# Innovative Dissolved Metals Removal Plus Replaceable Skin Layer Membranes to Treat Mine Impacted Water

ROB STEPHENSON PHD P.ENG. waterStrider Treatment Inc. Vancouver, BC, Canada

DAVID BROMLEY M.ENG., P.E. DBE Hytec Ltd. Vancouver, BC, Canada KEYWORDS: mine water treatment, electrochemical treatment, Replaceable Skin Layer, membranes, CO<sub>2</sub> pH neutralization, CO<sub>2</sub> scrubber, air scrubber, dissolved metals, iron oxidation, Amprey, Misty, membrane fouling

## ABSTRACT

A new mine-impacted water treatment process employed four novel unit operations: (1) magnesium and steel pellet anode electrochemical precipitation of dissolved metals to form insoluble solids, (2) scrubbing of  $CO_2$  from diesel generator exhaust to neutralize alkaline pH, (3) scrubbing of oxygen in air to oxidize ferrous iron, and (4) replaceable skin layer membranes removal of sub-micron metal precipitates.

The process electrochemically precipitated dissolved metals separated by replaceable skin layer membranes without fouling. The mine water treatment process met stringent regulatory discharge requirements at moderate operating cost and produced just small amounts of non-leachable solids for disposal.

## INTRODUCTION

A gold mine located in the wilderness of northern British Columbia in Canada discharges without dilution to an environmentally sensitive creek, resulting in extremely stringent regulatory discharge requirements for dissolved aluminum, antimony, arsenic, cadmium, copper, iron and zinc. Meeting dissolved metal contaminants of concern (CoCs) water quality requirements in this challenging environment necessitated developing a new mine water treatment process.

At the remote, wet, and seasonally cold area in northern BC, supply chains and expert assistance at mines were costly and un-predictable. Freezing temperatures, treacherous roads, and seasonal rainfall at the mine compounded risks of chemical supply, chemical handling, and chemical storage. Consequently, minimizing requirements for transport to the mine, complex materials handling, and storage of hazardous chemicals that entail high risks had particular value.

The mine's remote location and consequentially significant potential impact to facilities and personnel by possible mishaps during chemical transport and handling favored using benign and local inputs. Site-generated sources of water treatment consumable inputs that use inert feed stock for uncomplicated delivery and storage were preferred over imported solid, liquid or gas reagents.

This mine is permitted to discharge at up to 212 L/min into environmentally sensitive habitat with no dilution, thus requiring extraordinarily high levels of water treatment to meet water quality discharge requirements. Table 1 lists dissolved metals CoCs of mine water samples, showing that maximum levels exceeded monthly average permit limits of total suspended solids (TSS) and dissolved aluminum, antimony, cadmium, copper and zinc. Maximum levels also indicate exceedances of maximum permit requirements for TSS, dissolved cadmium and dissolved zinc.

# Table 1:

Parameter	Units	Maximum	Minimum	Standard	Mean	Permit Req	uirement
				Deviation		Maximum	Monthly
						in Any Sample	Average
Total Suspended Solids	mg/L	57.0	1.0	9.2	8.9	30	15
Dissolved Metals (Water):							
Aluminum (Al)-Dissolved	mg/L	0.1250	0.0010	0.0299	0.0137	0.5	0.1
Antimony (Sb)-Dissolved	mg/L	0.0320	0.0183	0.0040	0.0033	0.16	0.02
Arsenic (As)-Dissolved	mg/L	0.0054	0.0031	0.0006	0.0005	0.03	0.01
Cadmium (Cd)-Dissolved	mg/L	0.00907	0.00188	0.00208	0.00159	0.00012	0.00002
Copper (Cu)-Dissolved	mg/L	0.0138	0.0021	0.0032	0.0021	0.04	0.01
Iron (Fe)-Dissolved	mg/L	0.0930	0.0100	0.0201	0.0092	0.30	-
Zinc (Zn)-Dissolved	mg/L	1.2000	0.2270	0.2702	0.2001	0.18	0.03

Water Quality at a Mine in BC: Dissolved Metal Concentrations

Removing dissolved metals from mine water requires furnishing chemical conditions of pH, oxidation-reduction potential, and cations to minimize the solubility each metal contaminant of

concern. The resulting solid precipitate can then be removed by solid: liquid separation methods such as gravity clarification, air flotation, or filtration. The available chemistries that are able to precipitate dissolved metal CoCs are listed in Table 2.

