

In-Pulp Treatment of Dissolved Arsenic from a Gold Mine

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Abstract

Aurizon Mines Ltd., Casa Berardi, is a gold mine located approximately 3 hours north of Rouyn-Noranda, in Québec. The gold is recovered through conventional cyanide leaching and carbon-in-pulp technology. The tailings are then deposited in a tailings impoundment area with separate cells, a settling pond, and a process water pond for recycling water and for final discharge. In the leaching process, some arsenic is liberated. For the past few years, the settling pond in the tailings impoundment area was used for treatment of residual arsenic through co-precipitation with iron hydroxides. With a new tailings cell and with closure planning, it was determined that upstream treatment would be advantageous if possible. An extensive laboratory study was completed to optimise in-pulp ferric treatment of the arsenic in order to co-precipitate the arsenic and dispose of it with the tailings. The treatment is currently being applied at full-scale. This paper details the experimental design results, describing the dominant factors involved in controlling the arsenic concentrations during in-pulp treatment. The full-scale results are also presented showing successful treatment of arsenic without a dedicated treatment plant.

Introduction

Aurizon Mines Ltd. is a Canadian based gold producer, exploration, and development company. The Casa Berardi mine is situated 95 kilometres north of La Sarre, Québec and straddles a 37 kilometre section of the Casa Berardi fault. Between 1988 and 1997, approximately 690,000 ounces of gold were produced from two underground mines, approximately 5 kilometres apart, in the central portion of the property. Aurizon acquired a 100% interest in the property in 1998 and conducted deep exploration drilling in the area of the West Mine, which was successful in discovering several new gold zones. Of particular importance was the discovery of Zone 113, in the West Mine area, which contains high grade gold mineralization in quartz veins and forms the core of the current mining operation.

From 2004 to 2006, Aurizon developed new underground infrastructure, constructed surface facilities, and rehabilitated the milling facility and fleet of mining equipment, resulting in the commencement of production in November, 2006. It now operates at 2,000 tons per day. Casa Berardi Mine entered its fifth year of commercial operations in 2011 and is expected to continue operations for at least another 10 years.

The tailings are disposed of in the same tailings facility opened by the original owners in 1988. This facility is broken down into different cells, as described in Figure 1. The first cell used in the original operations (Cell #1) is actually located between cells #2 and #3. The current flow in the tailings facility is (from top to bottom): Cell #2, Cell#1, Cell#3, Old Polishing Pond (PP), Cell #4, New Polishing Pond, and Process Water Pond. This study was completed in 2008 and 2009, before construction of Cell #4 and the New PP which were built in 2010. At the time, the tailings most often were discharged into Cell #2, but tailings placement in other cells also occurred, depending on the filling stage and operational concerns.

The tailings impoundment includes a large water pond used for recycling water to the process (Process Water Pond). The runoff and process water discharge from the mine site is from this pond, as indicated in Figure 1 (identified as “DISCHARGE”). The discharge point is located in close proximity to the recycle pump house. In 2008, the arsenic concentrations in this pond were approaching the discharge limit of 0.5

mg/L. This initiated a study lead by the authors, to first identify the source of arsenic and optimise control.

