# Bioreactor for Passive Treatment of ARD at Tulsequah Chief

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## Abstract
A limestone-based bioreactor was tested at the bench and pilot-scale to treat ARD at the Tulsequah Chief underground mine. The pilot scale bioreactor was built inside the 5200 level drift and operated for 8 months. It removed Al, Cd, Cu, Fe, and Zn passively at 6-8ºC from pH 3.3 water when supplemented with ethylene glycol. Using this information, a 4-cell, 100 m long limestone-based bioreactor was constructed inside the 5200 level adit to treat the mine water. Neutral mine water, supplemented with a passive NaOH feed, was blended with the acidic mine water in a settling area to promote iron removal. This water was directed to a series of three downflow limestone cells to raise water pH and remove Al, Cu, and Fe. An additional cell was operated as downflow SRB bioreactor to remove Cd, Cu and Zn. This temporary system was designed to operate for two to five years, including unattended winter operation for periods of 3-6 months.

Although the bioreactor discharge was not free of metals, it enabled the company to continue its exploration program and proceed to feasibility design of the mine. The paper provides design details, monitoring results and lessons learned for future applications.

Key Words: acidic drainage, passive treatment, bioreactor, cold climate

## Introduction
The Tulsequah Chief was an underground, polymetallic (Au/Ag, Cu, Pb, Zn) mine abandoned in the late 1980's. The property is located in northern British Columbia, in the remote mountains of the BC-Yukon border (Figure 1).

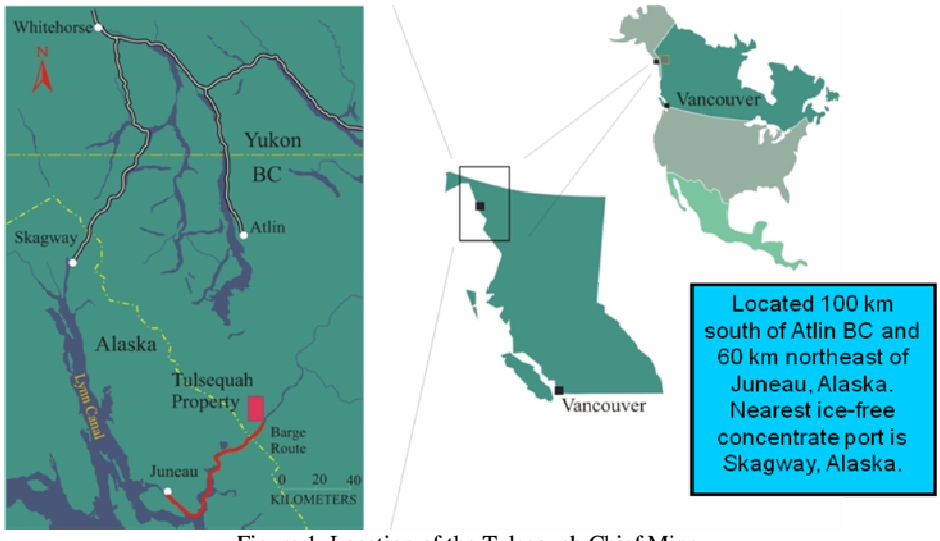



Figure 1. Location of the Tulsequah Chief Mine.

The mine was dug inside Mt Eaton, with the massive sulphide deposit dipping steeply downward. The ore was mine through several levels and extracted through portals at the 5900, 5400 and 5200 levels. When the mine was abandoned in 1989, broken chalcopyrite was left in an open stope, which produced metal-contaminated acid rock drainage (ARD) that flowed into the Tulsequah River. Historic water quality is shown in Table 1. "Mine Water" is collected inside the underground workings and is the most acidic water

at the site. “Portal Discharge” is water below the 5200 portal and represents a combination of acidic adit water and neutral groundwater. The data for presented in Table 1 show that mine water is strongly acidic and it contains several metals that exceed acceptable environmental limits, including aluminum, cadmium, copper, iron, and zinc.

Table 1. Historic water quality inside the mine and at the portal discharge.

| Parameter | Mine Water | Portal Discharge |
|---|---|---|
| pH | 2.8 | 3.1 |
| Al | 76 | 14 |
| Cd | 1.5 | 0.3 |
| Cu | 126 | 12 |
| Fe | 320 | 42 |
| Zn | 335 | 64 |

Metal concentrations are for dissolved metals and are presented in mg/L.

