State of the art of passive treatment technologies for the abatement of cyanides from the mining industry: Experiences in Asturias (Spain)

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ABSTRACT

Gold extraction operations generate a variety of waste products, which must be responsibly disposed of, in compliance with environmental regulations. During the last decades, increased emphasis has been placed on effluent control and treatment, being most immediate concern the threat to the environment presented by toxic constituents, such as certain cyanide species.

Almost all the modern technologies developed for cyanide detoxification from solution require further treatment in order to reach cyanide statutory limits for direct discharge. Taking this into account, and considering also that natural degradation processes reduce the toxicity of cyanide over time, a passive system can be considered as a viable technology for cyanide removal from mining effluents. A pilot scale passive system has been constructed and monitored during several months in a gold mine of North-Western Spain (Asturias). The results from this experience suggest that these technologies are able to detoxify cyanidation effluents in about 25% for dissolved cyanide and more than 90% for common metals, nitrite and nitrate.

INTRODUCTION

Due to intensive exploration and production along the centuries, gold mining operations have derived in the exploitation of low-graded mineralized areas. In addition to the low gold contents, it is also important to consider the fact that the great majority of the gold appears in the form of "refractory gold", being then the cyanide leaching ("cyanidation") the most suitable recovery process and the only one that avoids poor extraction rates. This is a hydrometallurgical process in which NaCN and CaO are used as primary reactives, forming a solution which is capable of dissolving the gold present as "refractory" (generally, in the crystalline structure of sulphides). Chemically, the process consists of the extraction of the gold from the grinded ore following Elsner´s equation:

$$4 \, NaCN + 2 \, Au + \tfrac{1}{2} O_2 + H_2O \Leftrightarrow 2 \, Na[Au(CN)_2] + 2 \, NaOH)$$

and the subsequent recovery of gold using activated carbon (CIP and CIL processes) or zinc oxide (Merill-Crowe process). After the leaching tanks, the residual slurry is driven to a "detoxification" process (generally, oxidation methods), before being stored in a tailings disposal facility. At this stage, standard solutions are still toxic due to the presence of cyanide compounds and other contaminants (metals, sulphate, ammonium, nitrate, etc).

In parallel with the resurgence of the gold mining industry (1972-1990), and the associated technological progress, an increasing environmental awareness and a major movement towards the control of factors affecting the environment worldwide (particularly, in the USA and Canada; Rubo & Gos, 2002) has occurred. As a result, increased emphasis has been placed on effluent control and treatment (Logsdon *et al.*, 1999; Smith & Mudder, 1999).

Due to the nature of the described hydrometallurgical extraction processes, the most problematic wastes, from an environmental viewpoint, are the liquid effluents (slurries/solutions). The immediate concern is usually the threat to the environment posed by toxic constituents of the liquid phase, such as various cyanide species.

On the other hand, the technologies referred as "passive treatment systems" have been successfully applied for the treatment of mine water, as well as some industrial effluents and storm and urban wastewaters during the last two decades in different parts of the world. In order to develop low-cost and environmental friendly long-term methods for treating leachates from tailing disposal facilities, wetland-based passive systems have been tested at a gold mine site in Spain. The aim of the study was to obtain relevant information concerning the performance, effectiveness and suitability of engineered wetland systems for the treatment of the liquid fraction of the waste generated in cyanidation operations. Taking into account the experimental data obtained through several experiments at laboratory scale, a pilot scale passive system was constructed and monitored at a local gold mine site. This research was supported by the PIRAMID Project (UE-00-EVK1-CT-9900021, European Commission, Fifth framework Programme)

CYANIDE CHEMISTRY

As it has been already stated, cyanide solutions are worldwide extensively applied for gold recovery, as they act as a very strong "bonding" agent, capable of complexing with virtually any heavy metal at low concentrations (Marsden & House, 1993; Smith & Mudder, 1991).

Generally, the different chemical species that attach the cyanide ion in their chemical composition can be categorized into the following categories:

- Cyanide ion: this term refers exclusively the CN^- ion.