# Table 2:

Chemical Precipitation of Dissolved Metal Contaminants of Concern

Parameter	Formation of Metal Precipitate*						
	Metal Hydroxide	Metal Sulphide	Metal Carbonate	Co-Precipitate			
Aluminum (Al)-Dissolved	$\checkmark$	×	×	×			
Antimony (Sb)-Dissolved	×	×	×	✓			
Arsenic (As)-Dissolved	×	×	×	$\checkmark$			
Cadmium (Cd)-Dissolved	$\checkmark$	$\checkmark$	$\checkmark$	×			
Copper (Cu)-Dissolved	$\checkmark$	$\checkmark$	×	×			
Iron (Fe)-Dissolved	$\checkmark$	$\checkmark$	$\checkmark$	×			
Zinc (Zn)-Dissolved	$\checkmark$	$\checkmark$	$\checkmark$	×			

\*✓ Forms insoluble solids. × Does not form insoluble solid.

Table 2 indicates that no single water treatment chemistry – neither hydroxide, sulphide, carbonate, nor cationic co-precipitation (such as with iron, aluminum, calcium, magnesium) - can remove all of the dissolved metal CoCs at the mine.

Figure 1 illustrates the impact of pH on minimum solubilities of various metal hydroxides.

# Figure 1:

Solubilities of Metal Hydroxides vs pH (Blais et al., 2008)

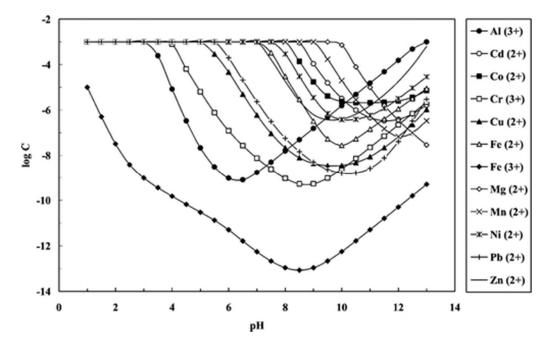


Figure 1 shows that minimum solubilities of dissolved metals occur at significantly different pHs. For example, whereas the minimum solubility of dissolved aluminum occurs at pH 6.5, the minimum solubility of cadmium is at pH 11.0 to 12.0. These differences in pH, where the solubilities of dissolved metals as hydroxides are minimized, indicate that more than one stage of metals precipitation plus solids separation is needed. Note that solid particulates must be separated from treated water under the pH and redox conditions that resulted in their formation. Otherwise, newly formed metal precipitates may be re-dissolved, un-doing dissolved metals removal.

ELECTROCHEMICAL TREATMENT OF MINE WATER - Since lime treatment of mine water is the industry standard, use of conventional lime mine water treatment was compared with the proposed electrochemical water treatment process. Table 3 compares the use of lime with electrochemical treatment. These methods are compared in terms of their abilities to remove permitted CoCs at a mine, the amount and nature of the metal sludge waste by-product that is generated by each process, the ability to control the process, and their relative cost.

## Table 3:

*Comparison Between Electrochemical Treatment vs Lime Treatment to Precipitate Dissolved Metals* 

Mine Water Treatment Method	Removes all CoCs	Sludge Production	Control Effectiveness	Relative Cost
Lime	Also requires dosing with iron salt to remove antimony or arsenic.	High volume of easy to dewater and chemically unstable (TCLP) solids	Site ambient moisture creates dry lime handling and storage difficulties. Constrained by cold temperatures, high maintenance. Challenges with automation for extended operations.	Moderate cost. Two stages of pH and solids separation + iron dosing are required. High cost of lime sludge handling and disposal.
Electro- chemical	Mg anode and Fe anode needed to remove all metal CoCs.	Low volume of easy to dewater, chemically stable (TCLP) solids	Handling of metal pellet anodes is unaffected by ambient moisture. Readily automated. for extended unattended operation in any climate.	Relatively low to moderate cost. Two stages of electrochemical treatment + solids separation are required. Low cost of sludge handling and disposal.

Table 3 indicates that electrochemical treatment has comparative advantages over lime since the dissolved metal CoCs at the mine can be removed electrochemically.

Different consumptive metal anodes serve different purposes to remove dissolved metals from mine water. For mine water treatment, the main choice is between using magnesium or steel anode pellets, with applications as follows:

(1) Magnesium anode electrochemical cells can lower redox potential, raise pH, and add reactive dissolved magnesium to agglomerate metal hydroxide precipitates of cadmium and zinc.

(2) Steel anode electrochemical cells introduce ferrous iron to form iron co-precipitates of antimony and arsenic and coagulate solids.

Lime treatment does not have this capability to remove dissolved antimony and arsenic and requires an additional step of iron addition to co-precipitate antimony and arsenic. Additionally, compared to electrochemical treatment, lime treatment of mine water yields high volumes of sludge, creating significant costs and liabilities for solids handling and waste disposal.