The new property owner, Redfern Resources, began exploring this property in the 1990’s, but received an Environment Canada Inspector Directive in 2002 that required it to treat the acidic discharge from the site. Although there was a bond available from the previous owner to cover closure costs, it was too small to allow for the development and operation of a full-scale treatment system. Moreover, it would be difficult for Redfern to use its limited exploration funds for this purpose. Redfern sought an interim solution to treat the ARD and allow the mine to be developed and generate a cash flow, which would sustain more permanent treatment.

The development of any kind of treatment system at this site was difficult. The site was only accessible by helicopter, which limited the size of equipment that could be used. ARD discharged by the lower level portals (5400 and 5200) flowed down steep mountain sides, with very little flat land available for construction of a treatment plant. Finally, the site was left unattended during winter months (approximately mid-November to April), with neither operator nor power being available, save for periodic inspections. Although these circumstances favour a passive treatment system, the cold winter temperatures at the site do not. Thus, the challenge at this site was to develop a passive treatment system for highly-contaminated ARD that could function unattended during cold winter months.

## Development of a passive treatment system

A limestone bed was constructed in the mid-1990’s to treat the portal discharges, but it quickly became armoured with iron oxides and was rendered ineffective. The system had been installed with little testing and it was decided that a more robust, systematic approach was needed. This became more urgent after Redfern received the Inspector Directive. The authors were tasked with assessing the site hydrological and geochemical characteristics and develop a treatment solution that could work passively and last long enough for a mine to be developed, at which time money can be raised to construct and operate a more permanent treatment system. The proposed treatment system was to be developed rapidly, yet be credible for acceptance by regulators.

A site visit was conducted to identify the sources of water into the underground workings and determine if clean water could be diverted. Boreholes were identified that conducted surface water into the stopes, and these were subsequently sealed. These two measures alone halved the volume of ARD that needed treatment. In addition, available resources were assessed, including a source of limestone, equipment, and potential locations for a passive treatment system. Finally, various options for passive treatment of mine drainage were evaluated at the site, bearing in mind the site restrictions and available resources. It was felt

that the best treatment option was to construct a bioreactor inside the (lowest) 5200 level adit. This bioreactor would have to operate semi-autonomously at ambient temperatures of 6-8 ºC.

**Treatment process**

The composition of mine water shown in Table 1 presents some challenges for passive treatment. Low pH, strong acidity and elevated aluminum and iron concentrations can be treated passively using limestone, but it will not affect cadmium and zinc concentrations. These metals can be removed as insoluble sulphides generated by sulphate-reducing bacteria (SRB), but SRB require neutral, anoxic waters. In addition, their metabolism is slow at low temperatures, though some species are known to live in Antarctic and arctic waters at between -5 and 4°C. Their application in a passive treatment system at this mine remained to be demonstrated.

Removing the large quantities of iron in mine water will produce a large volume of sludge. There is no way to recover this sludge in a clarifier on site, so managing this sludge will present a challenge. Another challenge to resolve is the process that supports SRB activity when the site is unattended. They can be supplied with carbon source either in solid or liquid form. Most solid organic materials decompose slowly at low temperatures, which practically precludes their use in treating anything but low flows. On the other hand, a mechanical device would be required to dispense a liquid carbon source and this presents a challenge when the site is unattended.

It was decided to treat this water using a bioreactor comprising three components: a pre-settling basing to remove as much aluminum and iron as possible, a limestone component for neutralizing mine water and removing the remaining aluminum and iron, and an SRB component in which sulphide is produced to remove the remaining toxic metals. A number of studies would be needed to resolve the following questions:

Is there a solid organic carbon source that can be degraded in the cold and support good SRB activity?
Will aluminum and iron precipitates cause plugging problems for the bioreactor or can they be removed in a pre-treatment step?
Will SRB activity at cold temperatures, regardless of carbon source, produce enough sulphide to remove all the toxic metals?
What will be the fate of the precipitated metal sulphides? Can the resulting sludge plug the bioreactor?

The questions were addressed in the laboratory and pilot studies presented below.

**Laboratory studies**

Several laboratory studies were conducted to test aspects of the bioreactor concept. A column study with limestone (from the site) and mulch demonstrated that acid water was neutralized within hours, but that mulch decomposition at 8 ºC does not support any significant SRB activity. No attempt was made to test more commonly-used organic materials like manure or compost because shipping them to the site would be cost-prohibitive.