▪ Hydrogen cyanide**:** HCN, as a neutral molecule. In analytical procedures, the cyanide ion and the hydrogen cyanide are included in a category known as "free cyanide". In aqueous solution the following chemical balance is established, where the stable compound depends almost exclusively on the pH of the solution (pH values above 9) :

$$CN^- + H_2O \Leftrightarrow HCN + OH^-$$

Free cyanide forms can react with different metals forming metal-cyanide complexes, following the next expression (Sharpe, 1976; Jay, 2000):

$$M^{x+} + y\ CN^- \Leftrightarrow M(CN)_y^{(y-x)-}$$
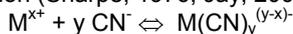
Depending on the relative stability of these complexes (K, stability constant for the described chemical equilibrium), are grouped in one of the following categories (Mudder, 1999):

▪ Weak Acid Dissociable (WAD) cyanide: if Log K ≤ 30. This group includes mainly copper, zinc and cadmium cyanides.

▪ Strong Acid Dissociable (SAD) cyanide: if Log K > 30, being the most representative species cyanides of gold, iron and cobalt.

▪ Total cyanide (TCN): include all cyanide species present in the sample (dissolved or undissolved).

▪ Cyanide related compounds: basically, these are non-toxic forms derived from cyanide degradation: thiocyanate (SCN^-), cyanate (CNO^-), nitrate (NO_3^{2-}), nitrite (NO_2^-) and ammonia (NH_3) (Sharer et al., 1999).

GOLD PRODUCTION PRINCIPLES. TYPES OF WASTES

Leaching
The grinded ore (mixed with CaO and sometimes having been pre-oxidized) is generally driven to a series of leaching tanks, were a poor solution of cyanide is added, and oxygen (air) is injected tanks to promote the slight oxidative conditions that the hydrometallurgical process needs. The most common reagent is sodium cyanide, although in some cases potassium or calcium cyanides are also employed. The residence time of the pulp in the leaching circuit should be enough to safeguard the complete dissolution of gold (and silver), following Elsner´s equation. Simultaneously, activated carbon is added in the leaching circuit (counter-current flow). Subsequently, the "discharged" solution is driven to a series of tanks, where the residual content of cyanide compounds (and other toxic chemical forms) is partially removed, in most cases by means of oxidation methods; this process is known as "detoxification". The final step of gold recovery (by the "leaching in tanks" process) is the storage of the partially detoxified solution in the tailings disposal facility of the metallurgical plant. Because about 50-100 mg/l of TCN remains (as a typical average concentration; Smith, 1994) in the stored solution, this waste is reciculated to the leaching process, optimizing both the economy of the process and the toxic waste generation (Venter et al., 2004; Marsden & House, 1993).

TREATMENT METHODS FOR CYANIDE REMOVAL
The detoxification processes are employed to remove toxic chemicals compounds. When dealing with liquid wastes from cyanidation operations, there are three different ways in which the detoxification can be carried out (Young et al., 1995b; Young & Jordan, 2000): i) Dilution; ii) Removal of toxic forms from solution and iii) Conversion of toxic forms into non-toxic forms.

Taking into account the toxicity of free cyanide, in most cases, the dilution is not allowed, and the removal of toxic forms from solution is economically prohibitive (mainly several physical, adsorption and complexation methods; Botz, 2001). Therefore, the technologies that are currently employed to detoxify cyanidation solutions are based on the conversion of toxic forms into non toxic forms (free cyanide is typically converted into cyanate) by means of different oxidation methods. Common industrial applications are listed below (Young & Jordan, 2000; Smith & Mudder, 1991):

▪ Natural degradation (oxidation may occur naturally)
▪ The hydrogen peroxide process
▪ The sulphur dioxide process
▪ Alkaline clhorination.
▪ Ozonation

Currently, the investigation of cyanide detoxification is based on the study of new oxidizers ($KMnO_4$), the biological assisted oxidations (*Pseudomonas Pseudoalcaligenes*) and the adsoption on a great variety of solids phases. Generally, the product of cyanide (CN^- and HCN forms) degradation is the cyanate ion (CNO^-), which is considered to be 10.000 times less toxical than free cyanide forms (Meehan, 2001). When the oxidant agent is the hypoclorite ion, the product of the oxidation is the chlorocyanogen.