In spite of advantages of electrochemical treatment to remove dissolved metals from mine water, electrochemical water treatment methods have rarely been adopted by mines. This may be due to limitations of commonly available electrochemical technologies:

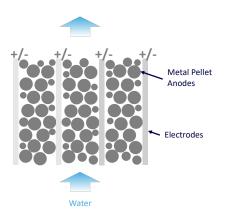
- Inability to treat water with low conductivity;
- Need for frequent operator intervention to remove chemical fouling of cell anodes and cathodes;
- Need to frequently re-set the gap between consumed anode and cathode plates and/or replace partially consumed anodes;
- Difficulty to scale up to treat large volumes of mine water;
- Complexity of mechanical and electrical systems; and
- High operating and capital costs.

Note that irrespective of how dissolved metals are precipitated to form insoluble solids, highly effective solids separation is essential to satisfy regulatory discharge limits and/or water reuse requirements.

The "Amprey<sup>TM</sup>" technology was developed to address the limitations of conventional electrochemical treatment of mine water as outlined above. Amprey's upflow expanded bed cell is filled with magnesium or steel consumable anode pellets. The electrochemical cell is electrified by AC power that is supplied to multiple pairs of non-consumptive titanium electrode rods inside the expanded bed of anode pellets. Figure 2 illustrates the Amprey cell.

# Figure 2:

Amprey Electrochemical Cell



GAS SCRUBBER - Removing dissolved metal CoCs from the mine impacted water required more than a single stage of treatment, each with its own pH and redox potential. At the mine, a

low cost and effective method was needed to lower pH and to oxidize ferrous iron to form ferric iron.

Rather than transporting and handling concentrated acid, using  $CO_2$  gas from filtered exhaust of a diesel generator was a safer, equally effective, and much less costly source of acid. A gas scrubber was used to produce a fine spray mist of Mg- treated alkaline treated mine water into an enclosed tank gas headspace that was supplied with filtered diesel exhaust to for-m carbonic acid and thus lower pH to controlled neutral pH conditions.

A second gas scrubber also produced a fine spray mist of treated mine water. The scrubber tank headspace was supplied with air to oxidize ferrous ( $Fe^{2+}$ ) iron in Fe-treated mine water to form less soluble ferric ( $Fe^{3+}$ ) iron, thereby aiding removal of iron and iron co-precipitates of dissolved antimony and dissolved arsenic.

By providing a high surface area of water droplets into a controlled gas environment, available waste  $CO_2$  gas and air were used to treat the mine impacted water at high rates of reaction and at low operating cost. Figure 3 illustrates the units to scrub  $CO_2$  and scrub oxygen or air.

# Figure 3:

## Carbon Dioxide Scrubber and Air/Oxygen Scrubber



SOLIDS SEPARATION - Although membrane filtration is a high cost alternative to separate solids at mines, membranes consistently attain high efficiency solids separation required to meet stringent discharge requirements. However, membranes are vulnerable to fouling by magnesium and aluminum silicates that are formed under high pH conditions that are needed to precipitate dissolved cadmium and zinc.

Mine water treatment testing that employed a conventional membrane system demonstrated effective solids removal of the electrochemically precipitated metals at the mine. However, the treatment conditions needed to remove dissolved metals also formed solids identified as aluminum silicates and magnesium silicates that resulted in membrane fouling. Clean in place (CIP) requirements to restore membrane flux were extremely high and threatened to negate the chemical-free advantage of the mine water treatment process by requiring frequent cleaning and significant volumes of sodium hydroxide and hydrochloric, sulfamic, and citric acids.

In desperate need to find a replacement to the complexity and high cost for CIP of a conventional membrane system, a removable skin layer membrane was operated to process electrochemically treated mine water for repeated cycles at a constant initial pressure and flow rate.

Unlike conventional membranes, replaceable skin layer membranes operate with a membrane pore size 25,000 times larger than a conventional ultrafiltration (UF) membrane yet achieve similar quality water. The use of large pore size membranes (5 to 10 microns) facilitates flux rates 10 times greater (300 to 500 L/m<sup>2</sup>/h) (Loganathan 2015, Bromley 2013) compared to conventional UF membranes, with 90% less energy, 95 to 99% recovery (i.e. very low reject volumes) (Murphy Oil, 2023) and membrane CIP requirements on a weekly or monthly basis, not daily.