Biodegradable plastics were tested to determine if they could support SRB in the cold, including Bionelle 1001 (Linear polybutylene succinate, from Showa Highpolymer Co.) and Tone P787 (Linear poly-caprolactone polyester, from Dow Chemicals). Tests were conducted in sealed serum bottles with SRB isolates from various sources, the test plastic, a mineral salts solution and a redox indicator at 8 and 27 ºC. Sulphide production was measured using the Methylene blue method described in Standard Methods (1995). Bionelle and Tone supported SRB activity at both temperatures, but the rate of sulphide production was only 0.0022 mg $HS^-$/g/d at 8 ºC, compared with ~3 mg $HS^-$/g/d at 27 ºC. In contrast, ethylene glycol supported a rate of 0.16 mg $HS^-$/g/d at 8 ºC, more than 70 times higher than for plastics. These tests demonstrated that SRB could be at cold temperatures with either substrate. However, these

tests cannot tell if the above rates are adequate to remove metals from mine water in a bioreactor. A pilot-scale bioreactor was constructed to answer this question and to determine the fate of metal precipitates.

**Pilot plant studies**

A pilot-scale bioreactor was constructed inside the 5200 level adit to determine its ability to remove metals, establish parameters for designing a full-scale facility, and determine the fate of metals removed from mine water. A secondary, but equally important set of objectives was to only utilize construction methods and materials that can be used on site. Thus, organic materials like manure or compost were not used because of the prohibitive expense in flying them to site, but wood mulch was used because it could be prepared using a commercial wood chipper flown to the site. Finally, the bioreactor was designed to provide treatment passively, with only periodic human intervention.

Before building the pilot-scale bioreactor, a settling reservoir was constructed by damming a portion of the 5200 adit to help precipitate aluminum and iron. Raw ARD was mixed with neutral water in an attempt to raise its pH and promote metal precipitation. In addition, coarse limestone was placed on the adit floor. These changes caused water pH to rise from 2.9 to 3.3 and iron concentrations to decrease slightly, but had no effect on the concentrations of other metals.

The pilot bioreactor was constructed as a 10 $m^3$ crib comprising four cells (Figure 2). It was sized to treat approximately one-tenth of the anticipated full flows, based on flows that were treated in the laboratory studies. The bioreactor comprises three layers:

A bottom drain of river rock

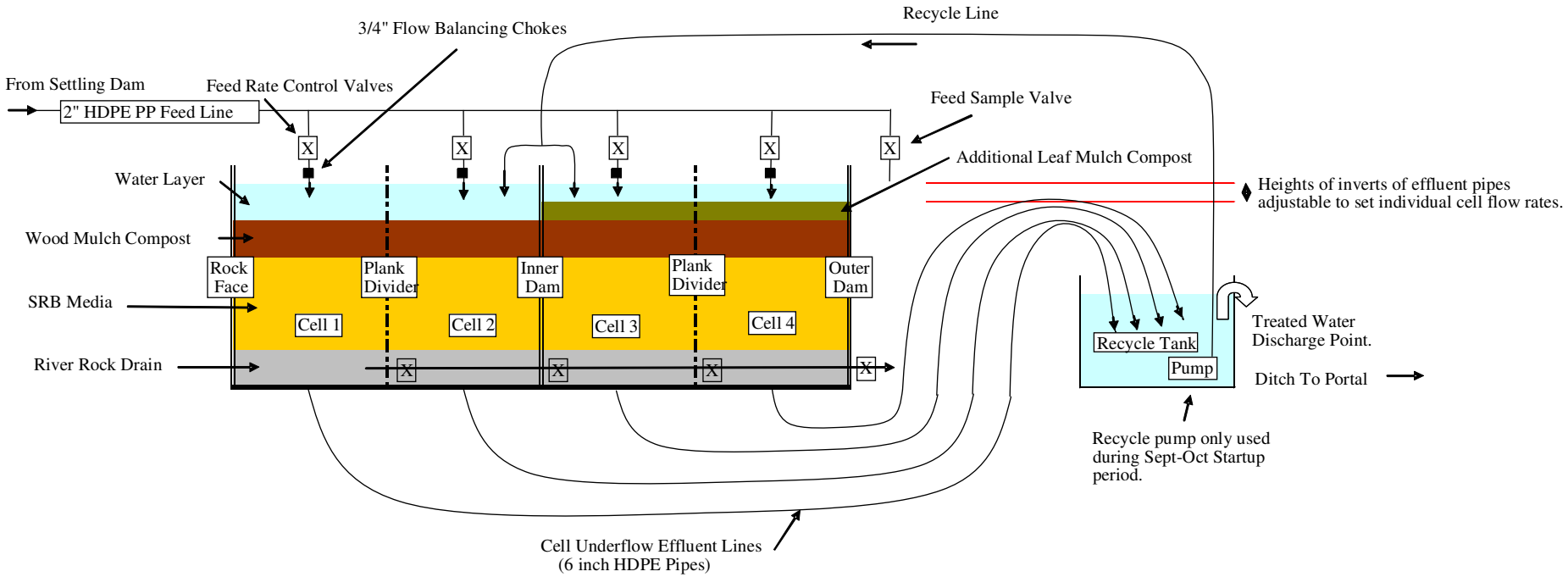
A deep middle fill layer made of 60% limestone, 12% wood mulch, 24% plastic, 4% sulphur prills and bone meal

