% (from 50 mg/l to 1 mg/l). Taking into consideration the experimental data, a pilot scale passive system, including aeration cascades and aerobic and anaerobic cells, has been constructed at the site of a local gold mine and it is currently being monitored.

1. Introduction

The chemistry of cyanide is complex and many forms of cyanide exist in mining solutions; free cyanide (HCN and CN^-), which form complexes with many metal species, principally the transition metals, which vary widely in stability and solubility:

$$M^{x+} + yCN^- \leftrightarrow M(CN)_y^{(y-x)-} \qquad (1.1)$$

These complexes may be grouped into two main categories, based on their stability: Weak Acid Dissociable Cyanides (CNwad) if $\text{Log } K \leq 30$ and Strong Acid Dissociable Cyanides (CNsad) if $\text{Log } K > 30$, where K represents K the equilibrium constant of reaction (1). These categories are widely used in the analysis of process solutions, since they help to describe the behaviour of the cyanide species present, while avoiding the need to provide detailed analytical information on every cyanide complex present and thus greatly simplifying analytical procedures (Mardsen and House, 1992).

The toxicity of cyanide in mine wastewaters is related to its form and concentration. Hydrogen cyanide (HCN) is considered to be the most dangerous form and it is a WAD form which, in solution, dissociates in a non-complete manner as follows:

$$HCN \leftrightarrow H^+ + CN^- \qquad (1.2)$$

The extent of this dissociation reaction at equilibrium is a function of pH. At pH 9.3, approximately half the total cyanide is present as HCN with the remaining part presenting itself as free cyanide ions. At pH 10.2 more than 90% of the Total Cyanide (TCN) is into the ionic (CN^-) form, while at pH 8.4, over 90% of the cyanide present takes the form of HCN. This is important because HCN has a relatively high vapour pressure (100 KPa) at 26ºC (Meehan, 2001) and consequently, under ambient conditions, it volatilizes readily from the liquid surface causing a loss of cyanide from the solution (thus most cyanide leaching systems are operated at pH values which minimize cyanide losses, ie. typically at pH>10).

2. Cyanide removal from mining solutions

In order to avoid environmental pollution by cyanide from the gold mining industry, different methods, based on physical, chemical and biological processes, have been traditionally used. Three basic types of technologies can be considered (Young, 1995):

A) *Control technologies*. These technologies attempt to prevent, or minimise, the formation of waste. In the context of gold mining, minimising the quantity of this waste form is difficult since this is a function of the process used and the quantity of material being mined and therefore processed.

B) *Pathway interrupt technologies*. These technologies attempt to contain or divert the cyanide-polluted waste following its generation but before its removal off site.

C) *Controlled release technologies*. These technologies are focussed on the treatment of the waste portion which could be released beyond the waste containment facility. Cyanide detoxification methods can be classified as follows (Mardsen and House, 1992): i) Cyanide removal by natural volatilization and/or adsorption onto minerals. ii) Cyanide oxidation to less toxic cyanate species by natural oxidation, biological oxidation and/or detoxification processes based on 'assisted oxidation' methods using hydrogen peroxide, sulphur dioxide, ozone, etc. iii) Complexation to less toxic Fe (II) cyanide, with the potential for removal as insoluble double salts.

Most remediation processes developed and used in the recent past to address cyanide-contaminated waste forms have been 'controlled release technologies'; some representative examples are the biological process developed by Homestake to destroy cyanide by oxidation; the hydrogen peroxide oxidation (Mudder et al, 1998) and the sulphur dioxide/air oxidation method.

Smith and Mudder (1991) reviewed a large number of laboratory and case studies carried out to determine the chemical pathways by which cyanide can be destroyed/transform. Results from these studies indicate that the most significant destruction/transformation pathways are likely to be the following: i) Off-gassing as HCN; ii) Hydrolysis (group of oxidative pathways, some mediated by bacteria that break the C≡N triple bond); iii) Sulphidation to thiocyanate (SCN^-); iv) Precipitation of insoluble cyanometallic compounds; v)Adsorption or co-precipitation on solid phases.