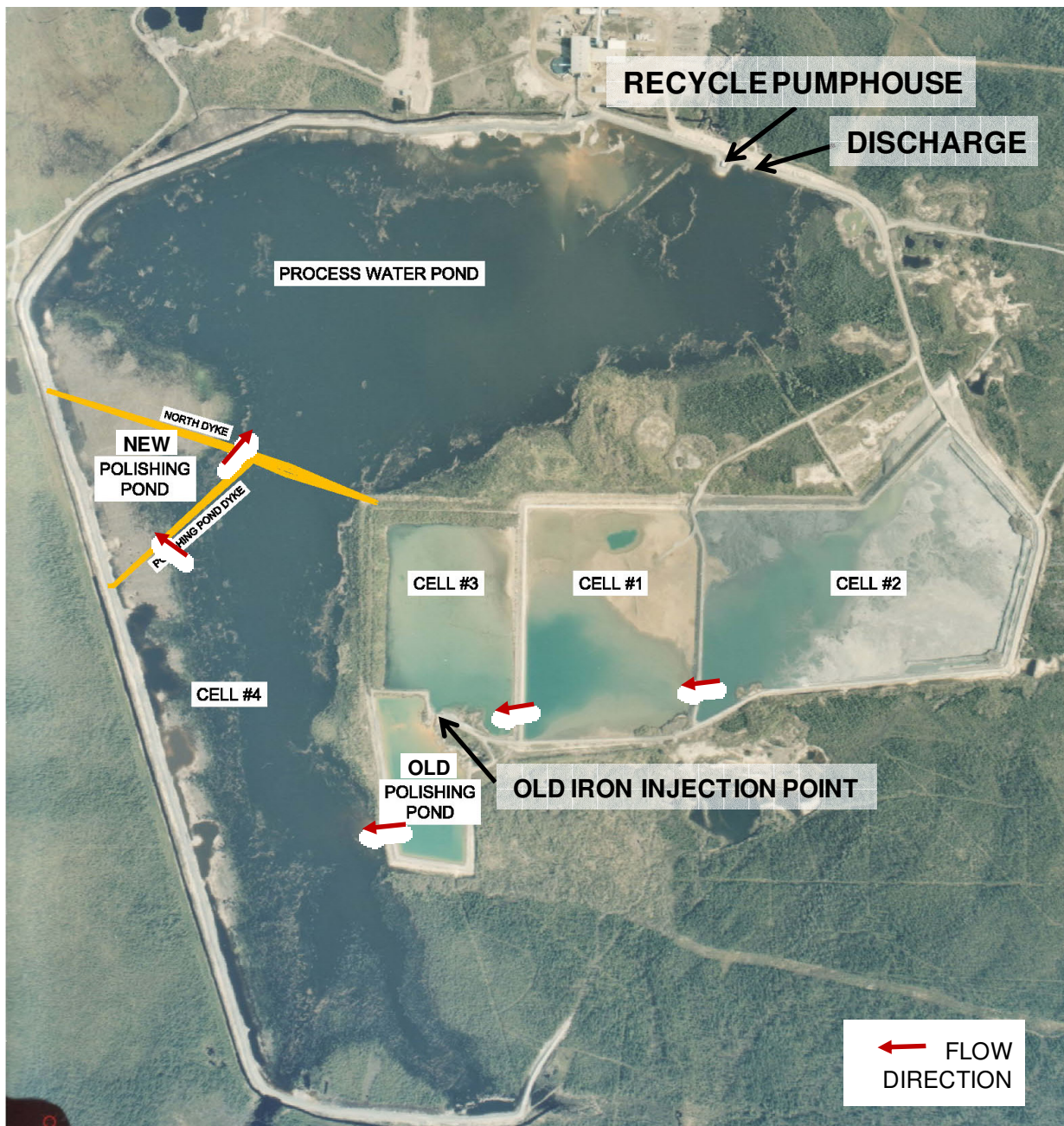


Figure 1: Casa Berardi Mine Tailings Disposal Facility

Mass Balance

Casa Berardi maintained an excellent database of metal concentration at many site locations. This chemistry database was combined with flow data from all locations (Figure 2) and a detailed mass balance of As in the pond system was completed within dotted line in Figure 2. The mass balance spanned 21 months, from January 2008 to September 2009. Note that the new dams shown as yellow

Arsenic Treatment Theory

There are many different technologies in use for treatment of dissolved arsenic (As) either for potable water use, or for environmental release. These treatment options include precipitation/co-precipitation, membrane technologies such as reverse osmosis, adsorption treatment, ion exchange, and permeable reactive barriers (US EPA, 2002). Arsenic can be removed as a calcium arsenate [$\text{Ca}_3(\text{AsO}_4)_2$] at very high pH but this precipitate is not very stable. The most widely used technology, co-precipitation of As with iron, is discussed in this paper.

Treatment of arsenic using co-precipitation with ferric iron is a proven technology applied in many situations where As must be removed from solution. Hydroxide precipitation of base metals such as copper and zinc has also been known to adsorb As. In all cases, oxidation of As(III) to As(V) can improve treatment efficiency and the production of a stable sludge. Many oxidants can be used with varying costs and degrees of effectiveness.

When treating with ferric iron, it is sometimes necessary to have a two-step process which precipitates most of the As at a slightly acidic pH (4 to 5), followed by a pH increase. Co-precipitation at a low pH is more efficient and can form a more stable precipitate (ferric arsenate) than at high pH where adsorption is most likely. When using a clarifier for solid/liquid separation, a sludge recycle can be used to increase treatment efficiency. This can result in significant savings in reagent addition but can also cause the arsenic to be mostly adsorbed as opposed to co-precipitated. Adsorbed arsenic is slightly less stable than when it is co-precipitated as a ferric arsenate. An excess of iron can be applied with any process to improve sludge stability. The final sludge disposal system can weigh into the decision as to whether or not a recycle is applied and what ratio of iron to arsenic is to be used.

