

# PASSIVE TREATMENT OF A CYANIDE AND ARSENIC LADEN PROCESS WATER AT THE RPM GOLD MINE, MINAS GERAIS, BRAZIL<sup>1</sup>

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**Abstract:** The barren water from a hydrometallurgical process at the RPM Gold Mine averages 100 mg/L of total cyanide, 20 mg/L of arsenic, and has a pH of 9.2. Treatment objectives were to reduce to the total cyanide and arsenic concentration to below 50 and 5 mg/L respectively. The concentration of copper in the water is 50 mg/L suggesting that most of the cyanide exists in the complexed form. A bench-scale passive treatment study was conducted that emphasized the use of common sulfate-reducing bacteria reactors (SRBR) for the elimination of the cyanide. For removal of the arsenic, zero valent iron (ZVI), and native lateritic soils were used in combination with the SRBRs. For total cyanide, the SRBRs reduced the concentrations to below 10 mg/L and those reactors with ZVI reduced the cyanide to an average of 5 mg/L. For arsenic, the SRBRs reduced concentrations to between 1.0 to 6.0 mg/L and the SRBRs with ZVI showed the best removal. The lateritic soils worked well in the beginning to lower the pH and to remove cyanide and arsenic. However, their removal ability became exhausted over the course of the six month study. The results show that a passive treatment system using SRBRs in combination with ZVI would be effective as a primary method for removal of cyanide and arsenic from processing waters

**Additional Key Words:** Arsenic, cyanide, sulfate-reducing bacteria, zero valent iron, gold processing waters

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## Introduction

Rio Paracatu Mineracao (RPM), Morro do Ouro Gold Mine, in Paracatu, Minas Gerais State, Brazil is a Rio Tinto open pit mine which has been in operation since December 1987. In late 1998, the company started mining and processing a sulfidic ore (pyrite and arsenopyrite – 1% S and 2500 ppm of As, on average). Environmental impact studies for the mining and processing of the sulfidic ore identified impacts related to this new operation. Consequently appropriate mitigation and control measure were designed and implemented. An in house extensive acid rock drainage (ARD) study, Taboada et al. (1997), determined that low levels of S (0.3% on average) and As (800 ppm) present in the tailings would result in gradual elevation of  $\text{SO}_4^{-2}$  and As levels in the tailings decant water, as the dam filled. As a precaution, the company planned to install an ion exchange plant if concentrations of As and  $\text{SO}_4^{-2}$  in the tailings dam drain water approached the pre-determined safety levels. In addition, the company decided to consider passive treatment as an innovative treatment method. The first phase of this research was a laboratory study conducted at RPM during a 6 week period, starting on March 11, 2000 (Pinto et al., 2001). The research objectives were: to identify materials nearby the mine that would be suitable to be used as a substrate in an anaerobic treatment system; and then determine which substrate mixtures are efficient in the removal of arsenic and sulfate from tailings dam water.

In 2001, it was decided to use the results of the laboratory study to test the removal of cyanide and arsenic in water from the carbon-in-leach (CIL) hydro-metallurgical circuit. Mineral processing at RPM includes crushing, milling, flotation, and hydro-metallurgy for recovery of Au. The tailings from the flotation process are sent directly to the tailings dam and the tailings from the CIL are sent to special holding ponds. In these ponds the solids are settled and the reclaim water is sent back into the plant to recover cyanide (CN) and precipitate As through an acid volatile recovery (AVR) process. The problem, as shown in Table 1, is that As and CN are in sufficient concentration in the CIL water to cause concern for it being held in an open pond due to potential wild life impacts. Thus, the treatment objective for the passive reactors was to reduce the concentration of arsenic to below 5 mg/L and CN to below 50 mg/L in the CIL water, concentrations that are known to provide protection of wild life, particularly water fowl.

Table 1. Concentrations of environmentally important metals and anions in mg/l in the CIL process water.

