



Álvarez, R., Ordóñez, A., Loredó, J., and Younger, P.L. (2013) Wetland-based passive treatment systems for gold ore processing effluents containing residual cyanide, metals and nitrogen species. *Environmental Science: Processes & Impacts*, 15 (11). pp. 2115-2124. ISSN 2050-7887

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Deposited on: 05 June 2014

Wetland-Based Passive Treatment Systems for Gold Ore Processing Effluents Containing Residual Cyanide, Metals and Nitrogen Species

R. Álvarez^a, A. Ordóñez*^a, J. Loredó^a and P.L. Younger^b

Gold extraction operations generate a variety of wastes requiring responsible disposal in compliance with current environmental regulations. During recent decades, increased emphasis has been placed on effluent control and treatment, in order to avoid the threat to the environment posed by toxic constituents. In many modern gold mining and ore processing operations, cyanide species are of most immediate concern. Given that natural degradation processes are known to reduce the toxicity of cyanide over time, trials have been made at laboratory and field scales into the feasibility of using wetland-based passive systems as low-cost and environmental friendly methods for long-term treatment of leachates from closed gold mine tailings disposal facilities. Laboratory experiments on discrete aerobic and anaerobic treatment units supported the development of design parameters for the construction of a field-scale passive system at a gold mine site in northern Spain. An in situ pilot-scale wetland treatment system was designed, constructed and monitored over a nine-month period. Overall, the results suggest that compost-based constructed wetlands are capable of detoxifying cyanidation effluents, removing about 21.6% of dissolved cyanide and 98% of Cu, as well as nitrite and nitrate. Wetland-based passive systems can therefore be considered as a viable technology for removal of residual concentrations of cyanide from leachates emanating from closed gold mine tailings disposal facilities.

Introduction

Most of the world's current gold production is derived from low-grade ores that are described as "refractory", because the gold which they contain is not readily recoverable using conventional physical separation methods (usually due to close association between the gold and sulphide mineral phases)^{1,2}. At present, "cyanidation" (i.e. leaching with cyanide solutions) is the only economic beneficiation process for refractory gold ores. The advent of cyanidation represented a significant step forward in the control of potential environmental contaminants during gold beneficiation³; in recent decades, it has become the technique of choice in the gold mining industry worldwide^{4,5}, even at artisanal scale⁶. Although a great improvement on previous beneficiation processes (such as those involving uncontrolled use of mercury)⁷, cyanidation remains controversial amongst opponents of mining, as some incidents with unintended releases of cyanide to the environment have negatively affected the image of the mining industry^{8,9,10}. It is a fact that occasional accidents demonstrate just how lethal elevated cyanide concentrations can be; a case in point

associated with properly-operated gold ore beneficiation plants.

Although modern cyanidation plants are designed to minimise the concentrations of cyanide in slurries dispatched to tailings dams for long-term storage, even the modest residual concentrations of cyanide present in tailings dam pore waters can render the leachate potentially toxic to freshwater organisms (and sometimes also to birds and terrestrial animals¹³; ecotoxic effects may also arise from other contaminants (metals, sulphate, ammonium, nitrate) present in these pore waters, as cyanide complexation has been proved to enhance the release of lots of heavy metals such as Co, Fe, Hg, Ni, Zn, Cu and Ag^{14,15,16,17}.

Secure, long-term decommissioning of gold mine tailings dams therefore demands low-cost cyanide destruction techniques which can be trusted to work long after ordinary site operations have ceased. Drawing on the paradigm of passive treatment, which has been widely pioneered for other forms of mine water pollution¹⁸, this paper explores a possible wetland-type process for the long-term treatment of residual concentrations of cyanide and allied contaminants found in gold tailings dam leachates.

Use of cyanide in gold ore beneficiation

Cyanide compounds are useful in gold recovery because they act as powerful ligands, capable of complexing virtually any heavy metal even at low concentrations^{17,19,20}. Primary reactants in cyanidation are typically NaCN and CaO, which together form a solution capable of dissolving any refractory gold present within the crystal lattices of sulphides. Cyanidation is either implemented by leaching of gold ores "in tank" or "in pulp". Leaching in tank involves mixing the crushed and ground ore (which has sometimes also been pre-oxidized and roasted, depending on mineralogy) with CaO to form a 'pulp' which is dispatched to a series of leaching tanks, where a weak cyanide

^aDep. Explotación y Prospección de Minas, University of Oviedo;

Escuela Técnica Superior de Ingenieros de Minas; c/Independencia, 13, 33004 Oviedo, Asturias, Spain;