For treating clear water at a slightly acidic pH, a molar ratio of Fe to As of 3 to 1 could bring the As concentrations down to the discharge limit. With neutral water, a ratio of up to 10 to 1 may be necessary to remove the As from solution (Aubé and Bernier, 2008). Tests completed on the clear water overflow from Cell #3 showed that an iron to arsenic ratio of 7.5:1 could bring the As concentrations down below 0.2 mg/L at this point.

Arsenic Treatment at Casa Berardi

Figure 2 shows different ferric sulphate injection points as blue squares in the diagram. Prior to 2009, ferric sulphate was injected at Fe 2 and Fe 3, but Fe 1 is a new injection point resulting from this study. The main point of arsenic control prior to this study was by ferric addition in the transfer ditch between Cell#3 and the Polishing Pond. The resulting ferric hydroxides produced from dosing ferric sulphate removed As from solution by either co-precipitation or adsorption. The solids formed then settled in the Polishing Pond. This system could control arsenic concentrations efficiently but was difficult to operate as there is no power available at this location. The remote location of this addition point and the “gravity feed” approach resulted in a system which was not as reliable as desired.

The mine water, where the Fe 2 addition point is located, did not contain significant concentrations of arsenic even before treatment. The pre-treatment dissolved arsenic concentrations were normally less than 0.3 mg/L. After iron addition, the arsenic concentrations were less than 0.2 mg/L.

Since the mass balance proved that the source of dissolved arsenic was from the mill, a study was initiated to see if it was possible to remove the arsenic from solution prior to tailings deposition. A series of tests were designed, starting with scoping tests to see if the arsenic could be removed. This was followed by a detailed design of experiments to define the effects of various critical parameters (factors). The treatment point selected was located immediately after the cyanide destruction system by the INCO-SO₂ Air technology. The tests were completed using the slurry (or pulp) collected at the final tailings pump box. During normal operations, the cyanide concentrations at this point are low.

Laboratory Testing Methods

The method used for treatment was to collect a sample of tailings slurry (or pulp), to add a pre-set dosage of ferric sulphate, mix the sample for 5 minutes, than allow settling for 24 hours. Samples were taken for dissolved arsenic both on the initial pulp and after the 24 hours of settling. These samples were also analysed for many other parameters, including Fe, CN, and Cu.

In many cases the pH was controlled, but in all cases, it was monitored. Control was completed using sulphuric acid to decrease the pH or lime to increase the pH. The temperature and redox were also measured. Slurry solid content was normally measured as well. As many tests could be completed in a day, a 20-L bucket was used for sampling and analysis of the initial conditions. Several tests were then completed and allowed to settle overnight prior to sampling, as shown in

Figure 3. Overall, 141 tests were completed over nearly one year of testing.



Figure 3: Arsenic Treatment Tests after Settling Overnight

Note that the ratios calculated and reported throughout this paper apply the concentration of arsenic to the entire volume of slurry, as opposed to the water portion only. This means that the actual molar ratios are approximately 30% higher than those reported here. This was done for simplicity in testing and interpretation of results. This is discussed in greater detail in the section on design parameters.

Laboratory Testing of In-Pulp Treatment

According to a number of samples collected prior to testing, the average dissolved arsenic concentration in the pulp was near 15 mg/L. The first scoping tests were completed assuming this was the concentration. These provided some indication that treatment was possible, but the results were not conclusive due to some success and some failures without knowing the reason for response. It was then decided that a rigorous design of experiment (DOE) was necessary.

The DOE objective was to determine the major effects of many parameters on arsenic treatment efficiency, including: Fe:As ratio, pH and Two-step pH, CN concentration, Mixing intensity, Retention time, and Aeration.

The target arsenic concentration for a successful test was set at 0.4 mg/L. This was chosen as the current limit is 0.5 mg/L at the effluent, but it may change to 0.2 mg/L of arsenic, as per the updated Directive 019 in Québec. When considering the average yearly precipitation in the ponds, there is 4 times as much water being discharged from the pond system, as compared to the water from the tailings, indicating that three quarters of the water discharge is from precipitation. This means that 0.4 mg/L in the slurry would result in an arsenic concentration of 0.1 mg/L in the final effluent.

Several DOE's were designed and carried out. These were based on the results of previous tests and sometimes were duplicated due to failure in attaining the desired setpoints. The greatest challenge in completing these tests was attaining the setpoint ratio of iron to arsenic. The problem is that proper treatment must not allow for aging of the samples as the slurry conditions coming out of the INCO-SO₂-air system are not at equilibrium. To ensure that treatment was representative, the tests were always done on a sample collected the same day. Unfortunately, there were no means on-site to measure arsenic concentrations rapidly. A desktop colorimeter system was used at times, but found to be inaccurate. Over the complete 141 tests, the dissolved arsenic concentration in the initial pulp varied from 6 to 25 mg/L, with an average of 12.3 mg/L. The variability was also quite rapid as the concentrations could change by 5 mg/L (or more than 30%) overnight. Taking samples on the evening prior to testing therefore proved to be inadequate as well. This led to the ratio often being far off the desired setpoint.