Parameter	Average Value
pH	9.15
Total CN (mg/L)	101
Total As (mg/L)	19.8
Sulfate (mg/L)	808
Copper (mg/L)	49.6

Nickel (mg/L)	8.19
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Removal of CN in a sulfate-reducing bacteria bioreactor (SRBR) from concentrations of 4 to less than 0.2 mg/L was documented in tailings water from a Au operation in Nevada (Wildman, et al., 1994). However, concentrations of CN greater than 100 mg/L may be toxic to the bacteria. The pH and Cu to CN ratio of the CIL water suggests that the Cu in solution exists as a CN complex. Consequently, treatment objectives for CN include whether the bacteria can handle a high concentration of CN and whether the Cu-CN complex can be broken so that removal is possible. For As, removal of As in an SRBR to concentrations of around 0.4 mg/L has also been documented, but removal to concentrations down to 0.010 mg/L has been difficult (Wildman, et al., 1994). However, in the RPM laboratory study of Pinto, et al., 2001, Fe (ZVI) was included in the usual types of materials that are used in an SRBR and removal was excellent. In addition, the RPM site is in a terrain of lateritic soils, and the Fe and Al oxides should be able to adsorb As from solution. Consequently, treatment objectives for As include how well ZVI can treat high concentrations of As and whether lateritic soils can be used to remove some of the As. This paper presents the results of this bench-scale study.

### **Methods and Materials**

In the laboratory study, the substrates containing alfalfa, begas and sawdust worked well as long as the pH does not decrease below 5, which will inhibit the sulfate reducers. An inocula of local dairy manure worked well, and the ZVI in mixtures of the organic materials worked well. Based on these results the recipes for the reactors shown in Table 2 were chosen. The lateritic soil reactors were tried before and after the reactors, and so the complete configuration of reactors is shown in Fig. 1. Based on the cell recipes and the placement of the laterite cells, answers were sought for the following questions:

- Is removal better with or without ZVI?
- Is removal better with more begas in the system?
- Is removal better if the water flows through the laterite before or after the SRBR?

Table 2. Substrate Compositions for the bench-scale SRBRs.

RPM Bench Scale Test - Substrate Composition					
	CAn-01	CAn-02	CAn-03	CAn-04	Aerobic
ZVI	10.0%	10.0%	0.0%	0.0%	Laterite
Wood Chips	30.0%	30.0%	30.0%	30.0%	
Limestone	20.0%	20.0%	30.0%	20.0%	
Hay	20.0%	10.0%	20.0%	20.0%	
Manure	10.0%	10.0%	10.0%	10.0%	
Begas	10.0%	20.0%	10.0%	20.0%	

The test containers were 200 L barrels for the anaerobic reactors and the same barrels cut open, laid horizontal, and filled with approximately 100 L of material for the laterite reactors. Figure 2 shows the configuration of the first series of cells. The flow through all four systems was set at 10 mL/min and the experiment was run for 6 months from late February to mid-

November of 2003. In June, the aerobic cell in line 2 was removed and replaced with 200 L cell that contained only ZVI. The objective for this change was to see if ZVI alone would be effective at removing CN and As.

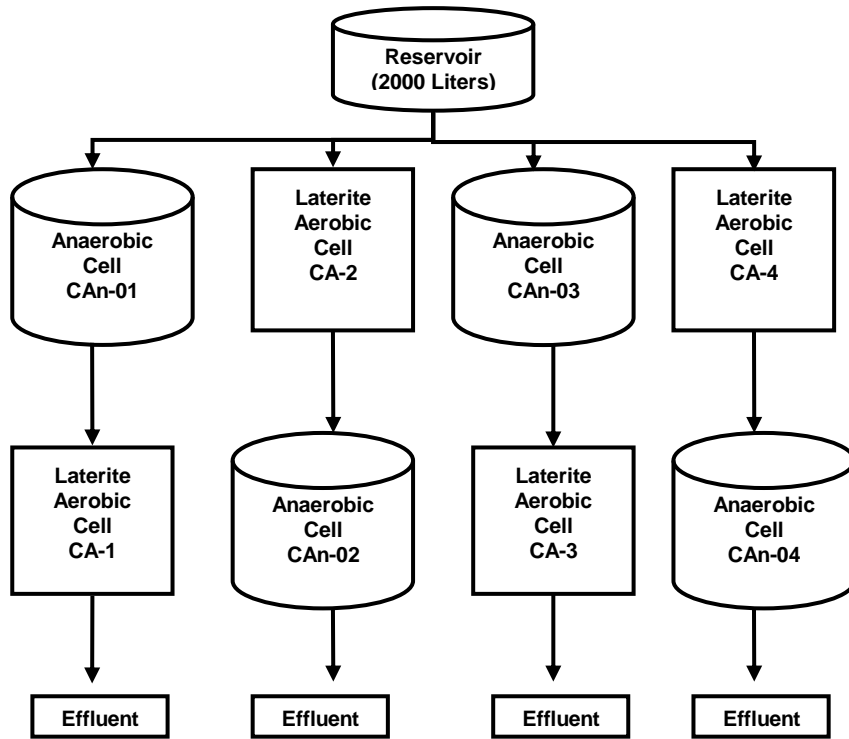


Figure 1. Diagram of the configuration of aerobic and anaerobic cells at RPM.