Using information from literature and other industrial and governmental sources, Wheathington (1988) and Young and Jordan (1995) noted that "*oxidation technologies were the only methods that destroyed free cyanides";* other technologies, a mix of physical, adsorption and complexation methods, produced a concentrated waste that required further treatment. The oxidative processes (that produce hydrocyanate and cyanate ions, formic acid and ammonium formate) are enhanced by the presence of ultraviolet light (which causes photochemical breakdown) and catalysts such as titanium dioxide and zinc oxide.

Cyanide is also degraded by microorganisms (many species, as *Bacillus pumilis* –Meehan, 2001- have been shown to tolerate high concentrations of cyanide), as it is a source of nitrogen and carbon which are required for sustenance.

3. Passive systems for cyanide abatement

Cyanide and cyanide-metal complexes can be removed from effluents by naturally occurring processes while the effluents are held in ponds (Scott, 1989), reducing the toxicity of cyanide processes over time. A natural degradation of cyanide in tailing ponds has been observed at Canadian gold mines for many years (Sobolewski, 1990). The most important mechanisms involved in the *natural degradation* process are the following (Mardsen and House, 1992):

-Volatilization: because of the low boiling point of the hydrogen cyanide (24ºC in aqueous solution), it volatilizes at the solution-air interface and diffuses into the atmosphere, following Henry´s Law of aqueous-gaseous phase equilibrium for a dissolved gas.

-Atmospheric oxidation: dissolved oxygen present in process solutions oxidizes cyanide to cyanate in the presence of activated carbon.

-Adsorption by other minerals: many minerals are known to attenuate cyanide compounds, being the best adsorption rates reached by carbonaceous materials (up to 0.5 mg/g).

-Other natural mechanisms: in a lesser extent, biological oxidation, hydrolysis reactions and photodegradation account for varying degrees of cyanide degradation, depending on specific conditions.

Passive treatment, according to the definition adopted by the European Union's PIRAMID (Passive In situ Remediation of Acidic Mine/Industry Drainage) R&D project (www.piramid.org) is "*the deliberate improvement of water quality using only naturally-available energy sources (e.g. gravity, microbial metabolic energy, photosynthesis,...) in systems which require only infrequent maintenance in order to operate effectively over the entire system design life*" (Younger et al., 2002).

On this basis, there has been renewed interest recently in the use of engineered wetland systems for the treatment of different mine waters and effluents. Although natural wetlands have been used as convenient wastewater discharge sites for long time, is recently, when monitoring was initiated at some of the existing discharges, and an awareness of the water quality purification was demonstrated, when potential of wetlands as treatment system began to emerge. Constructed wetlands, because of their ecosystem characteristics that are similar to natural wetlands, are generally accepted as an ecotechnology for treatment of various types of wastewaters. Wetland ecosystems characteristics are attributed to a combination of factors, such as high plant productivity, large adsorptive surfaces on sediments and plants, an aerobic-anaerobic interface, and an active microbial population (Urbanic-Bercic, 1994). Since these properties result in high rates of biological activity, they provide an opportunity to transform many pollutants to less harmful products or essential nutrients that can be used by the biota. But the problem of mine water treatment by means of engineered wetland systems is compounded when cyanidation wastewaters are considered, since the contaminant is not longer in the free and most readily treatable form.

There is virtually no data concerning the removal efficiencies of cyanide (and metals) from cyanidation wastewaters in wetlands, in spite of there have been several reports documenting microbial degradation of free cyanide in industrial wastewaters (Gormely et al., 1990). Climate is a major determinant in the success of this ecotechnology, because thermal conditions affect almost all removal processes, influencing then all stages of the planning, design, construction, and maintenance of constructed wetlands (Maehlum, 1999).