Figure 4 shows the initial arsenic concentrations measured for all tests completed.

Figure 5 shows the actual Fe:As ratios attained versus the desired setpoints.

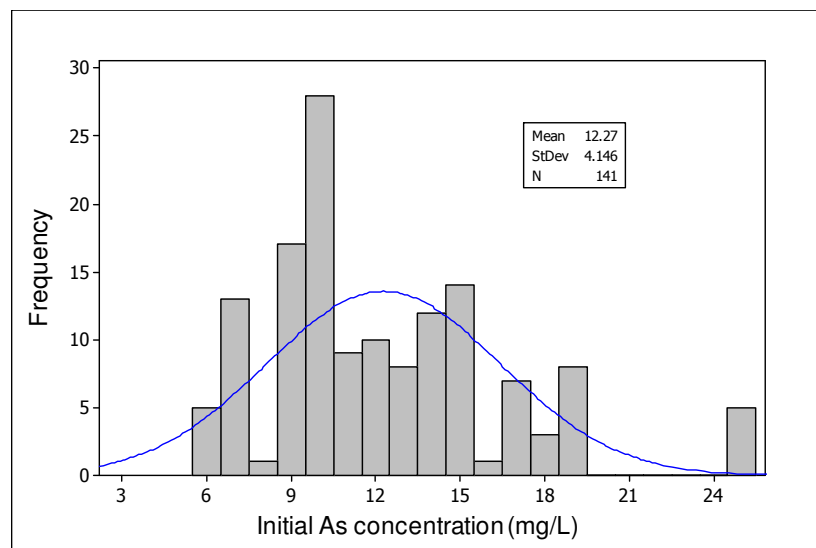


Figure 4: Distribution of Initial Arsenic Concentrations over the 141 Tests

There were also some difficulties due to variability in the efficiency of the cyanide destruction system. Occasional inefficiencies in this system were not critical to compliance as natural degradation in the pond system would remove residual cyanide to well below discharge limits. But as it will be shown in the results, the cyanide concentration affects arsenic treatment. Also, the pH was not always properly controlled as for two sets of tests, quicklime was used instead of hydrated lime and this resulted in a continuous increase in pH beyond the desired setpoint.

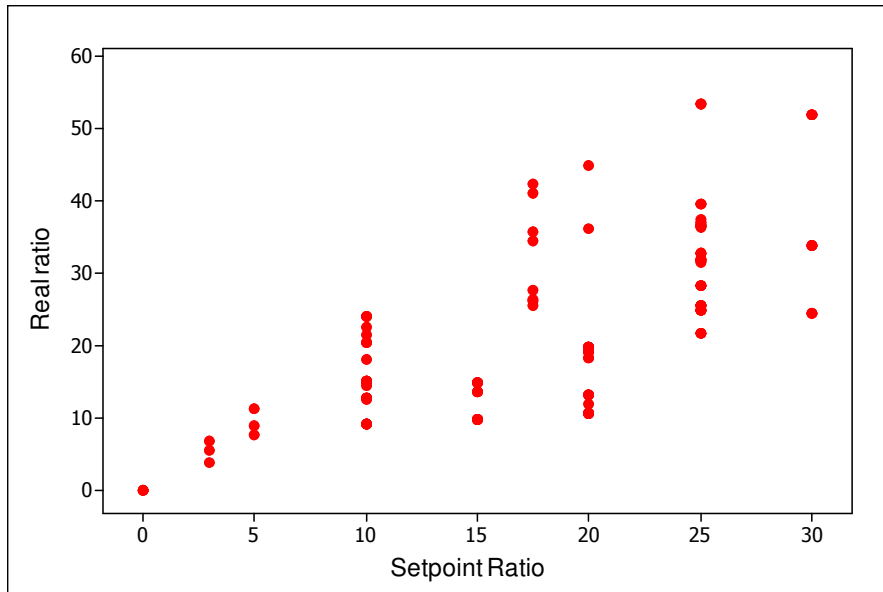


Figure 5: Real Fe:As Ratios Attained as a Function of the Setpoint Ratios

These difficulties in attaining the test setpoints made interpretation of the DOE results complex. In order to obtain bases for comparison, the results were grouped and ranges were used to describe certain concentrations. The values used for most interpretations are given in Table 1. This allowed for application of averages for a number of tests and thereby the use of typical DOE graphs.