A cap layer of wood chips and sulphur prills

The bottom river rock (-2”) facilitated draining the cells, if necessary. In addition, it would accumulate any dense sludge that would settle in the bottom of the bioreactor. The cap layer was intended to remove oxygen from mine water, even under acidic pH, and to prevent aluminum and iron precipitates from reaching the limestone layer. The middle layer would neutralize water and support the establishment of SRB, which would metabolise the mulch, plastic and/or sulphur prills to produce sulphide and precipitate metals. Limestone was mined from a nearby quarry and crushed using a dozer, then screened to -0.5”/+3” using a grizzly screen. Wood mulch was generated on site by chipping aspen in a small wood chipper and was mixed unscreened with coarse limestone for good drainage. The sulphur prills were added to consume oxygen in the cap layer and to enhance sulphide production in the limestone layer.

A 0.3 $m^3$ inoculum of SRB was prepared on site to inoculate the bioreactor limestone layer. These bacteria were isolated from a pool of stagnant, neutral mine water within the mine workings. They were grown in the laboratory, then scaled-up into a one gallon culture. This culture was shipped on site and mixed with wood mulch and liquid fish fertilizer in a tub, flooded with neutralized mine water and incubated outside the 5200 mine portal until a black precipitate was noted.

ARD was fed to the bioreactor at ~0.25 L/s during the pilot trial. Temperature, flow, pH dissolved oxygen (DO) and oxidation-reduction potential (ORP) were monitored daily in the influent and effluent, while metal concentrations were measured weekly. Sulphide levels were also measured periodically.




Notes: A pair of 2" ABS riser pipes are set to base of drain layer in each cell. Risers perforated and screened over bottom 15cm
Risers used for DO measurement and access for pumped sulphide sampling (risers not shown)

Cells are also equipped with 6" drain pipes and valves to permit flushing sludge from river rock drain layer.
Drain valve on cell 4 used for samples for sludge and sulphide testing.

Figure 2. Schematic of pilot plant cells and piping configuration.

Initial results showed that water pH increased from an average of 3.33 to 6.44 in the bioreactor (Table 2). Metal removal was evident during the first three months of operation, both from chemical analysis of influent and effluent, and by the deposit accumulating on top of the bioreactor. Removal of aluminum and iron can be accounted by the increased pH of mine water. Similarly, some copper removal may be due to increased pH, as well as adsorption onto organic matter. There was limited removal of zinc, some of which could also be accounted by initial adsorption onto organic matter. Tellingly, there was no evidence of sulphide generation during the first three months of operation. These results reflected a more limited success than hoped for and indicated that SRB activity was not supported by the mulch and plastic in the bioreactor at the ambient temperature of 7 ºC.

Table 2. Average influent and effluent chemistry for pilot bioreactor after 3 months of operation.

| Parameter | Feed | Cells 1/2 | Percent removal | Cells 3/4 | Percent removal |
|---|---|---|---|---|---|
| pH | 3.27 | 6.52 | NA | 6.22 | NA |
| Al | 16.5 | 1.69 | 90% | 1.89 | 89% |
| Cu | 31.0 | 3.40 | 89% | 3.89 | 87% |
| Fe | 64.5 | 3.38 | 95% | 2.96 | 95% |
| Zn | 97.9 | 52.9 | 46% | 76.0 | 22% |

Metal concentrations are for total metals and are presented in mg/L.