4. Experimental work

Laboratory and field-scale experimental work, focussed on the application and suitability of engineered passive systems for the treatment of mine wastewater containing cyanide and metals, has been undertaken. This experimental work was mainly directed towards the removal of cyanide complexes from mining solutions while trying to reproduce natural physical, chemical and biological processes occurring in natural wetlands.

4.1. Laboratory scale

For the purpose of this study, aerobic and anaerobic cells, and an aerobic/anaerobic wetland have been tested. The results obtained from laboratory studies allowed us to define the loading characteristics of passive systems for the treatment of cyanide-rich mine effluents. Monitoring was carried out through the analysis of water (for CNwad the picric-acid method was used), substrate and plant tissues samples.

Experience 1: Aerobic cells. Two independent 60 litres (0.6 m x 0.25 m x 0.4 m) cells have been used for aerobic experiments. Cell 1 was filled with a 5 cm deep limestone bed and a 10 cm deep compost bed, from bottom to top. Cell 2 was filled with a 3 cm deep limestone bed, a 18 cm deep compost bed, and a 3 cm grained iron oxide particles bed, from bottom to top. Both cells, placed in an opened air area, were watered at the beginning of the experiments with water from the tailings pond of an active gold mine. Measurements of pH, Redox Potential (ORP), Electrical Conductivity, and Dissolved Oxygen were taken daily over a period of two months and representative samples of water were collected weekly for analysis.

Throughout this experiment, pH in both cells gradually decreased from around 9.4 to 8.5. As a result of this, some cyanide ions are supposed to be converted into HCN and were partially removed by volatilization. Measured Eh in static cell 2 was higher than in static cell 1. No distinct pattern was observed in the two readings. Redox potential reached its minimum values (negative ones) in static cell 2 which guarantees the presence of reducing conditions inside that system due to the presence of Fe. In static cell 1, redox potential measurements were almost constant. The CNwad were reduced in both systems, although such reduction was more significant in static cell 1 whereas in static cell 2 the grained iron particles would sustain the complex cyanides.

Experience 2: Oxidation cascade. A unit (located in an opened air area) composed by four cells, each one placed at different height, was used as an oxidation cascade. The continuous water flow from each cell into the following one and the formation of cascades promote high oxidation conditions. Water samples were collected every two days for analysis. The experience took placed over a two months period.

After circulating through the four oxidation-promoting cells, water suffered a slight decrease in pH. At pH 8.5-9 most free cyanide was in the HCN form and cyanide reduction was mainly due to oxidation and volatilization. Electrical Conductivity reached average values of 8-10 mS/cm, according to a decreasing trend. Redox potential confirmed that the oxidizing conditions were being achieved throughout the experiment.

If degradation due to volatilization and oxidation, the major abiotic pathways, occurred it is reasonable to propose that a decline in concentrations would have occurred from the initiation of the experiments since these transformation pathways are often thermodynamically driven. The average reduction found in CNwad was 40%.

Experience 3: Anaerobic columns. Two 42 litres (1.2 m high and 0.21 m diameter) columns operating in a continuous flow-through mode have been used as anaerobic cells (or bioreactors). Column 1 was filled with a 20 cm thick layer of limestone and a 100 cm layer of compost, from bottom to top. Column 2 had the same content as the first one with an addition of grained iron particles mixed with the compost substrate.

Water from the cyanidation process of a local gold mine was made to circulate through the columns at a constant rate of 2.3 ml/min over 60 days. Daily measurements of pH, Eh and conductivity were made and every two days a sample of water collected for analysis.

These cells can be considered anaerobic systems (only the top of the columns is in contact with the atmosphere). A general increase in pH was measured during this experiment when comparing influent and effluent values. With regard to Eh, the behaviour is similar in both columns although slightly lower in column 2. The reduction of WAD´S and Cu is very important in both columns. CNwad removal is very important in both columns (60-70%) being slightly higher in column nº 2 (as high alkaline conditions are maintained, a dissociation effect can occur concerning WAD molecules, which may break down to form CN^- and the metallic positive ions). As reactive Fe is present in column 2, the liberated CN^- would precipitate as insoluble Fe salts. Cu removal rates are also more important in the column 2, probably due to the formation of complexes (Cu-Fe oxy-hydroxides) that would be absorbed in the compost.