Table 1: Values Used to Represent Ranges for DOE Interpretation

pH		CN (mg/L)		Ratio Fe: As	
Range	Value	Range	Value	Range	Value
< 8.5	8.25	<2	1	<12.5	10
8.5-9.0	8.75	2.5-5.0	3.5	12.5-17.5	15
9.0-9.5	9.25	5.0-10	7.5	17.5-22.5	20
9.5-10.0	9.75	10-20	15	22.5-27.5	25
10.0-11.0	10.5	>20	25	27.5-32.5	30
>11.0	11.5			>32.5	35

Laboratory Results – Ferric to Arsenic Ratios

The greatest effect measured was clearly the ratio of iron added to initial arsenic concentration. This is illustrated in Figure 6, as very high ratios result in low average arsenic concentrations. Unfortunately, ferric sulphate is expensive and to maintain ratios of 40 or more would be cost-prohibitive. A similar trend is seen in Figure 7, which shows the result of every specific test as a function of the actual ratio.

It is clear in

Figure 7 that there is significant variability for a given ratio. For example, with a ratio of 20:1, resulting arsenic concentrations vary from detection limit to 3.6 mg/L. This indicates that there are other factors that are also important. Before defining the effects of these other factors, some data can be removed from the series to simplify interpretation. It is clear that below a ratio of 10 to 1, there were no results that met the target of 0.4 mg/L. Although very high ratios seem to work well, the cost of controlling ferric addition to ratios of more than 40 would be completely cost-prohibitive. Therefore all tests with ferric addition ratios of less than 10 and more than 40 were removed from the database prior to detailed interpretation.

