HYBRID TREATMENT SYSTEMS FOR VERY ACIDIC MINING INFLUENCED WATER[1]

James J. Gusek, and Kevin W. Conroy[2]

Abstract. The treatment of mining influenced water (MIW) has traditionally been addressed with two distinct technologies: active treatment with its associated chronic operating costs that include labor, power, reagents, and residue disposal, and passive treatment with its typical requirement of acidity-dependent land areas for bioreactors, aeration wetland cells, and ponds. With the development of "semi-passive" lime-dosing and caustic soda dosing units driven by water wheels, the concept of a "hybrid" treatment system might be worth considering at some MIW sites, particularly those exhibiting high mineral acidity concentrations. The marriage of active and passive technologies is not new. It was first introduced at the Wheal Jane Mine test facility in Cornwall, England in the mid-1990's. However, technology advances that include semi-passive auto-dosing systems and highly-automated active systems might be applied in situations where land available for MIW treatment is in short supply or the MIW chemistry is too aggressive for passive treatment alone. An example comparing capital and operating costs and land requirements of passive, active, and hybrid systems shows the potential advantages of implementing hybrid systems.

The synergy of combining these two technologies in a multi-stage system might offer more than just cost savings. The separation of "non-revenue" metal residuals such as gypsum-rich iron oxy-hydroxides from potential revenue-generating residuals such as copper, lead, and zinc sulfides might facilitate sustainable metal recovery economics that could offset some of the treatment cost burden. Minimizing the footprint of the MIW treatment system compared to a purely passive installation would be an additional advantage.

Additional Keywords: passive treatment, active treatment, heavy metals, economics, sustainability

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[2] James J. Gusek, P.E., is a Senior Consultant with Golder Associates Inc., 44 Union Blvd #300, Lakewood, CO 80228, jgusek@golder.com Kevin W. Conroy, P.E., is a Principal and Water Treatment Group Leader at Golder Associates Inc., 44 Union Blvd #300, Lakewood, CO 80228, kconroy@golder.com

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Introduction

Passive treatment technologies have historically been viewed as direct "competition" with traditional active treatment technologies in improving the quality of mining influenced water (MIW). While some mining companies and government agencies have embraced passive treatment and its cost savings and hands-free operating protocols, this promising technology has some major limitations when confronted with relatively high flows of very acidic MIW characterized by elevated concentrations of Fe and Al. Current design criteria for passive treatment aerobic cells and anaerobic sulfate reducing bioreactors (SRBRs) include surface area as a function of mineral acidity. The higher the acidity loading, the more land area that is required. Sometimes implementing passive treatment systems becomes infeasible due to excessive land area requirements.

Traditional active treatment methods, in a perceived response to the needs of the coal mining industry in the Eastern US, have evolved into so-called "semi-passive" systems that utilize micro-hydropower (i.e., water wheels) to feed solid and liquid neutralizing reagents at set rates into acidic MIW. This technical approach is especially advantageous in situations with varying flow and nearly constant MIW chemistry: as MIW flow rates change, water wheel rotational speed increases or decreases proportionately and more or less reagent is released. Two off-the-shelf semi-passive units are the Aquafix™, which is fitted to feed solid pebble lime; and the Wheeltreater™, which is designed to feed caustic soda solutions. Each has its own advantages and disadvantages and these must be assessed by the treatment system design engineer on a case-by-case basis. For coal MIW, which typically manifests proton acidity and acidity mostly from Al and Fe, stand-alone semi-passive systems suffice in most situations, and further treatment is not required.

One disadvantage that semi-passive systems share with active treatment systems is not related to mechanical engineering, hydraulics, or sludge disposal. As shown in Fig. 1, complex MIW containing multiple heavy metals is difficult to address due to the wide range of minimum solubility concentrations as pH varies. The "ideal" pH for achieving the best water quality with respect to one metal may not be the best pH for meeting the same criterion for another. The highlighted data on Fig. 1 show that an MIW containing Al, Cu, and Cd might be problematic as the "best" pH varies from about 6 for Al, 8.8 for Cu, and 11.3 for Cd. In fact, as one approaches the desired pH for Cd, Al and Cu might be re-dissolved. This chart ignores the effects of adsorption and co-precipitation effects (assuming iron is present). However, this removal mechanism may not be adequate in all situations.