Fax: +34985104245; Tel: +34985104275; E-mail: aoalonso@uniovi.es

^bRankine Chair of Engineering, University of Glasgow, Scotland, UK.

has been the breaking of a cyanidation tailings dam at Baia Mare (Romania) in 2000, which caused severe contamination of some 2,000 km of the River Danube and its tributaries, resulting in the hundreds of thousands of fish kills^{11,12}. Of more widespread interest are the possible sources of long-term cyanide contamination

solution is added and air is injected to promote slightly oxidative conditions. The retention time of the pulp in the leaching circuit is adjusted to ensure complete dissolution of gold (and silver, if present). Simultaneously, activated carbon particles are added in the leaching circuit (in a counter-current flow) to adsorb the gold. The resultant 'spent' slurry, containing 50-100 mg l⁻¹ of total cyanide²¹, is passed to a series of tanks in which most of the cyanide compounds are recovered and recycled into the process^{2,20}. The bulk of the residual cyanide (and a range of potentially hazardous dissolved metals, most notably copper) is then 'detoxified', generally by oxidation and the water recycled²². Finally, this partly detoxified slurry is passed to a tailings pond. The alternative approach, "leaching in pulp", involves placing the crushed and ground ore on lined pads, forming heaps which are then irrigated with dilute cyanide solutions. The solution percolates through the heap and the cyanide dissolves the gold; the resultant leachate is then processed as described above.

There are two principal forms in which the cyanide ion couple C-N occurs in soluble form:

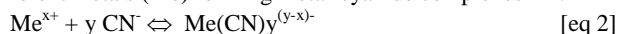
Cyanide ion: this term refers exclusively the CN⁻ ion.

Hydrogen cyanide: HCN, as a neutral molecule.

In laboratory analysis, the cyanide ion and the hydrogen cyanide are grouped together in the category "free cyanide". In aqueous solution the following chemical balance is established, where the stable compound depends almost exclusively on the pH of the solution (at pH above 9, the dominant species is the ionic form):



Free cyanide (active form to leach gold) forms can react with different metals (Me) forming metal-cyanide complexes^{23,24}:



Depending on their relative stabilities (characterised by the value of the chemical equilibrium constant (K) for the dissociation reaction in question), these complexes are categorised as^{25,26}:

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

Strong Acid Dissociable (SAD) cyanide (Log K > 30). The most representative species cyanides of gold, iron and cobalt belong to this group.

Total cyanide (TCN): include all cyanide species present (dissolved or not).

Cyanide related compounds: basically, these are non-toxic forms derived from cyanide degradation: thiocyanate (SCN⁻), cyanate (CNO⁻), nitrate (NO₃²⁻), nitrite (NO₂⁻) and ammonia (NH₃).

Free cyanide is the most toxic species, but it is also the quickest to attenuate, whereas the metal cyanide complexes, particularly the stronger ones, attenuate more slowly, so they control the long-term persistence of cyanide at sites where gold ores are processed²⁷.

Conventional treatment methods for removal of cyanide from spent process waters

The theoretical basis for defining the physico-chemical processes which contribute significantly to the removal of cyanide from solution is provided by the nitrogen cycle in general, and the cyanide cycle in particular¹⁷. The most important mechanism

effecting cyanide removal has been found to be the acidification of the solution by means of the action of the atmospheric CO₂^{25,28,29,30}. In accordance with [eq 1], as the pH of the solution drops, the predominant form of free cyanide becomes HCN, which is easily volatilized (boiling point in aqueous solution is 24°C)³¹. Important auxiliary processes include hydrolysis (yielding the formate ion and ammonium), bio-degradation^{32,33}, adsorption onto mineral surfaces^{34,35}, and photolytic degradation (to which SAD cyanides are especially sensitive)³⁶.

So-called 'detoxification' processes widely used in operational gold ore processing plants use one or more of three principal processes^{37,38}: *i*) Dilution *ii*) Direct removal of toxic species from solution, and/or *iii*) Conversion of toxic forms to non-toxic forms. As free cyanide forms are acutely toxic for humans and animals if ingested or inhaled (calculated lethal dose for humans ranges between 0.5-3.5 mg kg⁻¹ body weight)³¹, dilution is not a satisfactory approach in many cases. On the other hand, direct removal of toxic species from solution (which is feasible using several physical, adsorption and complexation methods)³⁹ is often prohibitively expensive. In most cases therefore, detoxification of cyanide usually relies on conversion of toxic forms into non-toxic forms by some oxidative method. Oxidative degradation of CN⁻ and HCN yields cyanate ions (CNO⁻), which are considered to be 10,000 times less toxic than free cyanide forms³¹. Oxidation at industrial scales may be achieved in a number of ways: natural degradation, the hydrogen peroxide process, the sulphur dioxide process, alkaline chlorination and the Caro's Acid process, among others^{17,37}.