Experience 4: Aerobic/anaerobic wetland. A 375 litres (1.5 m x 0.5 m x 0.5 m) galvanized steel container was used for this experimental work as support for the wetland simulation. The container was divided in 15 sections in which water was made to follow a circuitous path (7 m). The bottom of the wetland was filled with a thin layer of limestone with the remaining part being filled with an organic substrate (compost with a 45% of porosity) up to 30 cm (the calculated residence time of the water in the system was 7 days). Finally, *Typha Latifolia* plants collected in a natural donor site were planted on the organic substrate. A continuous flow of cyanide-rich water was maintained at a constant rate of 10 ml/min during the duration of the experiment (60 days).The systems were monitored by sampling the water weekly, before and after its entrance into the different treatment system units. pH, Redox potential and Electrical Conductivity were measured daily.

After having passed through the system, water pH decreased 1-1.5 units (from 8.7 to 7.5 units) (consequently affecting the HCN/CN^- balance, increasing HCN volatilization and promoting the cyanate formation). Electrical Conductivity decreased also, from 10 mS/cm to 6.5 mS/cm, without showing a constant trend. Best removal rates for CNwad (90%) were achieved through this experience.

The main mechanisms involved in CNwad removal are supposed to be complexation to solid phases (insoluble salts) and photodegradation. Cu was also successfully removed (98%). Plant tissues analyses (before and after the experiment) revealed high metal absorption capacity by *Thypa Latifolia*: mercury (which concentration increased 12 times) is mainly retained in the flower, whereas iron (4 times), copper (32 times) and lead (2 times) concentrate preferably in the root zone.

4.2. Pilot scale passive system at the mine site

Taking into consideration results from this experimental work, an *in situ* pilot scale system has been constructed at the gold mine site to treat water with residual contents of Cyanides and Cu through a passive system which is based in processes that naturally promote the removal of Cyanides from mining waters.

The system (fig.1) consists on four cells of 12 m x 1 m x 4 m designed as two parallel circuits . The first line (cells 1 and 2) constitutes the passive treatment itself while the second line (cells 3 and 4) is only intended as a reference and represents our 'control system'. Cells 1 and 2 have been designed taken into account previously described results from laboratory work.

Water flows into the system by means of a 30 m. long oxidation/aeration cascade (pre-treatment system). According to results obtained through experience 2, the CNwad concentration should be reduced and, by increasing the water/air interface, significant effects on the volatilisation rate of free cyanide are expected. Results show a decrease in TCN after pre-treatment of approximately 30% (from 312 mg/L to 220 mg/L). A significant part of the CNwad is converted into the free form. The Cyanide degradation is reached by HCN volatilization, oxidation pathways (ORP ~ +400 mV) and precipitation of Cyanide complexes (green crusts appeared on the bottom of the cascade blocks).

Cell 1 works under anaerobic conditions in order to promote Cyanide degradation below these conditions and by the interaction of microorganisms, Cyanide complex precipitation and adsorption, biological degradation and hydrolysis of HCN to formic acid and ammonium formate. The filling material is represented by a 40 cm deep layer of a mixture of cow manure and siliceous gravel. The cyanide degradation/attenuation mechanisms listed above are affected by the following parameters: the metal and oxygen content of the water, the water pH and the soil mineral content including clay, feldspar, organic carbon, free metals and (or) metal oxides. Although laboratory experiences have shown a reduction of 39% of CNwad in the water with an analogous treatment, no significant reduction of TCN was observed (the anaerobic treatment is thought to promote metals removal). Metal precipitation was successfully achieved (86,8% for Cu with average values in the outflow of 5.28 mg/L). The discharge is by overflow of a shallow water sheet.