Figure 2. The first series of cells at RPM. The anaerobic Cell 1 is on the left.

### Results

The average concentrations in the influent and in the effluents from each reactor for each line are given in Table 3. There is an issue in the results in Table 3 with respect to the CN analyses. A total CN analysis was prescribed and all of the analyses were performed in Brazil by a contract laboratory. No analyses of thiocyanate ( $\text{SCN}^-$ ) were done and quality control on the cyanide analyses were lacking. Thus there is some uncertainty in the results.

Table 3. Average concentrations of constituents in mg/L over six months in the influent and effluents in the RPM reactors. An. Means Anaerobic, Aer. Means aerobic, and the cells for each line are in order.

		Line 1		Line 2		Line 3		Line 4	
	Influent	Effluent An. 1	Effluent Aer 1	Effluent Aer. 2	Effluent An. 2	Effluent An. 3	Effluent Aer. 3	Effluent Aer. 4	Effluent An. 4
<b>pH</b>	8.6	6.8	7.6	8.0	7.0	6.8	8.0	7.9	6.8
<b>CN<sup>-</sup></b>	68	38	32	77	44	54	51	58	55
<b>As</b>	83	8.2	5.9	23	7.3	26	26	75	30
<b>SO<sub>4</sub><sup>=</sup></b>	914	398	857	952	440	602	950	1100	587
<b>Cu</b>	61	1.8	1.8	14	4.9	3.5	12.4	42	6.3
<b>Fe</b>	3.29	10	6	10.4	10	9.0	6.8	2.2	3.6
<b>Ni</b>	9.4	0.85	0.60	5.9	1.4	2.4	2.7	9.0	3.1

Most of the averages given in Table 3 are representative of the week to week removal results. However, for CN, there was a decreasing trend in the influent concentration for an average of 150 in the first two months to an average of 30 in the last two months. Also, for the reactors that contained ZVI, there were high concentrations of iron (~ 100 mg/L) in the effluent in the first month.

### Discussion of Results

#### pH

The effluents from the SRBRs had an average pH of 6.8, and this is probably because of the begas in the reactors, which is a potent source of low molecular weight organic acids. However, there was a trend of increasing pH over the course of the study so that the pH issuing from the anaerobic reactors was averaging about 8 at the end of the six month study. For the laterite cells, pH was slightly reduced in the beginning of the study but after four months, the laterite cells had no effect on the pH of the CIL water. This trend in pH is disturbing because a lower pH is better for adsorption of As onto the lateritic soils and forming hydrocyanic acid, which will aid in the

removal of CN in solution. Also, if the pH of the anaerobic cells increased to 9, the activity of the sulfate-reducing bacteria might be impaired.

### Arsenic

Arsenic removal was good, particularly in Lines 1 and 2 where the average influent concentration decreased from 83 to 5.9 and 7.3 respectively. The anaerobic cells were responsible for almost all of the removal especially in Lines 1 and 3 where the anaerobic cell preceded the aerobic cell. In Line 4, where the aerobic cell preceded the anaerobic cell removal by the laterite was about 90 % in the first month. But then, as the pH of the laterite decreased, removal decreased until the aerobic cell was not functioning after six months. Apparently, all adsorption sites were used after 2 months. If the laterite is used for arsenic removal, it should be placed after the anaerobic cell and considered a polishing system.

On Line 2, after 2 months, the aerobic cell was replaced by a 200 L vertical flow ZVI cell. Removal of As was immediate and the ZVI cell was as efficient as the anaerobic cell in removing As throughout the remainder of the study. In Lines 3 and 4, where there is no ZVI, As removal was noticeably less efficient. Consequently, even at high concentrations of As, ZVI, either alone or included in an SRBR, is best at removing As from water. However, to reduce the concentration of As to drinking water concentrations, another series of removal cells will be necessary.

### Cyanide

Besides the uncertainty in the analyses, removal of CN was confused by the influent concentration changing from over 150 to less than 50 mg/L over the course of the six month study. The anaerobic cells consistently removed CN and those cells with ZVI removed more CN than those without ZVI. However, in Line 2, when a cell with all ZVI was installed, CN removal did not occur within the cell. On the other hand, in the anaerobic cell after the ZVI cell, removal of CN was abrupt and much better than before with the laterite cell. For Lines 3 and 4, where there was no ZVI, CN removal was not as complete. Consequently, although it is not apparent that ZVI alone can remove CN, it certainly does aid in removal. It may be the case that Fe-CN complexes are formed and this could be a reason for better removal of Cu and Ni. With respect to using laterite for CN removal, again in the beginning of the study, when the laterite was capable of decreasing the pH, CN removal occurred. But at the end of the study no removal was occurring. This may be because early in the study the laterite changed the CN to the molecular acid and volatilization occurred.