Field measurements of dissolved oxygen confirmed that the bioreactor was aerobic throughout its depth. It was concluded that the bioreactor must be supplemented with liquid organic carbon to support SRB.

Two measures were taken to induce anaerobic conditions inside the bioreactor that are necessary for SRB activity. First, additional leaf mulch was added to the top organic layer of Cells 3 and 4 to increase oxygen consumption from mine water. Second, a timer-operated drip system (for hydroponic operations) was installed to supply ethylene glycol (EG) to these two cells, but not Cells 1 and 2. This reagent was chosen because it is not flammable (i.e., can be used underground), is relatively non-toxic and is readily metabolized by SRB. The cells were also supplemented with an SRB inoculum derived from runoff at the Whitehorse airport, where EG is used as a de-icing agent.

Sulphide became detectable in effluent from Cell 3 approximately two months after the above modifications were implemented. The effluent from this cell also exhibited a marked improvement in metal removal (Table 3).

Table 3. Influent and effluent chemistry after sulphide production was first detected.

| Parameter | Feed | Cells 1/2 | Percent removal | Cells 3/4 | Percent removal |
|---|---|---|---|---|---|
| pH | 3.45 | 6.86 | NA | 7.40 | NA |
| Al | 10.6 | 0.042 | 99% | 0.0056 | 99% |
| Cu | 12.4 | 1.71 | 86% | 0.00068 | 99% |
| Fe | 4.12 | <0.030 | 99% | 0.726 | 82% |
| Zn | 43.4 | 29.4 | 32% | 0.132 | 99% |
| $HS^-$ | - | <0.02 | NA | 3.2 | |

Metal concentrations are for *dissolved* metals and are presented in mg/L.

A site visit confirmed that SRB were active in the bioreactor. ORP readings inside Cells 3 and 4 registered below -250 mV. A small trench dug into the bioreactor matrix revealed blackened, sulphur-smelling organic material, indicative of SRB activity. Opening the valves from the cell underflow lines drew blackish liquor with a strong sulphurous smell, from which sulphide was detected through both field and subsequent lab analysis. The solids fraction of this slurry contained high levels of Al, Ca, Cu, Fe, and Zn (**Table 4**). These results supported the idea that zinc was removed as a sulphide.

Table 4. Metal content of solids in slurry drawn from pilot bioreactor underflow lines.

| Parameter | Al | Cd | Ca | Cu | Fe | Zn |
|---|---|---|---|---|---|---|
| mg/dry kg | 47,974 | 438 | 24,213 | 26,291 | 81,666 | 54,047 |

The pilot bioreactor was run in this mode for a few more months. Although subsequent removal rates were variable, removal of copper and zinc were always significantly better after SRB and sulphide production were established in the bioreactor. It is worth noting that gaseous hydrogen sulphide was never detected near the discharge tanks, despite being measured regularly after dissolved sulphide was first detected.

**Pilot plant teardown**

Following the pilot campaign, the bioreactor was dismantled to learn more about its state after eight months of operation. Exposing the inside of the bioreactor was instructive (Figure 3). The upper leaf mulch layer was brownish and had no evidence of SRB. In contrast, the middle limestone/mulch layer was blackened and had a strong sulphurous odour, indicative of SRB colonization. Limestone was free of any blinding from metal precipitates.

Figure 3. Section of the bioreactor matrix.

Interestingly, there were two layers of orange iron hydroxide precipitate: one on top of the leaf mulch and another between the top leaf mulch and middle limestone/mulch layer. The top layer resulted from a

combination of filtered particulates and iron precipitation from mine water. However, the intermediate layer is probably the result of iron dissolution from the middle layer, due to its reducing conditions, followed by its precipitation at the oxic/anoxic interface that existed between the two layers.

The sludge accumulated on top of the cells was worrisome, forming a ¼ to ½" thick layer after eight months of operation. Although it did not appear to impair flow through the bioreactor, this was clearly a concern for longer operation.

A thin layer of oozing, grey-black material was found coating the river rock. This sludge, with the consistency of toothpaste, had a similar metal content to the slurry sampled earlier, except that it contained half the calcium and twice the zinc (Table 5). Its consistency suggests that it would not be easily flushed out by backwashing the under drain lines.