Although natural degradation processes are effective in cyanide treatment, its kinetics are not often as fast as it is required for industrial purposes, being intensive the use of oxidation technologies (Smith & Mudder, 1991; Huiatt et al., 1983; Johnson et al., 1998).

PASSIVE TREATMENT SYSTEMS. GENERAL PRINCIPLES AND APPLICABILITY
The denomination of these technologies was born from the necessary distinction between them and the only systems that were available until 1980s to treat mine waters, known as "active systems".

During the last twenty years, the potential applicability of natural processes to the treatment of polluted water (storm, urban, industrial effluents,…) has led to the development of a new technology, known as "passive treatment", which has also been extensively and successfully applied to mine water. Passive treatment systems,

following the definition suggested by Younger *et al*. (2002) 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; PIRAMID Consortium, 2003).

A complete description of the different types of passive systems, their applicability and behaviour when applied to different contaminants can be consulted in Younger *et al*., 2002 and Watzlaf *et al*., 2004.

For the purposes of the present work, taking into account the physico-chemicals parameters of the tested residual effluent, different types of passive systems have been tested at laboratory scale (Álvarez *et al*., 2004, see also in this paper) and finally, a pilot-scale system (which included anaerobic and aerobic units) was constructed at a local gold mine site.

APPLICABILITY OF PASSIVE SYSTEMS TO THE DETOXIFICATION OF CYANIDE COMPOUNDS. PREVIOUS STUDIES.

It is well known nowadays that some natural degradation processes reduce cyanide toxicity with time (Mudder *et al*., 1999; Smith & Mudder, 1991; Botz & Mudder, 2000). The principal mechanisms responsible for this transformation, which consists mainly in the oxidation to cyanate of the free cyanide forms, are: volatilisation of hydrogen cyanide from solution, biological oxidation, hydrolysis, biodegradation, adsorption of toxic forms onto mineral surfaces and precipitation of insoluble salts from solution.

Currently, there is almost no information concerning the behaviour and suitability of passive systems to detoxify cyanide-rich solutions, with the exception of the following semi-passive systems:

-Star Lake and Jolu mines, Sasakatchewan district, (Canada).

Designed to treat residual solutions containing between 100 y 200 mg/l of Total Cyanide (TCN), using a natural wetland and two steps of treatment, TCN contents of 0,01 mg/l were obtained in the effluent. From this experience, a design criteria for wetlands surfaces, when treating cyanide rich solutions was suggested (Sobolewski, 1990): *"CN- loadings below 1 g/m^2·day are required in order to maintain cyanide content in the effluent below direct discharge values (Canada: 0.2 mg/L)"*.

-Homestake district, Dakota (USA)

Dr. Mudder (Mudder & Whitlock, 1983; Smith & Mudder, 1991; Waterman & Lien, 1996; Mudder *et al*., 1998) designed a bacteriological oxidation process to detoxify cyanide solutions. As non-natural energy sources were used to promote the bacterial activity, it cannot be strictly considered as a passive system.

-Nickel Plate Mine, Dakota (USA)

In this case, the process was similar to the above, but with the exception of the contaminant, as the cyanide present in the solution was in the form of thiocyanate. The bacteriological oxidation of thiocyanate produces ammonium and ammonia, which are later converted into nitrate in an aerobic circuit (Mudder *et al*., 1995).

-Colomac site, Yellowknife, (Canada)

Presenting average cyanide and thiocyanate contents of 12 mg/l and 228 mg/l respectively, the supernatant solution of the tailings ponds was treated by bacteriological oxidation, being this mechanism promoted by the addition of $NH_4H_2PO_4$ (Mono-Ammonium Phosphate) (Chapman *et al*., 2003)

-Bullfrog mine, Amargosa Desert, Nevada, (USA)

After the closure of the mining works, the stored solution of the cyanidation proccess (1,5 Mm^3) was evaporated by means of passive and forced evaporation (Kump, 2004).

LABORATORY EXPERIENCES.