In conclusion, the following observations can be made concerning cyanide removal:

- ZVI promotes CN removal in the anaerobic cell.
- ZVI alone does not cause CN removal but does change the chemistry of the water so that removal is easier in the anaerobic cell.
- The laterite soil removes CN as long as the pH is reduced as the water flows through the soil. Once the capacity for pH reduction is spent, removal apparently ceases.
- The cell sequence anaerobic- aerobic removal appears to remove CN better than the reverse sequence.

### Sulfate

Reductions in  $\text{SO}_4^{-2}$  concentration are the best indication that the SRBRs are acting properly, and for all four of the anaerobic cells sulfate concentrations were reduced throughout the study. Again, for Lines 1 and 2, which contained ZVI,  $\text{SO}_4^{-2}$  reduction was noticeably better than in Lines 3 and 4. The laterite cells had no effect on the concentration of  $\text{SO}_4^{-2}$ . In Line 2, when the ZVI cell was installed,  $\text{SO}_4^{-2}$  behaved in a similar fashion to CN. That is, the ZVI itself did not remove  $\text{SO}_4^{-2}$ , however, in the following anaerobic cell,  $\text{SO}_4^{-2}$  reduction was immediate and was slightly better than in any of the other anaerobic cells.

### Copper and Nickel

Copper is easily removed in SRBRs (Gusek, et al., 2005, Wildeman and Schmiermund, 2004), but in this process water it is undoubtedly complexed with CN, and its removal is less certain. What is found is that, consistent with how other parameters changed, Cu was removed in all of the anaerobic cells; however, its removal was better in the cells that contained ZVI. In the anaerobic cells, Cu removal was consistent throughout the study. The cell with ZVI alone did remove over 50 % of the Cu, and the laterite removed between 25 to 50 % of the Cu. All of these results imply that destroying the Cu-CN complex is not difficult.

Nickel sulfide is more soluble than  $\text{CuS}_2$ ; also Ni-CN is a stronger complex than  $\text{CuS}_2$ . Consequently, its removal is an indication of how well the SRBRs are functioning. In addition, Pinto (2004) found that ZVI removes Ni in the form of a magnetite compound. In this study, anaerobic cells with ZVI were best at removing Ni. The cell with ZVI alone removed between 25 to 50 % of the Ni. In Line 4, where the laterite preceded the anaerobic cell, no Ni removal was achieved. However, when the laterite followed the anaerobic cell (Lines 1 and 3) some polishing of Ni to lower values was achieved. These results suggest that an SRBR with ZVI is better at removing Ni than ZVI alone.

### Conclusions

One of the objectives in the formulation of the cell recipes was whether a larger amount of begas would aid in the operation of the SRBR. Observation of the pH changes in the four lines suggests that the anaerobic cells with more begas maintained lower pH's. However, the performance of Lines 2 and 4 that had the greater amount of begas was not substantially better. On the other hand, inclusion of ZVI in the SRBR cells definitely improved performance. Using the laterite cell before the anaerobic cells did not improve performance. Laterite cells after the anaerobic cells did help polish contaminants to lower concentrations. Based on the reduction in  $\text{SO}_4^{-2}$  concentration, it appeared that the anaerobic cells were still performing well after six months. However, the trend towards increasing pH in all of the lines strongly suggests that an optimum treatment configuration be tried on a pilot scale basis for a period of a year to make certain that removal can be maintained over longer periods of time. A pilot system could also test survival of the bacterial ecosystem over a longer time period.

The objective of making water with less than 50 mg/L of CN and 5 mg/L of As can be met using passive treatment. It also appears that breaking metal-CN complexes in an anaerobic cell is not a problem. However, an optimum design of a ZVI cell followed by a SRBR cell that also contained ZVI should be used to insure that these treatment objectives are met all of the time. Based on the results of this study it would not be possible to meet drinking water or aquatic life standards using only this treatment system, however, wild fowl protection is possible. A polishing system would have to be developed to remove more cyanide and arsenic. For this, a

shallow aerobic wetland or a ground infiltration system using lateritic soil is worthy of consideration.

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