Partial degradation of cyanide may occur naturally by microbial oxidation; Homestake Mining, Environment Canada and Dome Mines report natural degradation in their tailings ponds⁴⁰. Natural degradation processes can be influenced by variables such as the cyanide species in solution and their relative concentrations, temperature, pH, aeration, sunlight, and presence of bacteria. Although natural degradation processes are effective in cyanide treatment, their kinetics are not often as fast as required for industrial purposes; in such cases active oxidation technologies are demanded^{17,41,42}.

Currently, cyanide detoxification research is focusing on new chemical oxidants (such as KMnO₄ and ozone), biologically-assisted oxidation (mainly through the activity of cyanide-degrading bacteria such as *Pseudomonas pseudoalcaligenes*⁴³, ion exchange, reverse osmosis, precipitation of cyanide (as NaCN or KCN) and the adsorption of toxic forms on a range of solid phases, such as fly ash⁴⁴, feldspars,...

Emerging passive treatment technologies for cyanide abatement

As noted above, natural degradation processes are already harnessed in some conventional cyanide treatment plants^{17,25,28}. The main natural degradation mechanisms are volatilization of hydrogen cyanide from solution, biological degradation (that can be carried out by four general pathways: hydrolytic, oxidative, reductive and substitution/transfer)³³, adsorption of toxic forms onto mineral surfaces and precipitation of insoluble salts from solution. During the last twenty years, passive treatment systems based on natural processes have been successfully applied to treat a range of mine waters⁴⁵ (as well as other industrial effluents,

urban wastewaters and storm water, among others)⁴⁶. Passive treatment has been defined by the EU PIRAMID Consortium¹⁸, as “the deliberate improvement of water quality using only naturally-available energy sources (e.g. gravity, microbial metabolic energy, photosynthesis etc.), in systems which require only infrequent maintenance in order to operate effectively over the entire system design life”.

Although passive treatment has been extensively applied to mine waters¹⁸, research has been restricted almost exclusively to acidic and/or metalliferous leachates emanating from mine voids and/or waste rock piles, in which the principal contaminants are iron, aluminium, manganese and sulphate⁴⁵. There are a number of (successful) cyanide/gold mine wetlands in existence, but these generally have not been publicly described^{47,48}. Models of cyanide removal in treatment wetlands have been published^{49,50,51}, but little effort has been dedicated to passive treatment of cyanide-rich tailings leachates. Currently, there is little information concerning the behaviour and suitability of passive systems to detoxify cyanide-rich solutions. Some noticeable examples are the following ‘semi-passive’ systems: i) Star Lake and Jolu mines (Saskatchewan district, Canada, where a natural wetland was combined with a two-step active treatment)⁵²; ii) Homestake mining district (Dakota, USA, bacteriological oxidation technologies)^{17,53,54,55}; iii) Nickel Plate Mine (Dakota, USA, bacteriological oxidation of thiocyanate)⁵⁶; iv) Colomac site (Yellowknife, Canada, where the effluent was treated by bacteriological oxidation promoted by dosing with ammonium phosphate)⁵⁷ and v) Bullfrog mine, (Nevada, USA, passive and forced evaporation)⁵⁸.

None of these prior investigations resulted in a truly passive process that could be maintained after the closure of the associated ore processing plant. In the search for a more appropriate technology for the abatement of cyanide seeping from closed tailings ponds^{18,59,60}, experimental investigations into the laboratory- and field-scale passive treatment of cyanide-bearing leachates are reported here.

Experimental design

Taking into account the physico-chemical parameters of the effluents to be studied and knowledge of the main cyanide removal mechanisms⁶¹, a range of different types of passive systems (aerobic and anaerobic) were tested as individual units at laboratory scale, using a variety of reactor substrates and a range of flow rates. On the basis of these laboratory results, a pilot-scale system including both aerobic and anaerobic units was designed, constructed at the site of a gold mine in the municipality of Belmonte de Miranda (Asturias, northwestern Spain), and monitored over a period of 9 months.