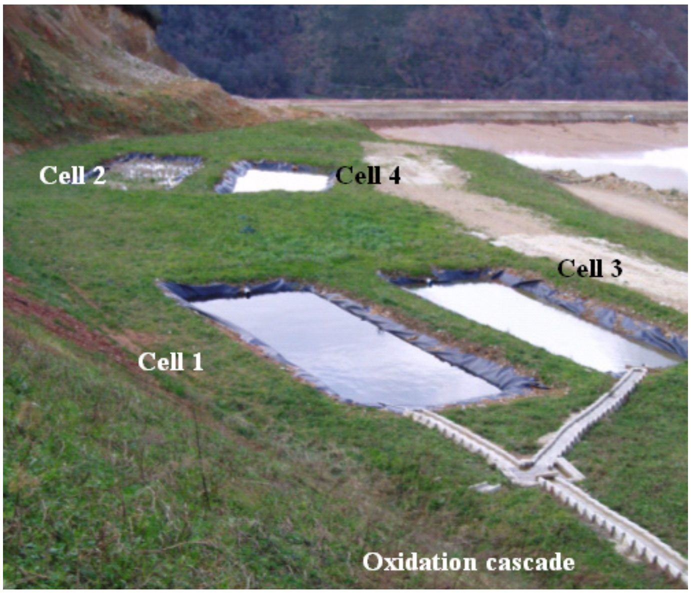

Fig. 1. View of the in-situ pilot-scale system.

Cell 2 works under aerobic (oxidising) conditions; it is formed by a layer of 50 cm. of compost (top soil), plants (about 225 units- 5 unit/m2 of *Typha latifolia*-) and a 10 cm deep water sheet. Main processes expected to take place in this cell are volatilisation of HCN, oxidation to cyanate and biological and photolytic degradation (revealed in experience 4 as a very important mechanism for CNwad dissociation). Surface effects (promoted by the relatively large surface area and the shallow depth) have been shown to contribute to a large proportion of the Cyanide losses in tailings systems. Average CNwad concentration in the influent is 38 mg/L, while the same parameter in the overflow from Cell 2 is below 10 mg/L.

The system design incorporates a final post-treatment phase, ie., a 12 meters aeration/oxidation cascade whose objective is to further encourage the volatilisation and photodegradation of HCN. The final treated effluent is collected into a receiving pond before being re-circulated to the mine tailings management facility.

Cell 3 and cell 4 constitute a ‘control system’ which will allow us to evaluate the real efficiency of the proposed passive treatment (anoxic and the aerobic cells). The control system consists of two cells containing inert material (siliceous gravel). The thickness of this layer was calculated so that the residence time of the water is the same in both systems ie., the treatment system and the control one. The comparison of the concentrations obtained for the blank line and the aforementioned results show that most of the CN reduction is achieved through the water aeration, more than the circulation through compost-based systems, which, on the other hand, are efficient for metal removal.

Sampling point	Free cyanide (mg/l)	WAD cyanide (mg/l)
Influent	275	37
After cascade 1	200	20
After Cell 1	190	18
After Cell 2	186	5
After cascade 2	165	2

Fig. 2. Average free and WAD cyanide concentrations in the effluent of the different phases of the in-situ system.

5. Conclusions

At the light of the experimental data obtained from laboratory and pilot scale work, it can be concluded that the use of passive treatment systems for the abatement of Cyanides and related compounds from mine effluents is possible.

When applied to treat leachates from tailing ponds, engineered wetlands may offer the following advantages:

-A relative inexpensive and environmental-friendly method.

-Significant reductions in Free and WAD cyanides concentrations.

-Absence of new toxic by-products formation.

-Reductions in the concentrations of other residual metals present in the waste water were also observed.

-Depending on the characteristics and specific cyanide contents of the waste waters the system could be viable as a primary treatment (combined with active methods) to meet environmental legal requirements for discharge into public water courses.

-The design of passive treatment systems should take advantage of natural features to reduce treatment costs.

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