For this mine-impacted water, replaceable skin layer membranes would need monthly CIP compared to daily CIP requirements for conventional membranes. To accomplish this, replaceable skin layer membranes rely on an aluminum oxide powder that creates a strong electric double layer (EDL) on the surface of the membrane substrate. The formulated metal precipitates also have a strong EDL which keeps the colloids in suspension and away from the surface of the aluminum oxide skin layer.

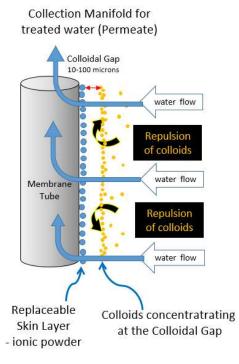
Replaceable skin layer membranes operate using three steps:

- 1. Application of aluminum oxide powder (replaceable skin layer) by injection of a powder slurry into a membrane housing where the membrane tubes are submerged with clean permeate water.
- 2. Filtration cycle of typically 4 to 20 hours until the transmembrane pressure (TMP) rises to a pressure difference of 70 kpa (10 psi).
- 3. When the TMP reaches 70 kpa (10 psi), compressed air backwash removes the replaceable aluminum oxide skin layer and the filtered solids. Next, permeate rinses the membranes. The replaceable skin layer membrane is then ready to start a new cycle.

Figure 4 illustrates a "replaceable skin layer" membrane provided by DBE Hytec Ltd. Figure 4a shows a graphic of the first phase (Zone A) of the filtration cycle where colloids are stabilized and a colloidal gap occurs in front of the replaceable skin layer. During Zone A, the TMP is close to zero.

# Figure 4a:

## Zone A First ("Stabilized") Phase of Filtration Cycle



Once the total suspended solids (TSS) in the housing concentrate to approximately 1.5%, the colloidal solids start to leak into the replaceable skin layer, causing the colloids to destabilize and create a floc on the surface of the replaceable skin layer.

Figure 4b graphically displays this phase of the filtration cycle. The TMP increases at a much faster rate than during the first Zone A (stabilized) phase of the filtration cycle.

### Figure 4b:

Zone B: Second ("Destabilized) Phase of Filtration Cycle

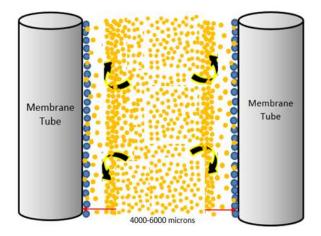
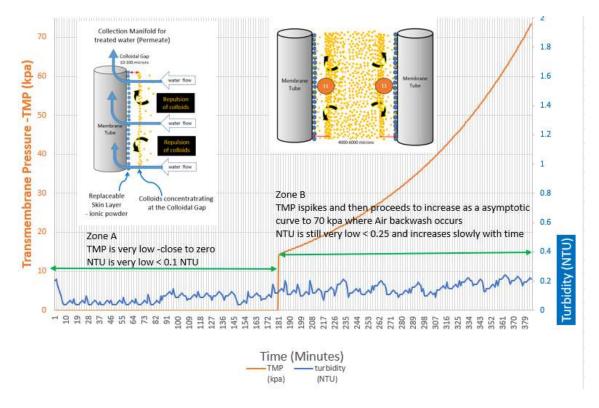


Figure 4c provides a typical plot of TMP (kpa) and turbidity (NTU) versus time. The  $350 \text{ L/m}^2/\text{h}$  flux rate is consistent throughout the filtration cycle. The TMP in Zone A is near zero kpa. In Zone B, the colloidal solids leak into the aluminum oxide replaceable skin layer. The colloids destabilize as they would in a coagulation process and attach to the powder and to each other. This creates floc on the surface of the replaceable skin layer. The TMP increases asymptotically to 70 kpa, prompting an air backwash to be initiated.

## Figure 4c:

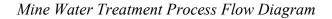


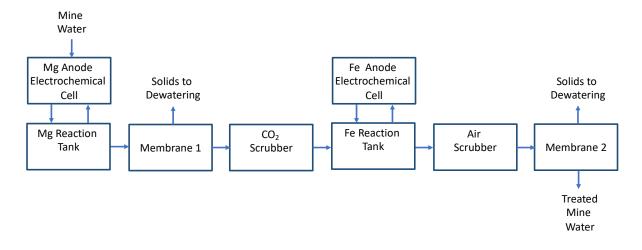
RSL Membranes Trans Membrane Pressure (kpa) vs Turbidity (NTU)

### MINE WATER TREATMENT PROCESS

Precipitation of dissolved metals, adjustment of pH and redox potential, and separation of precipitated metals solids were needed to remove dissolved metal CoCs to meet regulatory requirements. Figure 5 is the process flow diagram that integrates the unit operations to treat mine-impacted water at the mine.