This situation can be remedied somewhat by multi-step adjustments in pH followed by filtration. However, this would introduce a level of process complexity that would obviously push the semi-passive treatment system toward the "active" end of the passive-active treatment spectrum. Clearly, though, a multi-stage system would be difficult to avoid. The challenge is to find the most-appropriate "second stage" process to follow the semi-passive unit to create a hybrid system with a wide range of metal-sequestering capability.

In contrast to metal hydroxides, metal sulfides (e.g., PbS, CuS, ZnS) are virtually insoluble in a wide pH range above neutral. Therefore, combining a semi-passive lime dosing unit with a sulfate reducing bioreactor (in which sulfides are typically formed and sequestered) would be a logical fit for a hybrid system.

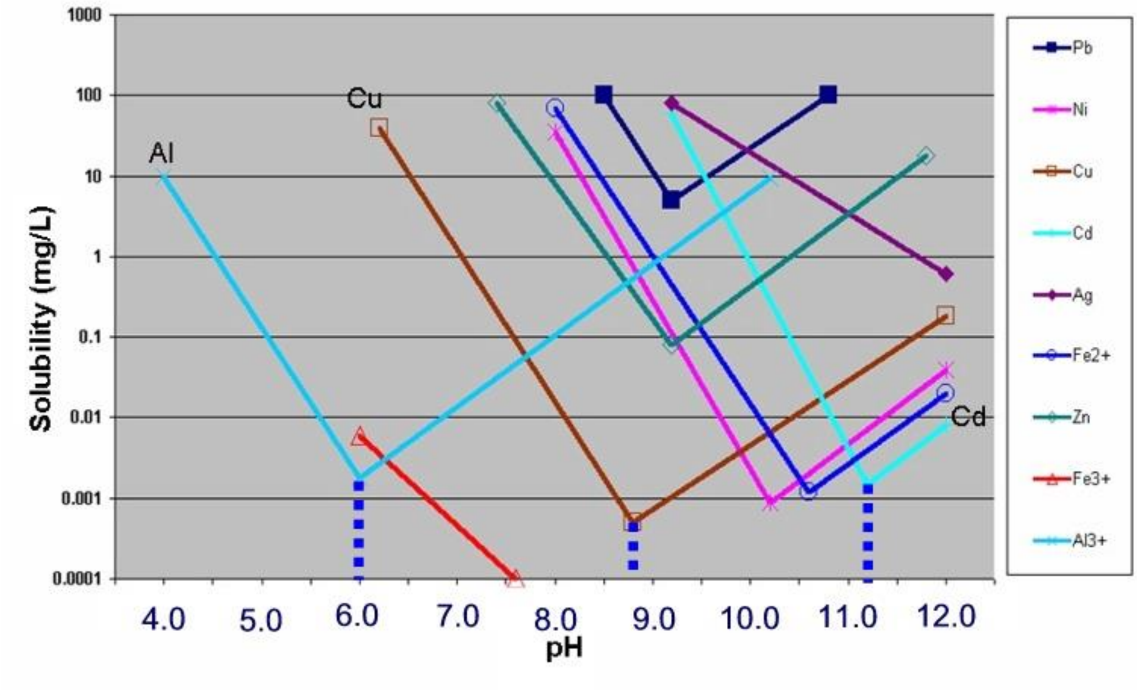

Figure 1. Solubility of metal cations as a function of pH adapted from Stumm and Morgan 1996

The prospect of resource recovery as discussed by Gusek and Clark-Whistler (2005) might be encouraged with a two-step hybrid system. If the primary semi-passive stage resulted in a pH adjustment to perhaps 6.0, virtually all the Al and Fe present in a particular MIW would be precipitated and settled. This product might be suitable for use as paint pigment as practiced by Hedin (2002). Site-specific testing should be conducted to verify this beneficial use. Consequently, (if present) the remaining higher-priced metals in the MIW (perhaps Cu, Zn, Cd, etc.) that report to an SRBR would be less "diluted" by the lesser-priced Al and Fe precipitates. Some of these metals might be adsorbed to iron hydroxides; close attention to the "optimum" pH will be required. Again, each case may be different, but the potential opportunity for resource recovery is certainly enhanced in a hybrid system.