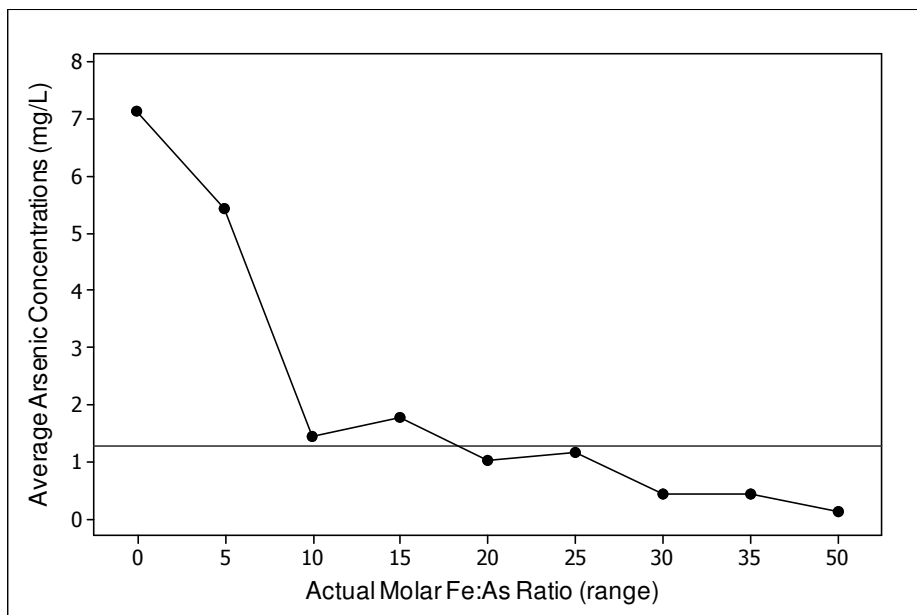


Figure 6: Average Treated As Concentrations vs. Fe:As Ratio

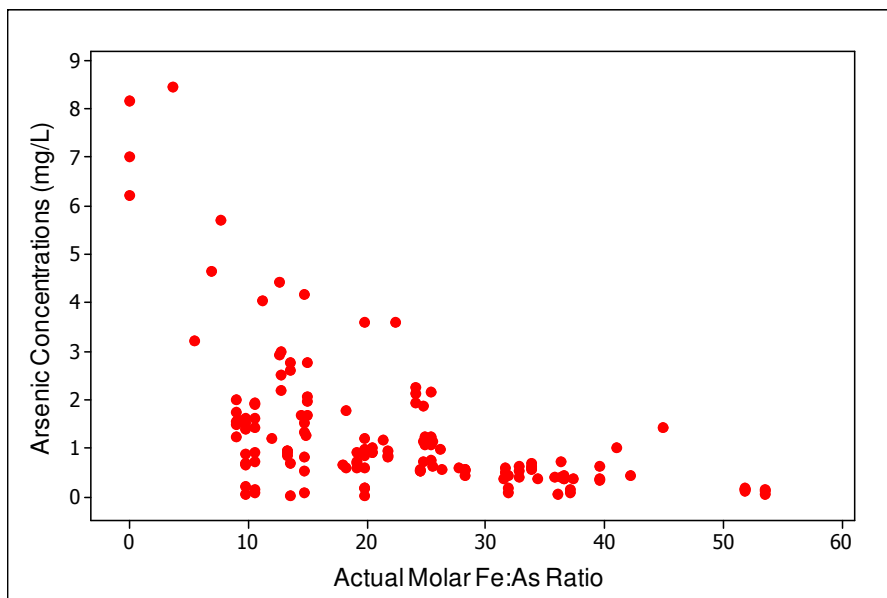


Figure 7: Arsenic Concentrations versus Actual Molar Ratios

Effects of pH

As with the ratio, a graph of all results shows a definite trend despite significant variability. It is clear that lower pH values improve treatment efficiency. Note that there were also two-step processes where the pH was increased after treatment. The two outlying arsenic concentrations near 4 mg/L at a pH of 4 are a result of this two-step process. It seems that the worst pH values are near 8 to 10.5 as the results improve at very high pH values. These higher values are suspected to be as a result of calcium arsenate precipitation. This is an unwanted precipitate as it is unstable and would be subject to redissolution in the

pond system. On the contrary, the ferric arsenate precipitates purposely formed with this treatment method are known to be quite stable.

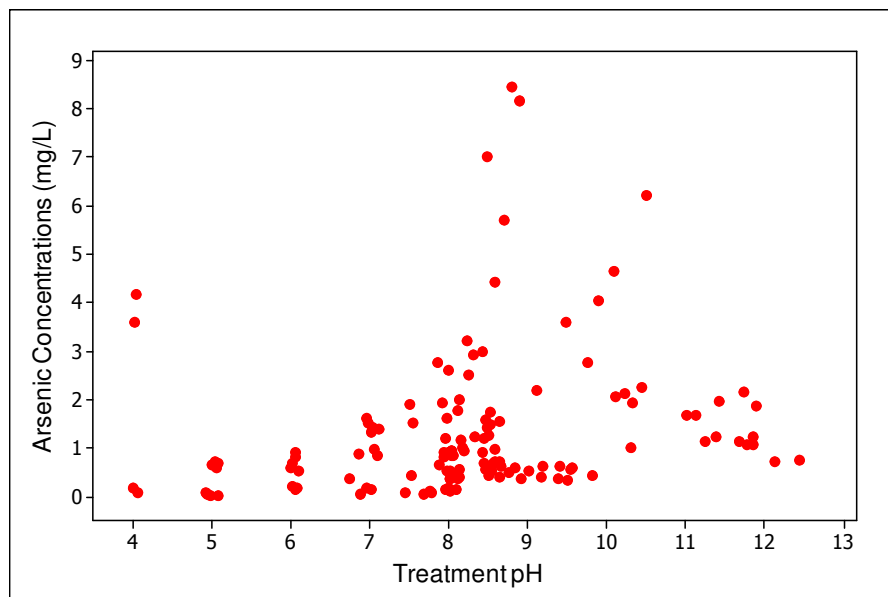


Figure 8: Arsenic Results as a Function of pH

Only one test with a pH of 9.5 or more met the objective of 0.4 mg/L arsenic and this test had a ratio of 40:1. It is clear that pH values of more than 9.5 are detrimental to the proper treatment of arsenic. For detailed interpretation, the tests with pH values of more than 9.5 were removed from the database.

Effects of Cyanide Concentration

To properly evaluate the effect of cyanide concentration,

Figure 9 was produced excluding tests with pH values of more than 9.5 and excluding tests with extreme ratios (<10 and >40). Each point on the graph represents the average of all tests that meet the indicated ratio range and CN concentration range. In some cases, a point represents only one test while other points represent the average of several tests.

Figure 9 shows that the CN concentration has a very strong influence on the efficiency of treatment when the Fe:As ratios are of 10 or 15 to 1. This effect is much less pronounced when the ratios are as high as 35 to 1. This can be explained by a reaction between CN and Fe forming iron cyanide complexes which then renders some of the iron unavailable for co-precipitation with arsenic.

Other Effects

Also included in the DOE interpretation were the responses to mixing intensity, retention time, and aeration. Aeration results were inconclusive. If there is an effect, it is not very pronounced. Mixing intensity and retention time showed no effect at all when in the normal operating ranges. Retention time did show a negative effect at very high pH values, but this will not be a desired operating condition.