Table 5. Metal content of solids in sludge obtained from river rock in pilot bioreactor.

| Parameter | Al | Cd | Ca | Cu | Fe | Zn |
|---|---|---|---|---|---|---|
| g/dry kg | 51.8 | 0.434 | 11.7 | 29.0 | 68.5 | 137 |

**Scale up considerations**

The pilot campaign showed that neutralization of mine water could be achieved within 6 hours, but that removal of copper and zinc required 24-48 hours. For a design flow of 7 L/sec, a 24-hour retention time would require 1,250 $m^3$, assuming a 50% void volume.

The above calculations were used to determine that 300 $m^3$ of limestone and 150 $m^3$ of chipped deciduous wood (aspen, alder or cottonwood) were required for the full-scale bioreactor. Surveys of the limestone quarry and of deciduous trees near the mine site confirmed that these quantities were available and allowed us to develop a schedule for mining and chipping these materials.

The estimated bioreactor volume presented an unexpected design challenge: how can we design a bioreactor that maintains enough head to push water along its length, if constructed inside the gently-sloping 5200 level adit? The ultimate number and dimensions (height and length) of treatment cells were largely dictated by the slope of the 5200 level adit.

Management of aluminum and iron precipitates represents one of the biggest challenges for the long-term operation of the bioreactor. The solution to this potential problem would be to either remove aluminum and iron more effectively in the settling reservoir (i.e., increase the pH of mine water) or to periodically remove the sludge accumulated at the top of the bioreactor. Both options can be applied to the full-scale bioreactor, if necessary.

## Full-scale bioreactor

The final design for the treatment bioreactor consisted of 3 x 20 m long limestone cells and a 28 m long SRB cell (Figure 4). A 1.8 m cell height allowed for mine water to flow horizontally through the cells, being collected at the bottom of each cell and directed to the top of the next one.

Each cell contained a river rock bottom layer with under drain lines, a middle limestone-mulch layer and a top mulch layer that would help keep water anoxic and retain aluminum and iron precipitates. Drip systems supplied EG at the head of the three anoxic limestone cells and at the head of the SRB cell to consume oxygen from mine water and to supply organic carbon for SRB. By-pass lines were also installed in case of irreparable blockage or failure of cells.

Mulch from the pilot system was used to inoculate the SRB cell in the full-scale bioreactor.