Previous Example of Hybrid MIW Treatment – Wheal Jane Mine, Cornwall

The first well-documented example of integrating an active treatment pre-treatment step with a passive treatment technology was at the Wheal Jane Mine in Cornwall, England (National Rivers Authority [NRA] 1996). The Wheal Jane Mine is an underground tin mine that closed in 1991 when dewatering ceased and the mine flooded. The subsequent breaching of an adit bulkhead in 1993 resulted in the release of a massive amount of acidic MIW into the Carrick Roads estuary, making world-wide news. In response to a need to identify and select a cost-effective, long-term remedy, three pilot scale passive systems were constructed in 1994; one of those systems included a lime-dosing step up-gradient of an aerobic wetland that was subsequently followed by a sulfate reducing bioreactor and an aerobic polishing cell. The other two systems were completely passive. One of these systems included the addition of alkalinity in the form of an anoxic limestone drain (ALD). All three systems were operated in parallel. The results of the initial research were summarized and it appeared that the system with the following components, the "ALD System" – See Fig. 2, provided the best metals and acidity removal performance:

- anoxic pond,
- anoxic limestone drain,
- aerobic wetland,
- sulfate reducing bioreactor (SRBR), and
- aerobic polishing cell.

The goal of the Wheal Jane lime dosing pilot "hybrid" system was not to precipitate iron hydroxide. Rather, it was to just add enough buffering alkalinity to allow passive iron removal in the downstream aerobic cells without generating large amounts of conventional iron hydroxide sludge that could cause operational difficulties.

Figure 2 – Wheel Jane Site Air Photo (NRA, 1996)

The influent Fe concentration to the pilot hybrid system was about 136 mg/L; due to the pilot system operating protocol, this was also the influent concentration to the aerobic cells. The Fe removal efficiency of the lime-dosed hybrid aerobic cells (3.7 grams/day/m^2) was virtually identical to the value observed in the totally passive "ALD" aerobic cells (3.5 grams/day/m^2). The Fe removal efficiency of the lime-free aerobic cells was only 1.2 grams/day/m^2, which demonstrated the benefits of pre-treatment, either by limestone or lime.

While the passive technology looked promising at Wheal Jane, limited land area constraints rendered this treatment alternative infeasible; active treatment with lime was the preferred alternative for the full-scale remedy. The lime-dosing system precipitates were conveniently deposited in a nearby tailings storage facility that had been originally associated with the Wheal Jane mine/mill complex.

Hypothetical Example of Hybrid MIW Treatment Evaluation

For this example, the authors have hypothesized a bulk-headed and flooded underground precious metal mine called "Adit Zero" in the Rocky Mountains of the western US. The portal of Adit Zero is assumed to be immediately adjacent to a relatively pristine stream and there is a limited amount of land area available for any kind of treatment, passive or active. The site is frequently inaccessible in the winter and keeping the access road snow-free is a significant expense. In addition, the flow from the mine during the spring freshet can nearly double. The mining company responsible for the situation (in perpetuity) naturally wishes to minimize cost. As part of a long term closure effort for the mine, the feasibility of three treatment scenarios were considered for the Adit Zero's MIW:

- Option 1 - Totally passive system (SRBR followed by aerobic polishing cells [APCs]),
- Option 2 - Traditional active treatment with hydrated lime,
- Option 3 - Hybrid Active/Passive System (Flash Semi-Passive pH Adjustment followed by SRBR and APCs)

The influent water quality and steady state flow assumed in the conceptual designs of the three treatment scenarios follow.