With the aim of designing a pilot-scale system with certain guarantees of success, different types of passive systems were tested at laboratory scale, combining aerobic and aerobic conditions and employing different flow rates and substrates. A detailed description of these systems and a Table 1, a summary of the effectiveness of each one of tested systems is presented. The results are expressed as percentage of removal of WAD cyanide achieved:

Table 1: Efficiency of WAD cyanide removal of different systems tested at laboratory scale

Experiment	Removal rate for WAD cyanide (%)
Aerobic Cells	**50-65**
Aeration cascade (simple)	**80**
Aeration cascade (recirculation)	**65-75**
Anaerobic Columns	**40-65**
Laboratory wetland	**90**

After analysing the behaviour of the different laboratory systems, a pilot-scale passive system was designed and constructed at a local gold mine site, very close to the tailings disposal facility of the cyanidation plant.

PILOT-SCALE PASSIVE SYSTEM FOR CYANIDE ABATEMENT

The tested system consisted of four elements: a 30 m long aeration-oxidation cascade as a pre-treatment, an anaerobic cell with cow manure mixed with siliceous gravel acting as substrate, an aerobic cell with aucthoctonous soil, also mixed with siliceous gravel, and a 12 m long aeration-oxidation cascade as post-treatment unit. In the aerobic cell surface, 160 *Thypa latifolia* units were planted. In parallel with the anaerobic and aerobic cells of the "treatment line", a "blank line" was also constructed. This included other two cells identical to

the first ones in size (12 m x 4 m) and filled with siliceous gravel (considered inert material), up to a pre-defined height, ensuring that the retention time of the solution in each one of these cells would be the same as the corresponding to the anaerobic and aerobic ones.

Solution to be treated

The tested solution, as it was already mentioned, was the residual waste from the cyanidation proccess of an Asturian gold mine. Its physico-chemical properties are highly dependent on the compounds that are in solution and suspension alike (i. e., the parameters of the cyanidation process, as well as the mineralogy of the ore). Taking this into account, it is easily understandable that this effluent is far from being homogeneous in composition. The average characteristics of this solution are summarised in Table 2.

Table 2: Ranges of values of the main physico-chemical parameters measured in the tested solution

Parameter	Range of variability	Parameter	Range of variability
pH	8-9	SiO_2	5-10 mg/l
Eh	8-10 mS/cm	Ca/Mg	100-200 mg/l
Temperature	10-25 ºC	S	1000-1500 mg/l
ORP	400 mV	SO_4^{2-}	3500-4000 mg/l
Dossolved oxygen	4-6 mg/l	Na	1500-2000 mg/l
Turbidity	Up to 100 ntu	K	50-100 mg/l
Total Cyanide (TCN)	Up to 200 mg/l	Cu	20-40 mg/l
WAD Cyanide	10-100 mg/l	Se + Mo	Hasta 5 mg/l
Amonnium	400-500 mg/l	$NO_3^- + NO_3^{2-}$	20-30 mg/l

Flow rate

Taking as a design criteria the suggested by Sobolewski (1990) already cited, and considering that the available surface of treatment is that which results for both cells, aerobic and anaerobic (i. e., 48 + 48 = 96 m^2), the flow should be defined by the following expression:

Q (l/min) · C (mg TCN/l) < 66,7

Due to the nature of the solution, which contained a great amount of suspended solids, it was no possible to establish a practical flow rate below 4 l/min. After going throughout the first unit of treatment (aeration cascade) in about 30 seconds, the solution enters the parallel series of cells, being then the flow equally divided in the two lines (2 l/min to the treatment line and the same for the blank line). Being this so, if the TCN content is above 33,3 mg/l (which happens most of the time), the system would be working far above of the way it should, according to the mentioned design criteria.

The depth of the substrates was 50 cm for both cells, with respective porosities of 35% (anaerobic) and 33% (aerobic). Thus, the calculated residence time of the solution into the cells was 70 hours for the first one and 66 hours in the second case.

Monitoring

During the operating time of the described system (9 months), it was monitored weekly, following the guidelines for monitoring passive systems described in *PIRAMID Consortium, 2003*. Electrical conductivity (EC), pH, Eh, salinity, turbidity, Dissolved oxygen (DO_2) and temperature were measured in situ. The solution was sampled at the inlet and outlet of each unit and analysed always for cyanide and in some cases for sulphate, nitrite and nitrate, ammonium and ammonia, according to U.S.EPA methodologies.

At the end of the experiment, substrates, as well as plant tissues were also collected and analysed for cyanide and metals.