# Figure 5:





The mine water treatment process used magnesium anode electrochemical treatment to raise pH to 11.0 to precipitate dissolved cadmium and zinc. Their insoluble hydroxides were separated from treated mine water using a removable skin layer membrane. The pH was lowered from pH 11.0 to 8.0 using a fine mist spray of treated mine water into an enclosed tank filled with CO<sub>2</sub> gas exhaust of a diesel generator to form carbonic acid. An electrochemical reactor filled with carbon steel pellet anodes formed insoluble metal hydroxides and iron co-precipitates of dissolved aluminum, antimony, arsenic, copper, and iron. A spray mist of ferrous iron treated water was oxidized by scrubbing with air to form less soluble ferric iron. Lastly, a second removable skin layer membrane separated insoluble solids for discharge of treated water to the environment.

PROCESS DESCRIPTION – Steps of the mine water treatment process were as follows:

- Mg Electrochemical Treatment: Water was pumped through the magnesium pellet anode electrochemical cell, powered by a controlled AC current. Electrochemically dissolved magnesium anode pellets increased pH, coagulated solids, and produced reducing conditions. Water upflow through the magnesium pellet bed flushed precipitated solids, hydrogen gas, hydrogen sulphide gas, ammonia gas, and carbon monoxide gas byproducts that were formed by hydrolytic reactions so the gases did not accumulate inside the cell. These gas by-products were collected in a Mg reaction tank and withdrawn under vacuum by a ventilation fan to the air intake of the diesel generator for combustion. Filtered diesel exhaust flowed to a CO<sub>2</sub> scrubber to form carbonic acid to pH neutralize the alkaline water.
- 2. Mg Reaction Tank: A pH setpoint of approximately 11.0 in Membrane 1 Feed Tank following Mg Reaction Tank regulated the electric current to the magnesium pellet anode electrochemical cell. Membrane 1 Feed Tank and Mg Reaction Tank were sealed, and their headspaces were continuously withdrawn by a Ventilation Fan for flow to the air intake of a diesel generator.

- 3. Replaceable Skin Layer Membrane 1: Overflow from Mg Reaction Tank flowed to Membrane 1 Feed Tank where a Level Sensor activated Membrane 1 Feed Pump.
- 4. CO<sub>2</sub> Scrubber: Permeate was pumped through spray mist nozzles into an enclosed headspace to scrub CO<sub>2</sub> in diesel generator exhaust and thus lower pH from 11.0 to 8.0.
- 5. Steel (Fe) Electrochemical Treatment: Water from the CO<sub>2</sub> scrubber was pumped up through the Fe cell, dissolving steel anode pellets to form dissolved ferrous iron (Fe<sup>2+</sup>) for cationic coagulation and to co-precipitate dissolved antimony and arsenic. Water upflow flushed hydrogen, hydrogen sulphide and carbon monoxide gas by-products formed by the hydrolytic reactions out of the Fe cell. The gas by-products were continuously withdrawn by a Ventilation Fan to the air intake of the diesel generator.
- 6. Air Scrubber: A blower supplied air to an enclosed tank where dissolved ferrous iron in Fe cell treated water was pumped through nozzles to form a fine mist spray and oxidize ferrous iron to form less soluble ferric iron. Dissolved iron agglomerated metal hydroxides and iron co-precipitates of arsenic and antimony.
- Replaceable Skin Layer Membrane 2: Overflow from the air scrubber flowed to Membrane 2 Feed Tank. Membrane 2 Feed Pump produced a permeate for discharge to the environment.
- 8. Filter Press: Back wash from Membrane 1 and Membrane 2 flowed to a Solids Holding Tank for dewatering by a Filter Press. The solids cake was disposed according to the mine's sludge management plan. Liquid filtrate from the Filter Press was returned to the mine's pond to be treated again by the water treatment process.

Table 4 lists the operating conditions used during three phases of on-site mine water treatment testing. Approximately 667,000 litres of water were treated during the tests.