The tested solution was the residual fluid from the cyanidation process of a Cu-Au skarn type gold mine. The physico-chemical properties of the solution reflect both the nature of the ore and the particulars of the cyanidation process implemented at this site. Consequently, the solution varies in composition quite widely over time; average characteristics are summarised in Table 1.

Table 1 Ranges of values of the main physico-chemical parameters measured in the tested solution.

Parameter	Range	Parameter	Range
pH	8-9	Ammonium	400-500 mg l ⁻¹
Electrical Conductivity	8-10 mS cm ⁻¹	Si	5-10 mg l ⁻¹
Temperature	10-25 °C	S	1,000-1,500 mg l ⁻¹
ORP	+300-+400 mV	SO ₄ ²⁻	3,500-4,000 mg l ⁻¹
Dissolved oxygen	4-6 mg l ⁻¹	Na	1,500-2,000 mg l ⁻¹
Turbidity	5-100 NTU	K	50-100 mg l ⁻¹
Total Cyanide (TCN)	50-200 mg l ⁻¹	Cu	20-40 mg l ⁻¹
WAD Cyanide	10-100 mg l ⁻¹	NO ₃ ⁻ + NO ₂ ⁻	20-30 mg l ⁻¹

Laboratory-scale experiments

The following laboratory experiments were undertaken:

Aerobic static cells: a batch system, consisted on two independent cells of 60 l (0.6 m x 0.25 m x 0.4 m) were used to test cyanide attenuation under aerobic conditions similar to those found in many constructed wetland systems. Cell 1 was filled with a 5 cm thick limestone bed, followed by a 10 cm thick compost layer, from bottom to top. Cell 2 was filled with a 3 cm thick limestone bed, and a 21 cm thick layer composed by organic compost mixed (1:50 volume) with grained iron particles. Both cells were placed in an open-air area, and were watered at the beginning of the experiments with the residual cyanidation solution (Table 1), which remained immobile until the end of the experiment (two months). Measurements of pH, ORP, electrical conductivity and dissolved oxygen were made daily over a period of two months; representative samples of solution were collected weekly for cyanide and metal analysis.

Oxidation cascade: in an open-air area, a unit comprising four

cells disposed at different heights was used as an oxidation cascade, with a continuous flow from one cell to another promoting aeration and oxidation (circulating system). Water samples were collected weekly for analysis, over a two months period. The used flow rate was 20 ml min⁻¹.

Anaerobic columns: Two columns of 42 l capacity (1.2 m high and 0.21 m diameter) were operated in continuous flow-through mode. Column 1 was filled with a 20 cm thick bed of crushed limestone beneath a 100 cm thick layer of organic compost. Column 2 had the same filling, with the addition of grained iron particles mixed with the organic compost substrate. The cyanidation residual solution was re-circulated through the columns at a constant rate of 2.3 ml min⁻¹ over 60 days (filling porosity: 33%; residence time: 91.3 h) with the help of peristaltic pumps. The effluent was sampled weekly and daily measurements of pH, ORP and electrical conductivity were made.

Laboratory scale aerobic/anaerobic wetland: A 375 l (1.5 m x 0.5 m x 0.5 m) galvanized steel container was used as a wetland

unit under laboratory conditions. The container was divided into 15 sections in partial communication, so that the water followed a circuitous path of 7 m inside it. A thin bed (5 cm) of limestone was placed at the bottom of the lab-wetland and the rest was filled with organic compost (porosity: 45%), up to 30 cm. Cattails (*Typha latifolia*) were planted on the organic substrate and no fertilizers or nutrients were added at any time. A continuous flow of cyanide-rich solution was maintained for 60 days at a constant rate of 10 ml min⁻¹ (flow-through mode) without pumping system. Calculated residence time of water in the system was 168 hours. pH, ORP, dissolved oxygen and electrical conductivity were measured daily, and influent and effluent solutions were sampled for cation and anion analysis on a weekly basis. Cattails were analysed before and after the experiment.

15 Pilot field-scale tests

A pilot-scale passive system was constructed between the cyanidation plant and the tailings disposal facility of a gold mine, within the perimeter of the latter, which is fenced and screened to prevent access by local wildlife (a potential handicap for engineered wetlands treating ecotoxic substances)⁶⁰. The in-situ pilot-scale system was designed in the light of the laboratory findings, and consisted of four units in series:

Unit 1: A 30 m long aeration-oxidation cascade acting as a pre-treatment.

25 *Unit 2:* An anaerobic cell whose substrate was constituted by a mixture of siliceous gravel and cow manure.