Table 1. Assumed Adit Zero MIW Chemistry and Flow

Design Parameter	Design Values	Design Parameter	Design Values
Flow	60 gallons per minute (gpm) [227 L/min], rising to 120 gpm/454 L/min	Copper	0.01 mg/L
pH	2.8	Iron	260 mg/L
Acidity	2,040 mg/L	Lead	6 µg/L
Aluminum	220 mg/L	Manganese	6 mg/L
Arsenic	200 µg/L	Nickel	300 µg/L
Cadmium	70 µg/L	Zinc	20 mg/L
Selenium	17 µg/L		

Option 1 - Hypothetical SRBR/APC Passive Treatment System

Design of Option 1 Passive Components

The organic medium in the SRBR component of the system was designed to be replaced on a 30-year schedule. The longevity of the aerobic polishing cell was estimated to be longer than 30 years since it will be exposed to relatively low levels of metal loading (minor concentrations of iron and manganese). The oldest SRBR system still in operation to date is about 12 years old (Gusek et al 1998). However, intrusive investigations of bench and pilot SRBR systems have provided visual evidence supporting the above estimates. For example, an excavation into a two-year-old pilot scale SRBR supervised by the authors revealed that some materials looked as fresh as the day the system was built.

To facilitate long term maintenance, the design flow of 60 gpm (227 L/min) was assumed to be evenly split between two SRBR cells. During the spring freshet, the excess MIW flow would by-pass the SRBRs and mix 50:50 with the steady-state SRBR effluent where the excess sulfide and alkalinity would remove additional metal loading in the APC.

The SRBR cell design criteria include satisfying a volumetric metal loading factor of 0.3 moles of metal loading per day per cubic meter of organic media as well as an acidity loading factor. Selenium removal in SRBR systems is typically observed; no special design changes are required. To satisfy the design criteria, each SRBR cell would have the following dimensions:

- A bottom area of about 115,000 square feet (10,700 m^2);
- organic medium thickness of four feet (1.21 m);
- 1.5 feet (0.5 m) of freeboard (distance from the top of the medium to the crest of the HDPE-lined earthen embankment/containment berm)

Thus, including side slopes and containment berms, the total footprint of each SRBR cell is 195,000 square feet (1.8 ha) for a total SRBR area of 390,000 square feet (3.6 ha) or about 9 acres.

SRBR cell effluents typically have low concentrations of dissolved oxygen. In fact, the discharge will have excess biochemical oxygen demand (BOD). Manganese removal in SRBR cells is typically low to non-existent; Fe removal efficiency may not be as high as other heavy metals such as Al, Cu, and Zn. To remedy this situation, an aerobic polishing cell (APC) is typically needed. An APC is sized based on combined Fe, Mn, and biochemical oxygen demand (BOD) area loading rates. For the assumed hypothetical conditions, the total APC footprint, including bottom area, berms, and a 1.25 safety factor, is 10,276 m^2, or approximately 110,600 square feet (2.5 acres/1.0 ha). The area of the mixing pond is a small proportion of the total SRBR/APC area, and the overall area required for this option is 11.5 acres (4.6 ha).

<u>Option 1 Construction and Operation Costs</u>

Figure 3 includes the conceptual plan view outlines of the various treatment components for Option 1. The approximate cost to construct this system is about $1.9 million as shown in Table 2 below.

Table 2. Option 1 Passive System SRBR and APC Construction Cost Estimate

Item	Amount
Clear & grub	$87,000
Topsoil strip & stockpile	$53,000
Compacted fill - berm	$52,000
Prepare subgrade	$77,000
HDPE liner	$402,000
Gravel bed purchase & delivery	$103,000
Geotextile	$96,000
Organic Substrate with 10% contingency	$990,000
Pipes and plumbing parts	$30,800
Seeding	$2,000
Total (rounded)	$1,900,000