# Table 4:

	Units	Phase 1	Phase 2	Phase 3
Volume of Water Treated	Litres	340,860	232,720	95,000
Unit Operations:				
Mg Electrochemical Cell				
Current / Voltage	amps / volts	60 / 39 - 48	130 / 70	130 / 70
Flow Rate	L/min	75, 100	75, 100	25, 50
pH Target	-	10.7	11.0	11.0
Mg Reactor HRT	minutes	60	none	60
Solids Separation 1	type	Flotation	Flotation	Membrane 1
CO₂ Scrubber				
HRT	minutes	30	30	30
Recirculation Rate	L/min	675	675	675
pH Target	-	8.0	8.5	7.5
Fe Electrochemical Cell				
Current / Voltage	amps / volts	NA	60 / 30	60 / 30
Flow Rate	L/min	NA	75, 100	25, 50
Fe Reactor HRT	minutes	NA	none	120
Recirculation Rate	L/min	NA	none	100
pH Target	-	NA	8.5	8.0
Oxidation	type	Air	Air	O <sub>2</sub>
Solids Separation 2	type	Flotation + Gravity Clarifier	Flotation + Gravity Clarifier	Membrane 2
Diesel Generator	type	Older Model	Murphy Tier 3	Murphy Tier 3
Filter	type	Donaldson	Donaldson	Donaldson
CO <sub>2</sub> Utilization	%	<10%	<10%	<10%

# Summary of Mine Water Treatment Test Conditions

### RESULTS

REMOVAL OF DISSOLVED METALS - The concentrations of total and dissolved metal CoCs are presented in Table 5 which shows that, like many mine waters, the metals in mine water were primarily dissolved. Aluminum and iron were the exceptions, present primarily as insoluble solids. Data from Table 5 indicates that changing the water chemistry was needed to remove the metals as insoluble solids for their removal.

# Table 5:

# Dissolved vs Total Metals Concentrations in Pond Water

Sample	Units	Al	Sb	As	Cd	Cu	Fe	Zn
Mean Dissolved Metal	μg/L	7.7	19.8	4.1	4.0**	5.3	10.3	484.8*
Concentration								
Mean Total Metal	μg/L	86.6	20.2	5.2	4.4	9.8	114.2	594.7
Concentration								
Mean Dissolved Metal	%	9	98	79	91	54	9	82
Concentration/ Mean Total								
Metal Concentration								

\*Exceeds permit maximum concentration in any sample. \*\*Exceeds permit monthly average.

Table 6 shows that dissolved metal concentration limits for regulatory compliance with BC Fresh Water Aquatic Life guidelines were achieved by means of the described mine water treatment process. Treated mine water resulted in 100% survival in Rainbow trout 96hLC50 bioassays. Clays (magnesium and aluminum silica oxides) formed by Mg electrochemical cell were separated from treated water by Membrane 1 filtration. Solids formed by CO<sub>2</sub> scrubber, Fe electrochemical cell, and air scrubber were removed by Membrane 2 filtration.

#### Table 6:

Sample	Units	s Permit Permit			Total Metals			<b>Dissolved Met</b>	als
	Maximum	Average	Feed	Discharge	%	Feed	Discharge	%	
		(Dissolved)	(Dissolved)			Removal			Removal
Aluminum	μg/L	500	100	60.4	10.4	83	5.7	<5.0	-
Antimony	μg/L	160	20	19.2	7.43	61	18.1	7.58	58
Arsenic	μg/L	30	5	5.62	0.88	84	4.55	0.5	89
Cadmium	μg/L	0.12	0.02	4.79	0.265	94	4.33	0.018	99.6
Copper	μg/L	40	7	9.66	5.23	46	5.87	0.79	87
Iron	μg/L	300	-	86	7,410	-	12	45	-
Zinc	μg/L	180	30	638	50.6	92	513	21.1	96

Removal of Total and Dissolved Metal Contaminants of Concern

The effectiveness of the treatment process to remove elevated concentrations of cadmium, iron and zinc was assessed by spiking the feed water with their chloride salts. Table 7 shows that high removal efficiencies were achieved when treating elevated metals concentrations.

### Table 7:

Removal of Total and Dissolved Metals from Spiked Feed

Units	Al	Sb	As	Cd	Cu	Fe	Zn
μg/L	119	26	5.35	11.7	28	1,360	2,400
μg/L	<5.0	3.69	0.57	0.115	0.72	<10	7.1
%	>96	86	89	99	97	>99	99.7
μg/L	10.4	19.6	1.21	8.8	4.82	10	1690
μg/L	<5.0	3.44	0.55	0.115**	0.86	<10	21.5
%	>52	82	55	99	82	-	99
	μg/L μg/L % μg/L μg/L	μg/L 119 μg/L <5.0 % >96 μg/L 10.4 μg/L <5.0	μg/L 119 26 μg/L <5.0 3.69 % >96 86 μg/L 10.4 19.6 μg/L <5.0 3.44	μg/L 119 26 5.35 μg/L <5.0 3.69 0.57 % >96 86 89 μg/L 10.4 19.6 1.21 μg/L <5.0 3.44 0.55	μg/L 119 26 5.35 11.7 μg/L <5.0 3.69 0.57 0.115 % >96 86 89 99 μg/L 10.4 19.6 1.21 8.8 μg/L <5.0 3.44 0.55 0.115**	μg/L 119 26 5.35 11.7 28 μg/L <5.0 3.69 0.57 0.115 0.72 % >96 86 89 99 97 μg/L 10.4 19.6 1.21 8.8 4.82 μg/L <5.0 3.44 0.55 0.115** 0.86	μg/L 119 26 5.35 11.7 28 1,360   μg/L <5.0