Unit 3: An aerobic cell whose substrate was constituted by a mixture of siliceous gravel and autochthonous soil. XRD analysis of this soil revealed that it was formed mainly by illite and kaolinite and quartz, dolomite and muscovite as secondary components. 160 *Typha latifolia* seedlings were planted in this cell. *Typha latifolia* was considered the optimum specie due to its hardness to aggressive conditions and toxic substances, in addition to its good behaviour at high pH values⁶².

35 *Unit 4:* A 12 m long aeration-oxidation cascade as post-treatment unit.

50 cm of substrate was installed in both Units 2 and 3, which were found to have porosities of 35% and 33% respectively. Calculated residence times of the solution in these units were 70 h (Unit 2) and 66 h (Unit 3).

In parallel with the treatment line, a “blank” line was also constructed, comprising two cells identical in size to the others (12 m x 4 m), but containing only an inert substrate (siliceous gravel; d₈₀<20 mm). The thickness of gravel in these cells was calculated so that the retention time of the solution in each one was comparable to that of the cells in the anaerobic and aerobic

treatment streams.

The test solution was obtained by diversion of part of the flow from the gold beneficiation plant to the tailings dam. The diverted flow was passed to a small settling pond, in which the current was divided evenly and passed to the treatment line and the blank line as shown in Figure 1.

The original intention was to base the design flow rate was based on a criterion suggested by : “CN⁻ loadings below 1 g m⁻² day⁻¹ are required in order to maintain cyanide content in the effluent below direct discharge values (Canada: 0.2 mg l⁻¹)”. Taking into account that the available surface for treatment is that which results for both cells -aerobic and anaerobic (i.e., 48 + 48 =96 m²), the system should be able to treat a loading of 96 g day⁻¹. As the cyanide loading entering the systems is defined by the flow rate and the effluent TCN content, the following expression links both parameters so that Sobolewski’s criterion is completed:

$$Q \text{ (l/min)} \cdot C \text{ (mg TCN l}^{-1}\text{)} \cdot (1 \text{ g}/10^3 \text{ mg)} \cdot (1440 \text{ min/day)} < 96 \text{ g TCN day}^{-1}$$

65 $Q \text{ (l/min)} \cdot C \text{ (mg TCN l}^{-1}\text{)} < 66.7$

where: Q = Flow rate (l min⁻¹) and C = Total cyanide concentration (mg l⁻¹).

Due to the nature of the processing plant effluent, which contains a great amount of suspended solids (5-15 g l⁻¹), it was not possible to establish a practical constant flow rate below 4 l min⁻¹. After going through the first unit of treatment (aeration cascade) in about 30 seconds, the solution enters the parallel series of cells, at which point the flow is equally divided between the two streams (2 l min⁻¹ to each one). This being the case, and with a TCN concentration > 33.3 mg l⁻¹ most of the time, the system was working far above the Sobolewski criterion.

During the operation of the described field system (9 months), it was monitored weekly, following the guidelines for monitoring passive systems described by the PIRAMID Consortium¹⁸. Electrical conductivity, pH, ORP, salinity, turbidity, dissolved oxygen and temperature were measured *in situ* using a multiparametric probe, which was frequently re-calibrated. Samples were analysed weekly for cyanide and monthly for sulphate, nitrite and nitrate, ammonium and ammonia, according to USEPA and APHA methods: EPA Methods 335.3 (total cyanide) and 9013 (cyanide extraction for solids); APHA Methods 4550-CN-I (WAD cyanide) and 4500-NH3-G (ammonia).

Substrates and plant tissues (root, stem and flower) in all tests were sampled before and after the experiment and analysed for cyanide and metals at the beginning and at the end of the experiments. Samples were oven dried and ground, recovering the fraction below 125 µm for analysis. Analysis of metals was carried out by Inductively coupled plasma mass spectrometry (ICP-MS) in ACME Analytical Laboratories Ltd (Vancouver, Canada). Analysis for cyanide was made according the above cited EPA 9013 method.