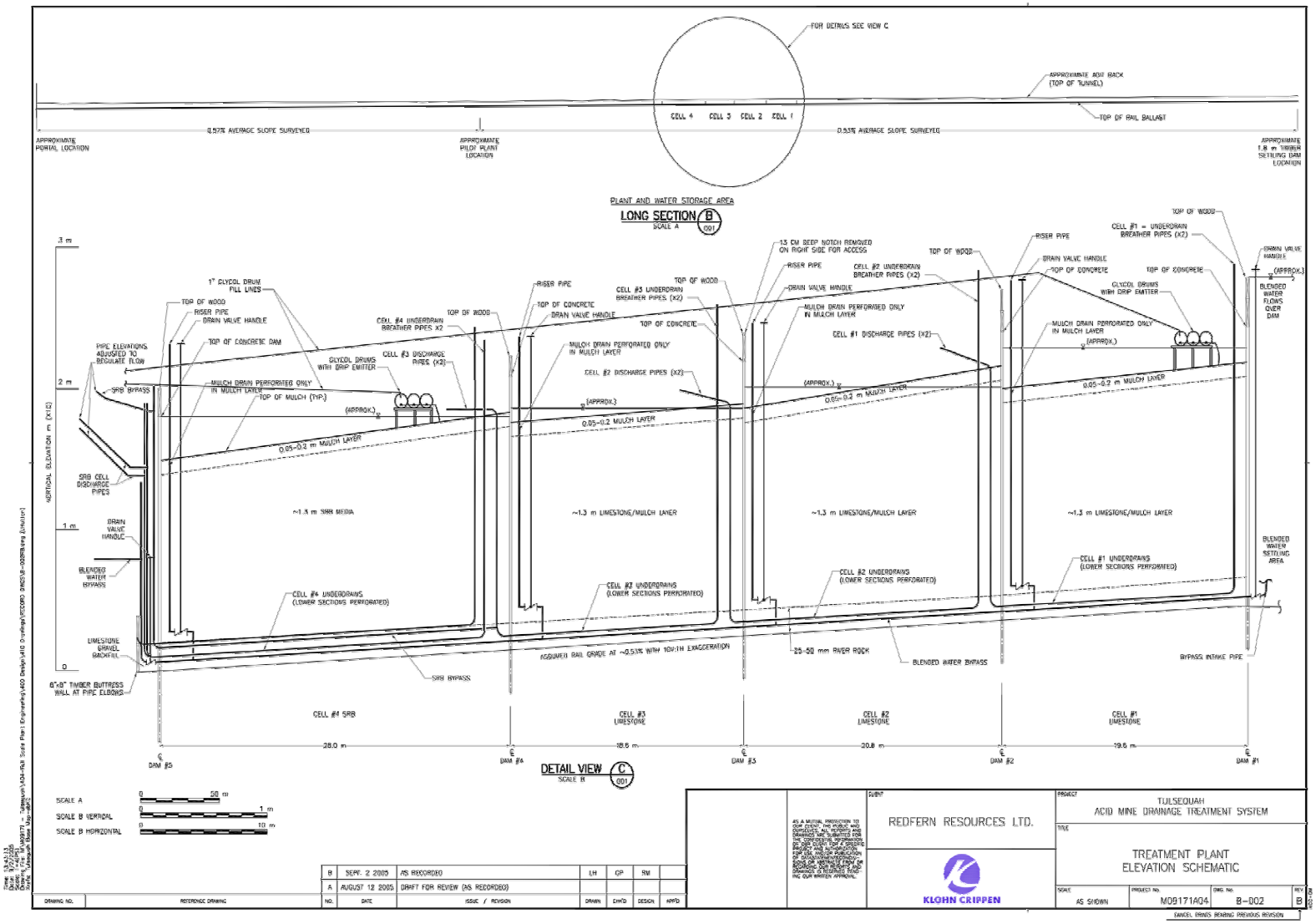



Figure 4. As-built drawing of full-scale bioreactor.

In the first few months of operation, mine water was fed to the bioreactor at 5-7 L/sec and its pH was approximately 3.2. Water neutralized in the limestone cells produced an effluent pH of 6.5-7.0. Aluminum and iron were removed at > 95%, as seen in the pilot bioreactor. However, copper removal was only 75% and zinc removal was <50%.

During that time, there were problems in maintaining good flow through some of the cells due to the build up of sludge. On two occasions, mine water bypassed some of the limestone cells, resulting in incomplete neutralization of water and sending acidic (pH 4, 5) water to the SRB cell. These upsets caused much lower metal removal rates. Although the SRB cell recovered some time thereafter, proper performance required manually removing sludge accumulated in the cells, which was very time-consuming. There was a distinct possibility that cells would become plugged while left unattended during the winter, possibly leading to failure of the system.

To avoid this problem, a caustic (NaOH) drip system comprising 2 x 2 $m^3$ plastic tanks and metered pumps was installed in a service raise to increase the pH of mine water and promote aluminum and iron removal in the settling reservoir upstream of the bioreactor. The system was sized to increase the pH of mine water to ~3.6 by dispensing a 20% NaOH solution, thereby removing most of the iron from solution.

Although this target pH was achieved inconsistently due to variation in flows and water acidity, treatment performance improved after the caustic drip system was installed. Iron concentrations in the bioreactor feed decreased more than ten-fold, from >50 to <5 mg/L. Copper concentrations in the feed steadied at 15 mg/L, and its discharge concentrations varied between 0.1 and 1.0 mg/L. Zinc concentrations in the bioreactor feed also decreased, from approximately 130 to 60 mg/L. However, the zinc concentrations in the discharge remained elevated at 20-30 mg/L. Sludge accumulation was curtailed, and its removal became an annual maintenance activity, rather than a monthly requirement. More importantly, the SRB cell was no longer exposed to acidic water and it functioned properly thereafter.

The treatment system is not perfect, but it produced a marked improvement in water quality that was acceptable to regulatory authorities. The bioreactor did not interfere with exploration activities that continued for a few years afterwards and which allowed the company to delineate resources that supported the re-opening of the mine. This treatment continues while the property owner obtains the financing needed for this project. In this regard, the bioreactor succeeded in accomplishing its main objectives.

## References

APHA (1995). Standard Methods for the Extraction of Water and Wastewater 19th ed, p. 4-124, method 4500-S2- D.

## Acronyms

EG: Ethylene Glycol
NA: Not Applicable
SRB: Sulphate-reducing bacteria