RESULTS

This section is divided in three parts, concerning the different systems tested (solution, substrates and plant tissues).

Solution

Unit 1: Aeration-oxidation cascade: using a mean flow of 4 l/min, the solution took 1 minute to complete the path. After going throughout the cascade, the pH of the solution decreased 0,3-0,5 units, as well as the Eh value, increasing its DO_2 content in an average value of 1,2 mg/l. Other physico-chemical properties are not affected, with the exception of a removal of 3 mg/l for dissolved cyanide and 5,5 mg/l of nitrite and nitrate.

Unit 2: anaerobic cell: once the solution has flowed through across the substrate, its pH, Eh and EC values do not show clear trends, varying with a high dependence on the temperature. On the other hand, the mixture acts as a clarifier, as the values of the turbidity decrease in 16 ntu. The DO_2 decreased in a mean value of 2,5 mg/l. In anaerobic conditions, and for the calculated retention time, the following average removal rates were achieved: 6,5 mg/l for dissolved cyanide, 48 mg/l for ammonia, 9,4 mg/l for nitrate and nitrite and 26,5 mg/l of copper (respective efficiencies of 8,6%, 9,8%, 48,5% and 89,5%).

Unit 3: aerobic cell: comparing the paired values influent-effluent, no significant difference has been found for pH and Eh. In contrast, the EC presented a slightly decreasing trend (about 1 mS/cm); the DO_2 content of the solution increased 0,5 mg/l and its turbidity 6 ntu. In aerobic conditions and after 66 h of retention time, the effectiveness was better than that found for unit 2: 9,8 mg/l for dissolved cyanide, 37 mg/l for ammonia, 6,2 mg/l for nitrate and nitrite and 2,6 mg/l for copper (i.e., removal rates of 14,2%, 8,4%, 62% and 82% respectively).

In Table 3, a comparison between the total efficiency of the "treatment line" (anaerobic and aerobic cells) and the "blank line" is presented, including most of the analysed compounds.

Table 3: Comparison of removal rates achieved both in treatment and blank lines

Unit	Compound	X_{in} (mg/l)	X_{ef} (mg/l)	$X_{in} - X_{ef}$ (mg/l)	X_{rem} (g/day)	X_{rem} (g/day/m^2)	%
Anaerobic cell and aerobic cell	Disolved CN	75,4	59,1	16,3	46,94	**0,49**	21,6
	WAD CN	15	0,14	14,86	41,60	**0,43**	99,1
	SAD CN	20	4	16	46,08	**0,48**	80
	Amonnia	491	406	85	244,8	**2,55**	17,3
	Nitrate[*]	19,4	3,8	15,6	44,92	**0,47**	80,4
	Copper	29,6	0,56	29,04	83,63	**0,87**	98,1
Blank line	Disolved CN	75,4	64,8	10,6	30,53	**0,31**	14,1
	WAD CN	15	0,5	14,5	41,76	**0,43**	96,7
	SAD CN	20	7	13	37,44	**0,39**	65
	Ammonia	491	348	143	411,84	**4,29**	29,1
	Nitrate[*]	19,4	22,6	-	0	**0**	0
	Copper	29,6	9,5	20,1	57,89	**0,60**	67,9

(*)"Nitrate" refers to the sum of nitrate and nitrite ions.

Substrates

Before the beginning of the experiment, it was proved that the substrates employed were free of cyanide, by means of an acid wet digestion of the grinded substrate, followed by a distillation to recover the cyanide in an alkaline media. At the end of the experiment, two samples of 2 kg each were collected in each one of the cells (near the inlet and the outlet). These samples were oven dried, grinded and the fraction below 125 µm was analysed using the same methodology, in the University of Bochum (Germany). In both cases similar values for the samples of each cell were obtained. The organic substrate mixed with gravel that was used in the anaerobic cell, showed a capacity to retain an average of 6,7 mg of TCN/kg. This is slightly under the mean value obtained for the autochthonous soil used in the aerobic cell (a XRD analysis of this soil revealed that it was formed by a mixture of illite and caolinite and as secondary components, quartz, dolomite and muscovite), which resulted of 10,7 mg TCN/kg.