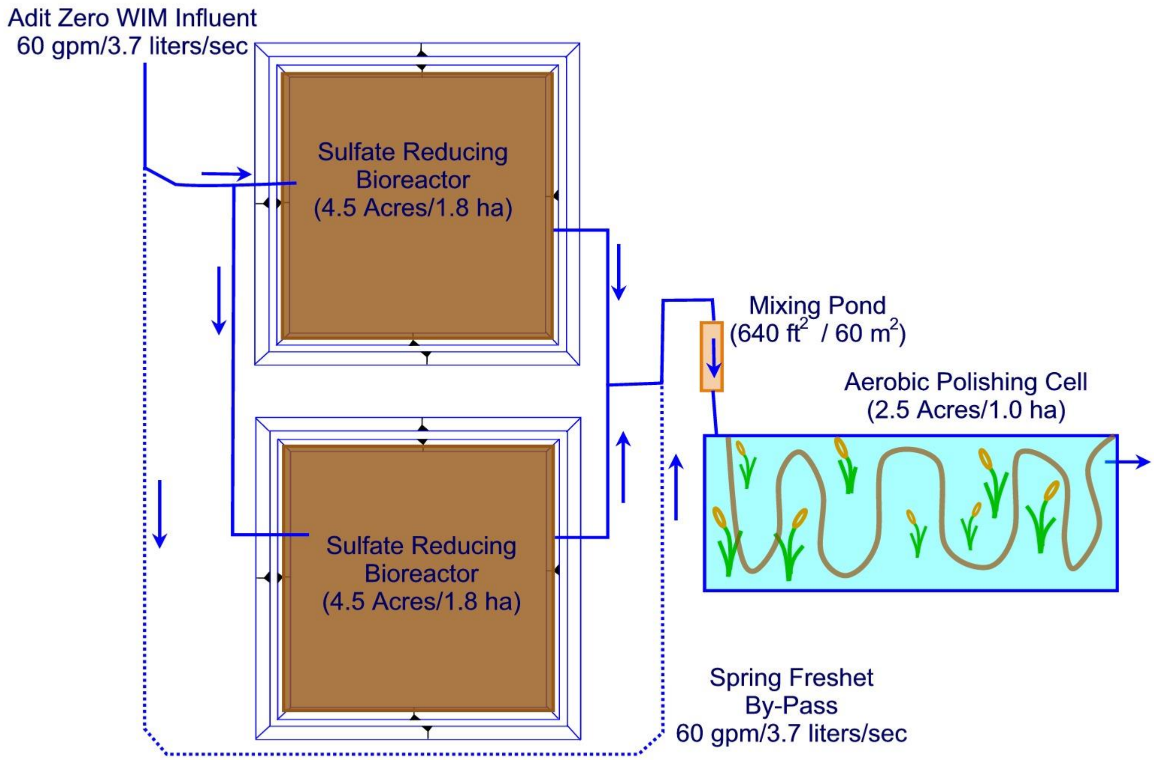

Figure 3. Option 1 - Passive System Layout

Maintenance is assumed to consist of replacing the organic media and cleaning out the mixing pond every 30 years. The APC may require refurbishing but its cost is considered negligible. Ignoring inflation, the 30-year system refurbishment cost should be approximately $1.25 million; this could be allocated evenly over 30 years at $42,000 per annum.

Option 2 - Hypothetical Active Treatment System

Design of Option 2 Components

Active treatment for the Adit Zero MIW water is based on using $Ca(OH)_2$ treatment for gross metals removal and TDS reduction. Lime treatment is the gold standard of active treatment of acidic MIW. With the exception of Se, all of the metals in the Zero Adit MIW that are at elevated levels can be reduced to low levels by lime treatment. Selenium is typically in the selenate form and therefore will not precipitate with lime; therefore, a biological Se removal step is included in the conceptual design. In addition, Al precipitates at a much lower (5.5 to 6.5) pH than the other metals species which are effectively removed in the 9.5 to 10.5 range. Therefore, a two-stage lime treatment system is proposed to achieve reduction of Al as well as the other metals.

For this two-stage conceptual design, the authors used the results of the modeling program Geochemist Workbench (Bethke 2005) to project treated water quality and lime utilization at various treatment pH levels. These results were tempered with data from actual treatability studies, which were used to estimate hypothetical sludge production. The conceptual Option 2 design included solids recycling, a typical design feature found in lime treatment plants because it provides more efficient lime utilization, contaminant removal, and contributes to lower dewatered sludge volumes (higher percent solids) in the sludge. The major equipment required for Option 2 is provided in Table 3. Flow through the majority of the plant is assumed to be by gravity.