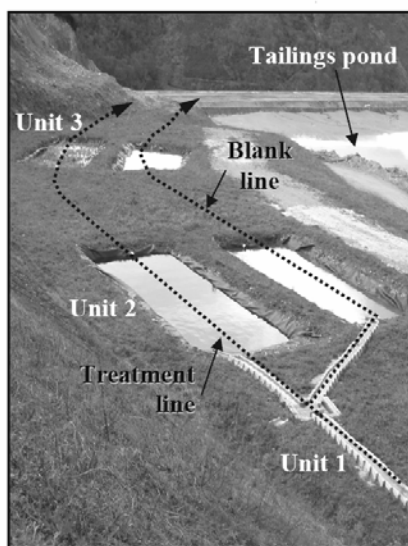
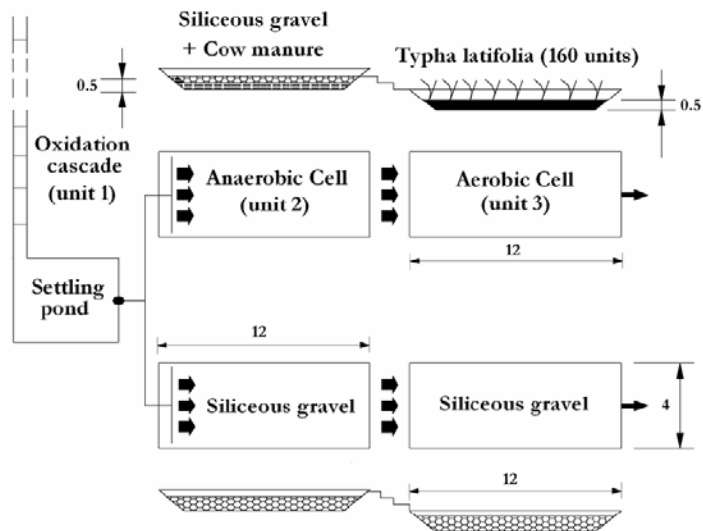


Fig 1 Detailed draw and view of the pilot-scale system. All dimensions are expressed in meters

Results and Discussion

5 Laboratory-scale experiments

In the laboratory aerobic cells, pH gradually decreased from 9.4 to 7.9 during the life of the experiment, probably due to dissolution of atmospheric CO₂. This acidification could be expected to result in the conversion of ionic cyanide forms into HCN, which is easily volatilized at low temperatures. WAD cyanide concentrations decreased by 50-65% over the experimental period. The addition of iron particles did not seem to improve the overall rate of decrease.

The circulation of the solution through the laboratory oxidation cascade resulted in pH decreasing slightly (from 8.8 to 8.5, as an average). Electrical conductivity reached values in the range 8-10 mS cm⁻¹ before commencing a gentle decreasing trend. ORP measurements confirmed that oxidizing conditions were achieved throughout the experimental cells. The average decrease in WAD cyanide concentrations over the life of the experiment was almost 80%.

During the experiments in anaerobic columns, no significant change in pH was observed. The electrical conductivity showed a decreasing trend, which was more marked in the column which

25 contained iron particles within the compost. WAD cyanide decrease ranged from 60% to 70%, being slightly higher in the column with iron particles. In this case, as reactive Fe is present, the liberated CN⁻ would precipitate as insoluble Fe salts, which are highly stable in the tested conditions (absence of ultraviolet radiation). The addition of iron particles seemed to help also Cu removal, reaching elimination rates of 60%, probably due to the formation of insoluble iron-copper cyanide complexes.

In the laboratory-scale wetland, the solution pH decreased from 8.7 to 7.5 units, thus presumably increasing HCN volatilization rates and promoting cyanate formation. Electrical conductivity decreased from 9 to 6.5 mS cm⁻¹. Removal rates of 90% for WAD cyanide were achieved and the main mechanisms involved are likely to be complexation to insoluble solid phases, photodegradation and oxidation. Cu removal rates of 98% were obtained. The analysis of *Typha latifolia* revealed high metal adsorption capacity, but poor absorption/adsorption capacity for cyanide and its complexes (below 1 mg kg⁻¹).

A summary of the effectiveness of each one of tested systems is presented in Table 2, where results are expressed as percentage of the achieved WAD cyanide removal.

Table 2 Efficiency of WAD cyanide removal of different systems tested at laboratory scale, after two months

Experimental Unit	% decrease in WAD cyanide concentrations
Aerobic Cells	50-65
Aeration cascade	80
Anaerobic Columns	40-65
Laboratory wetland	90

Field-scale tests

Oxidation cascade: On flowing through this unit, the pH of the solution decreased by 0.3-0.5, and increases were observed in dissolved oxygen (average rise of 1.2 mg l⁻¹) and ORP (35 mV increase). Other physico-chemical properties were not affected, with the exception of a mean removal of 3 mg l⁻¹ for dissolved cyanide and 5.5 mg l⁻¹ for nitrite and nitrate. Only moderate removal rates for dissolved cyanide and nitrite+nitrate were observed in this unit. HCN volatilisation seems to be the main process responsible for cyanide removal from solution, as the retention time is too short for appreciable photolytic effects to occur.