Plant tissues

Analyses for metal and cyanide in plant tissue (root, stem and flower) were carried out before and after the experiment. Although the specie *Thypa latifolia* supported the aggressive conditions it was submitted to, all analyses showed cyanide concentrations below 1 mg/kg, so no incorporation of cyanide to plant tissues could be confirmed. On the contrary, these plants are capable of incorporating several times their original contents in copper, arsenic or manganese, among others.

INTERPRETATION

Main processes involved in cyanide removal

The theoretical basis to define the relevant physico-chemical processes that play an important role on cyanide removal from solution, depending on the specific case, are the cyanide cycle (described in Smith & Mudder, 1991) and the nitrogen cycle.

The most important mechanism that affects the cyanide removal is, according with previous studies (Botz & Mudder, 2000; Mudder, 1999; Simovic *et al.*, 1984) the acidification of the solution because the action of the atmospheric CO_2. As the pH of the solution drops, free cyanide presents HCN as stable phase, which volatilizes at 26 ºC. Furthermore, another processes like hydrolysis (to produce formate ion and ammonium), biological oxidation (specially free and WAD cyanides, Boucabeille *et al.*, 1994), adsorption onto mineral surfaces (Alesii & Fuller, 1976; Chatwin, 1990) and photolytic degradation (SAD cyanides are very sensitive, Young *et al*., 1995b) are supposed to play a main role in the studied conditions.

Unit 1: aeration cascade: as it was stated previously, only moderate removal rates for dissolved cyanide and nitrate were obtained in this unit, which acted also decreasing the pH of the solution in about 0,5 units and increasing the values of DO_2 and Eh. Being that so, HCN volatilisation seems to be the main responsible for cyanide removal from solution. The retention time is believed to be too short to consider remarkable photolytic degradation effects.

Unit 2: anaerobic cell: After flowing accross the organic susbtrate, all the analysed compounds are removed in a certain extent, reaching, typically, valuable removal rates for WAD and SAD cyanide (93% and 65%, respectively), and also for copper (89,5%). For dissolved cyanide, ammonia and nitrate, the removal rates are moderate, although acceptable (8,6%, 9,8% and 48,5%, respectively). Under anaerobic conditions, the biological degradation and the adsorption onto mineral surfaces appear as dominant mechanisms, being the latter the only one that affects copper removal.

Unit 3: aerobic cell: The analyses of cyanide (TCN) in substrates can be translated in a partial removal rate of 1.6% due to the adsoption/absorption onto/in mineral phases of the substrate. A total average TCN removal of 14.2% was obtained in this cell due to other mechanisms, such as biological oxidation (the presence of several species of the *Pseudomonas genus* –potentially cyanide degradators- was proved), hydrolysis and volatilisation of HCN and photolytic degradation (this cells worked with a water sheet of 15-20 cm, suitable for the vegetation). Residual levels of copper, WAD and SAD cyanides were also successfully removed (respective efficiencies of 82%, 86% and 43%). Finally, these conditions seem to be suitable for nitrate removal (62%) and clearly non appropriate for ammonia removal (8.4%).

CONCLUSIONS

From this study, the following conclusions about the treatment of effluents of cyanidation processes using passive treatment systems, can be established:

▪ Both the high cyanide levels and the great amount of suspended solids of the tested solution cause that the slurries from cyanidation processes are not suitable to be successfully detoxified employing only passive treatment systems. In any case, once the tailings pond facility is closured, the stored liquid fraction (homogeneous and pre-degraded) can be treated employing these technologies.

▪ With total cyanide levels in the range of tens of mg/l and using low flow rates, removal rates of 20-25% (0,5 g/día/m^2) can be obtained for dissolved cyanide and above 75% for WAD and SAD cyanide.

▪ Nitrite and nitrate ions, as well as the great majority of the present metals are removed from solution with high efficiencies (80% and more).

▪ The main mechanisms involved in cyanide removal using passive systems are four: volatilisation of HCN, adsorption onto solid phases, biological oxidation and photolytic degradation.

▪ Aerobic conditions are more effective than anaerobic ones for this type of solutions.

▪ Mineral-nature substrates have demonstrated to be more suitable as absorbents/adsorbents of cyanide compounds than organic-nature substrates.

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