Table 3. Option 2 Active Treatment Equipment List

Equipment	Description
Mixing Tank 1	10 minute retention time for lime and recycled solids. 300 gal. working volume.
Reaction Tank 1	40 minute retention time for influent water plus feed from mix tank. 4,500 gal. working volume.
Floc Tank 1	5 minute retention time. 500 gal. working volume
Thickener/Clarifier 1	16 ft diameter, 12 ft deep
Mixing Tank 2	10 minute retention time for lime and recycled solids. 300 gal. working volume.
Reaction Tank 2	40 minute retention time for influent water plus feed from mix tank. 4,500 gal. working volume.
Floc Tank 2	5 minute retention time. 500 gal. working volume
Thickener/Clarifier 2	16 ft diameter, 12 ft deep
Sludge Holding Tanks	Two days sludge storage per tank, 4,000 gal. working volume, cone bottom tanks.
Filter Press	20 ft^3 press sized for dewatering of 3-4 days of sludge in single operational day.
Plant Water Tank	2,500 gal. tank
Potable Water Storage Tank	2,500 gal. tank
Lime Silo/Slurry Tank	Sized to receive a bulk load of lime with some capacity still available. Lime slurry tank is included with silo system.
Selenium Biotreatment System	Anaerobic 30,000 gal. tankage with media; aerobic polish tank 10,000 gallon and media; supporting mechanical equipment

Option 2 Construction and Operating Costs

The total cost for the key pieces of active-treatment equipment listed in Table 3 is about $1.2 million. The costs for tanks, pumps, mixers; other small equipment items, and instrumentation and controls would add about $120,000 or about 10%. Buildings and infrastructure were estimated at an additional $1 million for a total system capital cost of $2.3 million. If Se removal were not required, the total system capital cost could be reduced by up to $0.8 million. The primary components of the operating cost were estimated as follows:

- Hydrated lime: approximately 1,000 pounds per day (455 kg/day) at $150/ton ($165 per tonne) including delivery to the remote site = $27,400 per annum
- Labor: average of three operators for 12 hours per day or 36 man-hours per day @$40/man-hour (24/7) w/benefits = $525,600 per annum. It is assumed that the plant can operate unattended for approximately 12 hours per day, however, this is dependent upon the design and level of instrumentation. Due to the inclusion of the selenium bio-treatment component

which adds a level of complexity, the labor costs are somewhat inflated above a typical lime dosing plant without this treatment component. The labor cost includes snow removal in winter months.

- Sludge disposal: approximately 40 ft^3 per day at 30% solids. Non-hazardous landfill disposal cost (including transport) is \$30/cy (\$39 per m^3) = \$16,400 per annum.

The total Option 2 operating cost would be about \$570,000 per annum, most of which would be labor. The construction footprint would be about 0.2 acres (0.01 ha).

Option 3 - Hybrid Semi-Passive/Passive System

Design of Option 3 Components

Treatment Option 3 for the Adit Zero MIW consists of pebble lime pretreatment prior to an SRBR and APC. The pebble lime pretreatment shrinks the area required for the SRBR cells by reducing the metals loading and acidity of the SRBR-influent water. The pretreatment step would include a water-powered dosing unit, a lime pebble storage silo, a sludge retention pond and a sludge drying bed.

Due to the extreme winter conditions commonly found at Adit Zero site, pH adjustment using caustic soda or other liquid chemical was not considered. While power could be made available at the treatment site, a water-powered pebble lime dosing unit (Aquafix or similar) was selected for the sake of simplicity. As with Options 1 and 2, all flows are assumed to be by gravity. AMD Treat software (OSMRE 2005) was used to determine the lime dosing rate, required storage, delivery frequency, and system sizing. The retention pond was sized for sludge removal twice a year and a retention time of 24 hours. It is assumed that the Adit Zero MIW chemistry does not change appreciably during the spring freshet and that the increased flow during that time is matched by the proportionate increase in the water wheel rotational speed.

The Option 3 SRBR cells were sized based on expected effluent water quality from the pebble lime/retention pond pretreatment units. Since the pebble lime dose was calculated to neutralize the proton and mineral acidity contained in the Adit Zero MIW, the SRBR influent water is assumed to be pH-neutral and contain negligible amounts of Fe and Al. However, other base metal concentrations are assumed to remain unchanged from the raw Adit Zero MIW. The other base metals, including Zn, Ni, and As, remain in solution at a pH of seven. It could be argued that the arsenic would be adsorbed on to the Fe oxyhydroxides, but this was conservatively ignored in SRBR sizing. The SRBR cell design is based on the following assumed retention pond effluent water.