\*Exceeds permit maximum concentration in any sample. \*\*Exceeds permit monthly average.

pH NEUTRALIZATION -  $CO_2$  gas from filtered exhaust of a diesel generator that was to power the mine water treatment facility could produce sufficient  $CO_2$  gas to pH neutralize alkaline treated mine water at the permitted rate of mine water discharge. Table 8 indicates that pH neutralization used 22% of the  $CO_2$  gas that was produced by the diesel generator.

# Table 8:

Parameter	Units	Value	
Initial pH	-	11.0	
Final pH	-	7.5	
$CO_2$ to Remove OH- (minimum amount)*	g/m <sup>3</sup>	44	
CO <sub>2</sub> at Saturation	g/m <sup>3</sup>	2,000	
Total CO <sub>2</sub> Consumed	kg/m <sup>3</sup>	2.0	
CO <sub>2</sub> Generation Rate	kg CO <sub>2</sub> /L Diesel	2.7	
Rate of Diesel Consumption @ 75% load**	L Diesel/h	41	
CO <sub>2</sub> Generation from Diesel Generator	kg CO <sub>2</sub> /h	110	
Mine Water pH Neutralization Capacity	L Water/min	894	
Requirements for $CO_2$ @ 200 L/min	% CO <sub>2</sub> Consumed/ CO <sub>2</sub> Available	22	

## CO<sub>2</sub> Requirements for pH Neutralization vs CO<sub>2</sub> from Diesel Generator at the Mine

Table Notes:

 $*=(10^{(-(14-pH_i))-10^{(-(14-pH_f))})*44.01$ 

\*\*A 175-kW diesel generator operating at 75% of full load (131 kW) to maximize fuel efficiency and cleanliness of the burnt diesel exhaust consumes 0.31 L of diesel/kWh or 40.6 L of diesel/h.

SLUDGE CHARACTERISTICS - Removing dissolved metals from mine water produced an insoluble metals slurry that required solids dewatering and disposal. Ideally, sludge volume should be minimized, chemically stable, and readily dewaterable.

Table 9 shows the concentrations of total metals in the sludge were high. Since metals can be removed from mine water but not destroyed, a high concentration of metals in the solid waste reflects a correspondingly small amount of waste sludge produced. However, Table 9 also shows that the concentrations of leachable metals in sludge produced by electrochemical treatment at the mine were less than detection limits. This indicates that the sludge produced by the mine water treatment process was chemically stable, in contrast with a general chemical instability of sludge from mine water treatment that is produced by chemical dosing methods such as with lime. Consequently, the sludge produced by the electrochemical mine water treatment process would not be classified as a hazardous waste.

In general, sludge produced by electrochemical treatment tends to be stable chemically, yielding toxicity characteristic leaching procedure (TCLP) (US EPA, 1992) values far below regulatory requirements for disposal at industrial waste landfills.

Treatability testing using lime was conducted in parallel electrochemical treatment of the mine water. Testing revealed that the weight of dry solids produced by the electrochemical mine water treatment process for this mine water treatment application was 11% compared to the weight of dry solids produced by lime treatment of the same mine water.

## Table 9:

Metal	Filter Cake RL [mg/kg dry]	Filter Cake Strong Acid Leachable Metals [mg/kg dry]	Filter Cake TCLP Leachate [mg/L]	HWR LQS [mg/L]
Arsenic	0.3	28.6	<0.010	2.5
Barium	1	338.5	<1.0	100
Boron	2	5.6	<0.50	500
Cadmium	0.04	26.3	<0.001	0.5
Chromium	1	33.3	<0.050	5.0
Copper	0.4	91.0	<0.10	100
Lead	0.2	27.3	<0.010	5.0
Mercury	0.04	0.05	<0.002	0.1
Nickel	0.6	69.5	<0.10	500
Selenium	0.2	<0.20	<0.020	1.0
Silver	0.1	0.59	<0.002	5.0
Uranium	0.05	0.29	<0.020	10
Zinc	2	4,005	<0.50	500

Dewatered Solids Cake from Water Treatment at a Mine: Total Metals and Leachability

Table Notes:

RL = Reporting limit, SALM = Strong Acid Leachable Metals (standard BC ENV total metals analysis method, TCLP = US EPA Method 1311, Toxicity Characteristic Leaching Procedure, HWR LQS = BC Hazardous Waste Regulation Leachate Quality Standards for determination of a Hazardous Waste.