Anaerobic cell: Although the pH, ORP and electrical conductivity of the solution do not show clear trends as the solution flows through the organic substrate, this substrate does seem to act as a clarifier, as the values of the turbidity decrease by 16 NTU. The dissolved oxygen content decreased by 2.5 mg l⁻¹ on average, and all analysed compounds were removed to a certain extent (average reductions of 6.5, 48, 9.4 and 26.5 mg l⁻¹ of dissolved cyanide, ammonia, nitrate and nitrite and Cu, respectively). Impressive removal rates were obtained for WAD and SAD cyanide (93 and 65%, respectively), and for Cu (89.5%). Under anaerobic conditions, the dominant cyanide removal processes include biological degradation and adsorption onto mineral surfaces; the latter process also explains Cu removal, although a modest contribution from sulphide precipitation cannot be ruled out.

Aerobic cell: Comparing the paired influent-effluent values, no significant changes were found in either pH or ORP. In contrast, the electrical conductivity showed a slightly decreasing trend (reduction of 1 mS cm⁻¹). The dissolved oxygen content of the solution increased slightly (averaging 0.5 mg l⁻¹), as did turbidity (by 6 NTU). In aerobic conditions, the effectiveness of removal of analysed substances was better than that found under anaerobic

conditions (average reductions of 9.8, 37, 6.2 and 2.6 mg l⁻¹ of dissolved cyanide, ammonia, nitrate and nitrite and Cu, respectively). A total average TCN removal of 14.2% was obtained in this cell. Most of this can be ascribed to a combination of biological oxidation (microbiological analyses proved the presence of several species of cyanide-oxidising *Pseudomonas*), hydrolysis, photolysis (favoured by a shallow water depth of only 15–20 cm) and volatilization of HCN. Analyses of TCN in the substrate before and after the experiment indicates that adsorption/absorption onto/into mineral phases of the substrate can account for the removal of only 1.6% of the TCN. Cu, WAD and SAD cyanides were also successfully removed, reaching removal efficiencies of 82%, 86% and 43% respectively. Finally, while conditions in this unit seemed to be suitable for nitrite+nitrate removal (62%), although they were clearly non-optimal for ammonia removal (8.4%).

In Table 3, a comparison between the total efficiency of the “treatment line” (anaerobic and aerobic cells with reactive substrate and plants) and the “blank line” (cells with inert substrate) is presented, including most of the analysed compounds. Both lines displayed noticeable removal of metal-cyanide complexes (WAD and SAD cyanide) and copper, though rates were clearly greater in the treatment line. More significant are the differences in removal rates between dissolved cyanide (21.6% in the treatment line, compared with 14.1% in the blank line), and nitrate/nitrite ions (80% in the treatment line, 0% for the sum of nitrate and nitrite in the blank line). The organic substrate mixed with gravel that was used in the anaerobic cell of the treatment line, showed a capacity to retain an average of 6.7 mg of TCN kg⁻¹. This is slightly under the mean value obtained for the autochthonous soil used in the aerobic cell (10.7 mg TCN kg⁻¹). Removal rates of the analysed compounds for each unit of treatment are shown in Fig. 2.

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

Unit	Compound	X _{in} (mg l ⁻¹)	X _{ef} (mg l ⁻¹)	X _{in} - X _{ef} (mg l ⁻¹)	X _{rem} (g day ⁻¹ m ⁻²)	Removal rate (%)
Treatment line Anaerobic + aerobic cells	Dissolved CN	75.4	59.1	16.3	0.5	21.6
	WAD CN	15	0.1	14.8	0.4	99.1
	SAD CN	20	4.0	16	0.5	80.0
	Ammonia	491	406	85	2.6	17.3
	Nitrite+ Nitrate	19.4	3.8	15.6	0.5	80.4
	Cu	29.6	0.6	29.1	0.9	98.1
Blank line Anaerobic + aerobic cells	Dissolved CN	75.4	64.8	10.6	0.3	14.1
	WAD CN	15	0.5	14.5	0.4	96.7
	SAD CN	20	7.0	13	0.4	65.0
	Ammonia	491	348	143	4.3	29.1
	Nitrate*	19.4	22.6	NA	0.0	0.0
	Cu	29.6	9.5	20.1	0.6	67.9

X: concentration of each compound; *in*: influent; *ef*: effluent; *rem*: removed; NA: Not available