Table 4. Assumed Retention Pond Effluent Chemistry fed to SRBR Cells

Design Parameter	Design Values	Design Parameter	Design Values
pH	7	Copper	0.01 mg/L
Acidity	Net alkaline	Iron	1.0 mg/L
Aluminum	1.0 mg/L	Lead	0.006 mg/L
Arsenic	0.2 mg/L	Manganese	6 mg/L
Cadmium	0.07 mg/L	Nickel	0.3 mg/L
Zinc	20 mg/L	Selenium	17 µg/L

Based on the SRBR design criteria previously discussed, the total SRBR bottom area required is about 5,800 feet (540 m^2). Dividing the bottom area into two separate cells and adding surface area for side slopes and berms yields two 22,300 square foot (2,072 m^2) SRBR cells for a total SRBR area of 44,600 square feet (4,145 m^2), or 1.0 acres/0.41 ha. As with Option 1, this design concept assumes an SRBR organic media longevity of 30 years.

Based on the APC design criteria previously discussed, the Option 3 APC can be significantly smaller that the Option 1 APC. Given the lime pretreatment step, significant iron concentrations are not expected in the APC influent. Therefore, iron was not included in the Option 3 APC sizing calculations. Required areas for BOD and manganese removal are identical to Option 1. Including berms, the total APC footprint will be 12,200 square feet (1,134 m^2).

Option 3 Construction and Operating Costs

Figure 5 includes the conceptual plan view outlines of the various treatment components for Option 3. The necessary land areas required to implement this option follow.

- Lime silo – 35 ton storage silo (negligible)
- Primary Retention Pond – 11,200 square feet (1,041m^2)
- SRBR - 31,100 square feet (2,890 m^2)
- APC – 12,200 square feet (1,134 m^2)
- Sludge Drying Bed – 1,000 square feet (93 m^2)
- Option 3 Total Area – 55,500 square feet (5,158 m^2)

The approximate cost to construct the Option 3 system is about \$0.3 million as shown in Table 5. The operating cost is allocated between the pretreatment and SRBR/APC steps; the primary components of the operating costs follow.

- Pebble lime: approximately 962 pounds per day (437 kg/day) at \$200/ton (\$210 per tonne) including delivery to the remote site = \$35,000 per annum. The delivery cost includes snow removal in winter months.
- Labor: the detention pond would be cleaned out twice a year; two persons with a trash pump would transfer sludge to a dedicated sludge drying bed; approximately 40 man-hours per year @\$40/man-hour w/benefits = \$1,600 per annum.
- Sludge disposal: approximately 1,510 cy per annum at 30% solids. Non-hazardous landfill disposal cost (including transport) is \$30/cy (\$39 per m^3) = \$45,300 per annum.

SRBR maintenance is assumed to consist of replacing the organic media every 30 years. Ignoring inflation, the SRBR refurbishment cost should be approximately \$50,000; this would be about \$1,700 per annum allocated over 30 years. Total Option 3 operating cost would be about \$84,000 per annum, most of which would be comprised of pebble lime cost and sludge disposal.