MEMBRANE FOULING - A removable skin layer membrane was operated to process electrochemically treated mine water for repeated cycles at a constant initial pressure and flow rate. During the constant pressure operating cycle, once the flow rate decreased to less than 50% of the initial flow, the membrane system was backwashed, the aluminum oxide powder was re-applied, and a new membrane operations cycle was run. Ten repeated cycles showed no change in the initial pressure and flow rate or cycle time, indicating a lack of permanent fouling of the membranes. Longer term, this suggest no or substantially reduced CIP requirements, thereby decreasing chemical costs and waste for disposal.

## ESTIMATE OF OPERATING COSTS

A preliminary estimate of operating costs of the unit operations to treat the mine impacted water are presented in Table 10.

Aluminum oxide powder is applied on the surface of the membrane tube at the beginning of each filtration cycle. For a 12-hour filtration cycle, the cost of aluminum oxide replacement is estimated as 0.085 per m<sup>3</sup>.

Since sludge disposal costs vary significantly, no estimate of cost savings to dispose of metals sludge that is lower in volume and non-leachable was made.

# Table 10:

Unit Operation	Treatment Objective	Ballpark Cost [\$/m <sup>3</sup> ]
Mg Amprey	>> pH to precipitate metals	0.337
Membrane 1	Separate high pH precipitated solids	0.085
Misty CO <sub>2</sub>	Lower pH for metals precipitation at pH 8.0	0.045
Fe Amprey	Fe co-precipitate of As, Sb	0.166
Misty Air	Convert Fe <sup>2+</sup> to Fe <sup>3+</sup> to minimize solubility of Fe and co-precipitates	0.045
Membrane 2	Separate mid pH precipitated solids	0.085
Preliminary Estimate	e of Costs to Operate Unit Operations	0.763

#### Ballpark Operating Costs to Treat Mine-Impacted Water at a BC Gold Mine

Table Notes:

Operating costs do not include: operating costs outside of costs for unit operations, operator labour, disposal of solid residuals, clean-in-place chemicals, maintenance and parts replacement, building lighting, heat, ventilation, maintenance, permit related costs, amortization of capital, on-going technology support, technology license fee.

# CONCLUSIONS

- 1. The mine water treatment process removed dissolved metal CoCs down to extraordinarily low concentrations to meet regulatory requirements for discharge to an environmentally sensitive receiving water.
- 2. The electrochemical cell with consumptive magnesium anode pellets elevated pH to precipitate cadmium and zinc as metal hydroxides at elevated pH for their removal by membranes.
- 3. The CO<sub>2</sub> scrubber supplied with filtered diesel generator exhaust lowered pH for removal of dissolved metals and for regulatory compliance for pH.
- 4. The electrochemical cells with consumptive steel anode pellets co-precipitated dissolved antimony and arsenic.
- 5. The air scrubber oxidized ferrous iron to enable removal of iron and iron-co-precipitates by membranes.
- 6. The solids precipitate by-product from both membranes was readily dewatered to form a non-leachable solids cake for disposal.
- 7. Full-scale testing confirmed meeting regulatory compliance for all dissolved metal CoCs. The treated effluent was not acutely toxic, meeting regulatory requirements.
- 8. The replaceable skin layer membranes had long filtration cycles, and, operating under extreme pH conditions, showed no indication of fouling after ten cycles of operation.
- 9. Precipitated metal solids were easily dewatered and chemically stable. Leachate (TCLP) concentrations were below detection limits, and the mass of solids produced was 11% compared to solids produced by lime treatment of the same mine water.

10. A preliminary estimate of operating cost to treat this mine water at  $1 \text{ m}^3/\text{min}$  was  $0.76/\text{m}^3$ .

### REFERENCES

Blais, J; et al (2008), Metals Precipitation from Effluents: Review, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management,* 12:3 (135).

Method 1311: Toxicity Characteristic Leaching Procedure, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, July 1992, *United States Environmental Protection Agency*.

Loganathan, K, et al (2015). A hybrid froth flotation-filtration system as a pretreatment for oil sands tailings pond recycling water management. *Journal of Environmental Management 161 113-123* 

Bromley, D. and Loganathan, K (2013). Nanoflotation-New Water Treatment Technology for petroleum exploration and production. *IWC 13-23* 

McConnell, A – Murphy Oil (2023). Public Reference, RSL Membranes™ Email Oct 17,2023