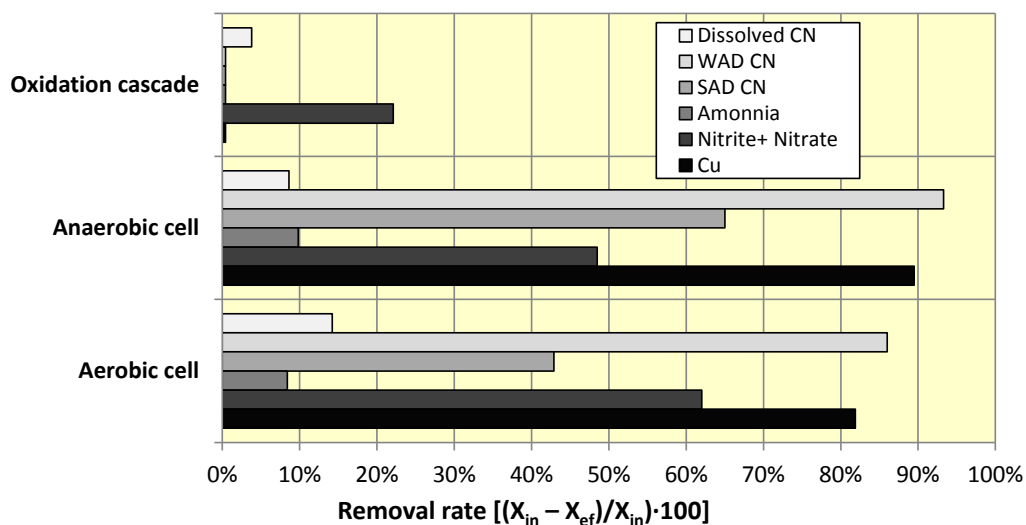


Fig 2 Removal rates achieved at each unit of treatment

Although the wetland plant *Typha latifolia* survived the aggressive conditions that it was submitted to, all analyses showed cyanide concentrations below 1 mg kg⁻¹, so no incorporation of cyanide to plant tissues could be confirmed. By

contrast, these plants have proven to be capable of incorporating several times their original contents in Cu or Mn, among other metals^{63,64}. Results of plant tissue analyses are summarized in Table 4.

Table 4 Analyses of *Typha latifolia* planted in the field-scale passive treatment system (all concentrations expressed in mg·kg⁻¹, excepting Fe)

Element	Root		Stem		Flower	
	(1)	(2)	(1)	(2)	(1)	(2)
Mo	10	11	1	3	2	5
Cu	5	1569	3	332	5.5	715
Pb	20.5	12.7	16	9	6.5	8
Zn	39	67	29	59	27	63
Mn	387	900	115	816	354	1458
Fe (%)	1.07	0.57	0.80	0.12	0.21	0.32
As	57	54	38	8	9	21.5
Hg	<1	<1	<1	<1	2	5

(1): original concentration

(2): concentration after 9 months of treatment

Conclusions

From this study, some conclusions about the applicability of passive systems for the abatement of cyanide species in effluents from cyanidation processes can be established.

Both the high cyanide content and the great amount of suspended solids of the tested effluents cause problems for passive systems application. The characteristics of this type of solutions during mining activity make them not suitable to be successfully detoxified employing only passive treatment systems. Once the tailings disposal facility is closed, however, leachates produced by tailings compaction (which can be expected to have a less variable chemical composition and to contain less cyanide and virtually no suspended solids) would be surely amenable to passive treatment using engineered aerobic-anaerobic wetlands, which offer significant removal of free cyanide and metal-cyanide complexes concentrations. With total cyanide levels in the range of tens of mg l⁻¹ and using low flow rates in the order of 2 l min⁻¹, removal rates for dissolved cyanide range from 20 to 25% (0.5 g day⁻¹ m⁻²), generally insufficient to achieve direct discharge limits for these parameter if this technology is used without any other complementary treatment. Removal rates for WAD's and SAD's cyanides are above 80%.

The principal mechanisms of cyanide removal using passive systems are HCN volatilization, adsorption onto solid phases, biological oxidation and photolytic degradation. In general, aerobic conditions are more effective than anaerobic for cyanide removal. Nitrite and nitrate ions, as well as the great majority of potentially ecotoxic metals (such as Cu), are removed from solution with high efficiencies (>80%). Finally, mineral-based substrates have demonstrated to be more suitable as adsorbents/adsorbents of cyanide compounds than organic-based substrates.

Acknowledgements

We are extremely grateful to Río Narcea Gold Mines S.A. for site access and assistance with pilot plant construction and maintenance.

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