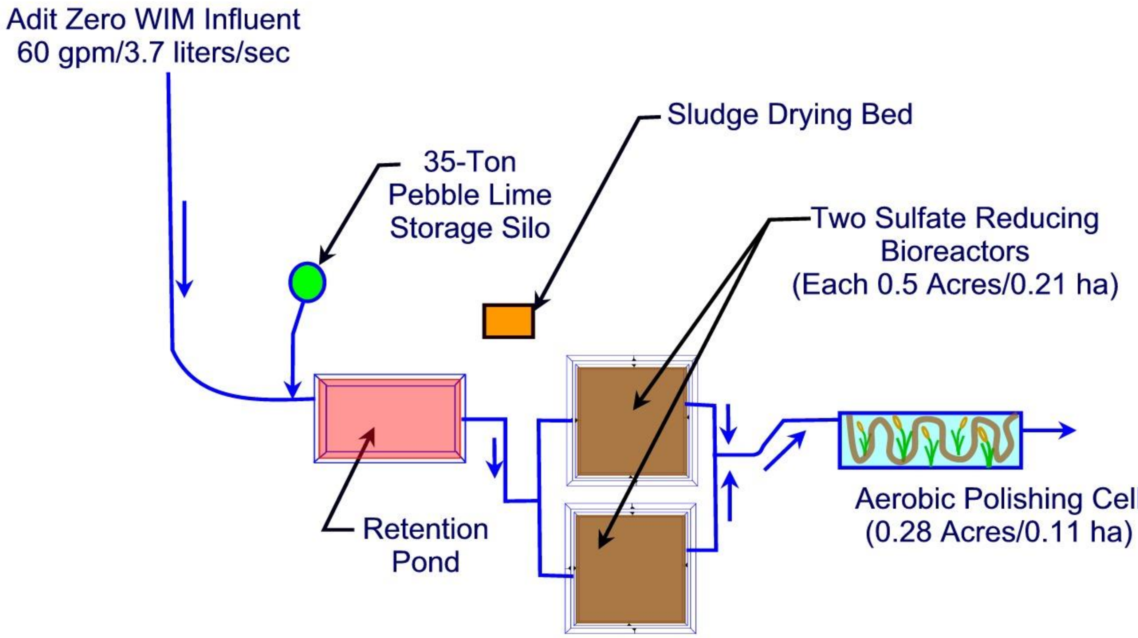

Figure 5. Option 3 Hybrid Semi-Passive/Passive System

Table 5. Option 3 Hybrid System: Pebble Lime Doser, Sludge Retention Pond, SRBR, and APC Construction Cost Estimate

Item	Amount
Clear & grub	$36,000
Topsoil strip & stockpile	$15,000
Compacted fill - berm	$21,000
Prepare subgrade	$9,000
HDPE liner	$45,000
Gravel bed purchase & delivery	$3,000
Geotextile	$11,000
Organic Substrate with 10% contingency	$40,000
Pipes and plumbing parts	$3,600
Seeding	$1,000
35 Ton Silo Storage System, installed (Jenkins, 2007)	120,000
Total (rounded)	**$305,000**

<u>Comparison of Options</u>

Table 6 summarizes the land area and cost information for the Adit Zero MIW treatment options. As the Adit Zero site is hypothetical, the available land area is subject to conjecture; however, it may be safe to say that it would be easier to find enough space to construct Options 2 and 3 compared to Option 1 in the typical mountainous terrain of the western US. Ignoring the land surface requirements, the comparisons suggest the following additional observations:

- Option 1 has the second-highest construction cost, but is the least expensive to maintain;
- Option 2 is more expensive than Option 1 to construct and about three years of labor-driven Option 2 O & M cost almost equal the Option 1 construction cost;
- Option 3, the hybrid, is the least expensive to construct and its annual O & M cost is on the same order of magnitude as Option 1;
- The active treatment option has the highest 30-year life cycle cost by a significant amount;
- The passive and hybrid treatment options have a similar 30-year life cycle cost. However, the land area required for the hybrid option (Option 3) is almost 90% less than that required for the totally passive system.

Table 6. Comparison of Treatment Option Economics and Required Land Areas

Option	Construction Cost	Projected Annual O & M Cost	30-Yr Life Cycle Cost	Land Area Required
1 – Passive Treatment	$1.9MM	$42,000	$3.2MM	11.5 ac/4.6 ha
2 – Active Treatment	$2.3MM	$570,000	$19.4MM	< 0.2ac/0.01ha
3 - Hybrid	$0.3 MM	$84,000	$2.8MM	1.3 ac/ 0.52 ha

Summary

The synergy of combining semi-passive and SRBR technologies in a multi-stage system might offer more than just cost savings and reduced land requirements. As discussed in Gusek and Clark-Whistler (2005), the recovery of select metals from depleted SRBR organic media may provide sustainable resource recovery opportunities. The separation of "non-revenue" metal residuals such as gypsum-rich Fe oxy-hydroxides in the pretreatment step from potential revenue-generating residuals such as Cu, Pb, and Zn sulfides sequestered in the SRBR media might facilitate sustainable metal recovery economics. The revenues from recovering this resource could offset some of the treatment cost burden. While minimizing the footprint of the MIW treatment system compared to a purely passive installation would be an additional advantage, the overall economics of the hybrid also appear to be more favorable than the other two options considered.

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