Effects on Other Parameters

The arsenic concentration was the main parameter measured and the one where a specific objective was set. The concentrations of other potential contaminants were also measured throughout the tests. These

parameters include iron, copper, and cyanide concentrations. Effects were measured and interpreted and some issues were identified with high copper or iron concentrations. Essentially, if the initial CN concentration is controlled within a reasonable range and the pH is maintained neutral to slightly alkaline, there should be no issues with other parameters.

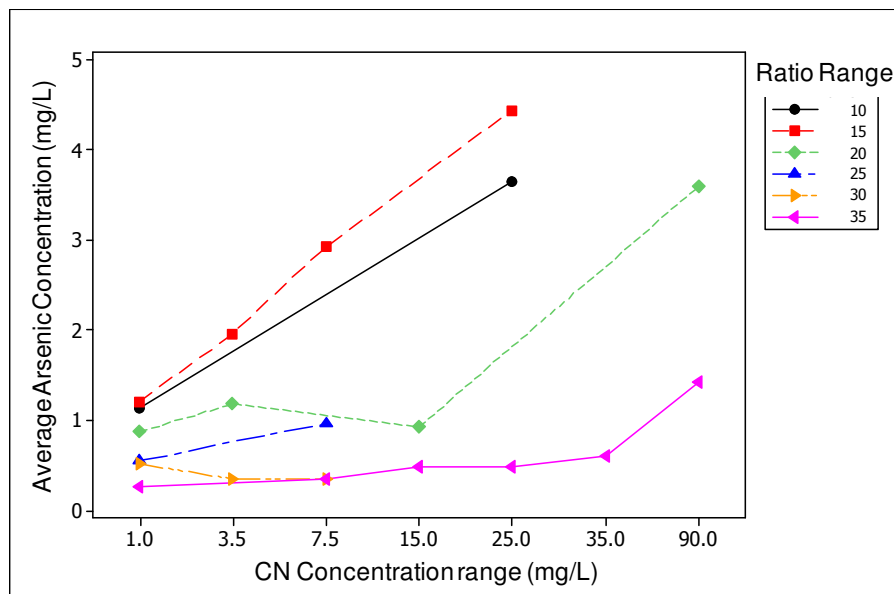


Figure 9: Average Arsenic Concentrations as a Function of CN Concentration and Ferric Ratio

Design Parameters

There were 21 tests that met the objective of 0.4 mg/L arsenic. After removing tests with elevated final concentrations of iron, copper (acidic conditions), or CN, 11 successful tests remained. These are illustrated in Figure 10 as a function of pH and ratio. The pH is currently controlled for cyanide destruction using the INCO SO_2 -air process. This process can operate at lesser pH values without negatively impacting the CN destruction process. The only significant operating cost for the removal of arsenic is therefore the ferric sulphate.

Figure 10 shows that the ferric sulphate consumption rates (and therefore costs) are clearly higher at higher pH values.

One point to be made in the full-scale design of this treatment system is that this entire study was completed using concentrations and slurry volumes while disregarding the solid content of the slurry in the dosages. This means that the real molar ratios are higher than those illustrated here and discussed throughout this document. The pulp (tailings slurry) normally contained approximately 45% solids. Taking into account the specific gravity of the solids, this means that 1 litre of slurry contained approximately 0.77 L of water. Applying this fraction to all results indicates that the actual molar ratios were higher by 30%. This practice was made for simplicity in testing and interpretation. It will also be simpler to operate using this off-set in the full scale as the volumetric flowrate of tailings can be measured on-line and used to control the ferric addition rate.

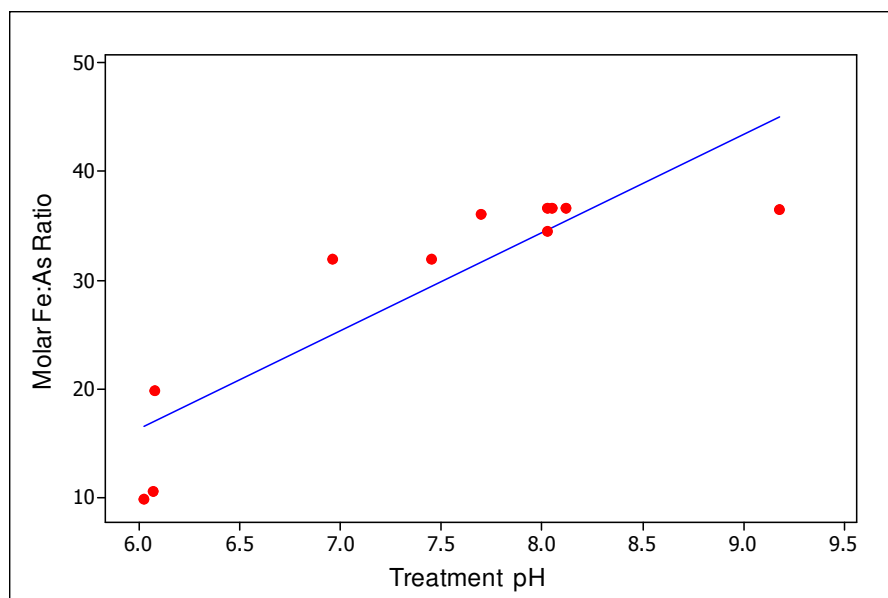


Figure 10: Fe:As Ratios and pH Values of Successful Tests

Applying the offset discussed above indicates that the best actual molar ratio (Fe:As) that successfully treated the arsenic was of approximately 13:1 (as opposed to the reported 10:1). This is considerably higher than the ratios obtained at other locations, even in neutral pH conditions. As this was a practical study, the precise reason why this occurs was not reviewed, but it could be postulated that the high solid contents from the tailings interfere with the co-precipitation process. Suffice it to say that when treating arsenic in the Casa Berardi tailings slurry with neutral to alkaline pH conditions, molar ratios of at least 13:1 are required to meet an objective of 0.4 mg/L arsenic.

Full Scale Treatment

As a result of the laboratory study, it was recommended that a reactor with pH control and ferric sulphate addition be implemented in the full scale. A ferric sulphate addition system had already been put in place at the mill during the study because the results showed promise. This simple system consists of a reagent pump feeding a ferric sulphate solution to the tailings pump box. Mixing is completed through turbulence in the pump box, by the pump itself, and in-line on the way to the tailings deposition. Approximately 3 litres per minute of ferric sulphate is currently being added in this way. Samples are taken regularly at the feed to the tailings pump box and near the outlet of the tailings pipe.

In the first 10 months of 2011, the average concentration of dissolved arsenic in the tailings pulp before iron addition was 8.1 mg/L. Just before discharge in the tailings cells, the average dissolved arsenic concentration for 2011 was 0.6 mg/L. This falls short of the target of 0.4 mg/L but still means that 93% of the arsenic was treated in the preferred manner.

The daily tonnage throughput at the mill varies, which means that the amount of solids and water going to tailings can be different from day to day. During the study, the tonnages were relatively steady near 1800 tonnes per day. In 2011, tonnages as high as 3000 t/day have been achieved. These tonnages can also be down to 1800 t/day at times. These variations, along with the changes in arsenic concentration make it difficult to control the Fe:As ratio.

In order to ensure that the arsenic concentrations in the Process Water Pond (Figure 1) are maintained low, there continues to be ferric sulphate addition in the pond system, at the feed point to the new

polishing pond. The dosages here are not very high as the arsenic concentrations are low. The arsenic has been efficiently controlled since the beginning of this study. Overall, the arsenic concentration in the Process Water Pond has been maintained below the discharge limit of 0.5 mg/L and is normally less than 0.2 mg/L.

Treatment Optimisation

In order to improve arsenic treatment and reduce ferric sulphate consumption rates, a reactor should be put in place before the tailings pump box. A twice daily sample with rapid analysis of dissolved arsenic concentrations would help improve the ferric addition rate based on recommended ratios. This analysis could be completed by the site laboratory using atomic adsorption. The actual flowrate of pulp should be used in conjunction with this concentration to define the total flux of arsenic. The ferric addition can then be controlled to obtain a known ratio. An improved pH control system, preventing any excursions above pH 8.5 would also improve treatment results.

If all of the above recommendations are put in place, the secondary ferric addition at the feed to the new Polishing Pond could be discontinued.

Conclusion

A study completed at Aurizon Mines Ltd., Casa Berardi Mine showed that it is possible to treat arsenic in the tailings slurry before deposition of the tailings. This allows for the arsenic to be stabilised with the tailings from the mine and removes the need for additional sludge management. An iron to arsenic molar ratio of about 13 to 1 is required to properly treat the dissolved arsenic in-pulp. This ratio is significantly higher than normally required for treating arsenic in clear waters. Despite this disadvantage, the in-pulp treatment system eliminated the need to build a separate treatment plant specifically for arsenic removal. The fact that the arsenic is treated and stabilised within the tailings pores also represents a significant advantage for long-term sludge management.

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