

September 2, 2011

Chuck Hubert Environmental Assessment Officer Mackenzie Valley Review Board Suite 200, 5102 50<sup>th</sup> Avenue, Yellowknife, NT X1A 2N7

Dear Mr. Hubert

#### RE: <u>Environmental Assessment EA0809-002, Prairie Creek Mine</u> Desk Study of Process Water Treatment Options

Please find attached a report by SNC-Lavalin. The report summarizes a desk study on treatment options for process water expected to be generated by the Prairie Creek operation. This work is one component of a framework for consideration of site specific water quality objectives. The framework proposed by Canadian Zinc Corporation (CZN) was submitted to the Review Board on July 4, 2011.

CZN will be adopting the recommendations of the report. Plans are being made to collect necessary samples, and embark on a further testing and evaluation program.

Yours truly, CANADIAN ZINC CORPORATION

David P. Harpley, P. Geo. VP, Environment and Permitting Affairs

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CLIENT:	Canadian Zinc Corp.
PROJECT:	Prairie Creek Mine

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#### **ISSUE/REVISION INDEX**

Issue			Revis	ion		
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RR	PB	ALN/DL	BM		2011-08-03	Issued for comments
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Issue Codes: RC = Released for Construction, RD = Released for Design, RF = Released for Fabrication, RI = Released for Information, RP = Released for Purchase, RQ = Released for Quotation, RR = Released for Review and Comments.

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## APPENDICES

APPENDIX A	SNC Draft Report dated August 3, 2011-08-24
APPENDIX B	Comments from Water Engineering Technologies Inc.

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## INTRODUCTION

SNC-Lavalin was requested to undertake a desk-based review of process water treatment alternatives by Canadian Zinc Corporation (CZN), based on water expected to be produced from the Mill at their Prairie Creek Mine. A draft report was completed in early August, 2011 (see Appendix A) and circulated to CZN and Aboriginal Affairs and Northern Development Canada (AANDC). Written comments were received from a consultant for AANDC (see Appendix B), and a conference call was subsequently held to discuss the comments on August 19, 2011. This final report incorporates the comments made.

## 1.1 Location

The Prairie Creek Mine site is located in the southern Mackenzie Mountains in the south-west corner of the Northwest Territories. The mine site facilities are situated on the eastern side of and adjacent to Prairie Creek, about 43 km upstream from its confluence with the South Nahanni River.

## **1.2** Background to Process Water Treatment Review

The water treatment plant at Prairie Creek is intended for the treatment of mine underground water and a portion of process plant effluent water.

Early bench-scale treatment testing of representative water samples for metals removal and subsequent optimization of reagent and settling characteristics performed by SGS-CEMI in 2006 led to the development of the currently proposed water treatment processes for the two water streams to be produced during operations. The proposed treatment processes include hydrated lime for mine water, and a combination of sulphide/lime/iron III treatment for process water.

Data reported in 2010 by SGS-CEMI confirmed the required treatment processes to remove metals from both waters and optimized the processes.

The currently proposed process water treatment scheme consists of first adding sulphuric acid to lower the pH to 4.5. Sodium sulphide is added at this time to react with the dissolved metals to form insoluble metal sulphides, which are stable throughout the remainder of the treatment process. The sodium sulphide treated process water then proceeds to a rapid mix in-line mixer where hydrated lime is added to adjust the pH from 4.5 to 9.0. The precipitated solids are maintained in suspension. Iron III Sulphate is then added to promote settling of the metals. Compressed air is added into this reactor to ensure full oxidation of all ions in

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solution. Flocculant is added to help unite smaller particles, and the solution flows into a clarifier where settled solids and treated decant water are separated.

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## 1.3 Scope of "Process Water Screening Review"

The purpose of this study is to perform a 'process water screening review' of base metal and heavy metal removal technologies which can be used successfully to produce an effluent meeting the most stringent requirements for discharge to the environment. Sulphate and total dissolved solids (TDS) removal were a secondary consideration for this study. The purpose is neither to review the correct selection of the treatment scheme for process water, nor to critique the design of the water treatment facility presently proposed for the Prairie Creek Mine Site.

The process water treatment option review will include the current treatment technology proposed for Prairie Creek; several membrane processes; treatment with barium hydroxide; ion exchange, and biological treatment alternatives. "Screening" criteria that were assumed included full-scale plant reliability; waste product disposal, consistent and reproducible effluent quality, order of magnitude capital and operating costs, and suitability to laboratory level bench-scale testing (since a full-scale plant would not be built if satisfactory results could not be generated on a bench-scale).

## 1.4 Current recommended Water Treatment Process

Selective laboratory tests on simulated mill water effluent and their subsequent engineering review have defined the best practical available technology to remove metals from the waste water at Prairie Creek. The use of sulphide/lime precipitation can be considered the 'base case' for this review.

The success of metal precipitation processes whether using sulphide or lime, depends to a large extent on other water quality parameters such as alkalinity and suspended solids in the treated water streams. It should be noted that metal hydroxide and sulphide precipitates are generally very fine and require additional steps of coagulation and flocculation coupled with high performance clarification to obtain very low levels of total metals in the treated effluent.

## 1.5 Explosive Management and Ammonia/Nitrate in Mine Water

CZN is planning to use emulsion explosives for 100% of their blasting needs. This is because of the level of nitrogen residues that would occur if ANFO is used. Use of emulsions would not avoid theses residues, but with appropriate handling, hole charging and excess product management, emulsion losses and thus residues are expected to be low.

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Mine water is to be pumped from underground to a large storage pond on surface, where the water will be stored for several months before either being recycled to the Mill or sent to the Water Treatment Plant. The several month residence time is expected to allow the low concentrations of nitrogen residues from blasting to oxidize and degrade.

Therefore, these factors, together with CZN's water treatment and discharge plan which will reduce or avoid discharge in the winter and during periods of low creek flow, means that water treatment to reduce nitrogen species concentrations may not be necessary.

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# 2.0 SUMMARY OF TREATMENT TECHNOLOGIES

This review is an evaluation of prescribed techniques and industrially-accepted operations to determine their performance in the removal of metals and reduction of dissolved solids content.

The 'case by case' consideration of each treatment approach is performed using 'Best Professional Judgment' standards to meet the purpose of the study.

## > Membrane Processes

## (i) Reverse Osmosis

Reverse osmosis (RO) units force water through a semi-permeable membrane under pressure, leaving contaminants behind. Reverse osmosis assemblies can treat approximately three times more water than they discharge. 75% of the water fed to the RO becomes treated water, while 25% becomes a waste brine flow. However, the actual recovery of the system (i.e. treated flow over total flow fed to the unit), will vary greatly based on the feed water quality. Reverse osmosis removes turbidity, microbes and virtually all dissolved substances. However, while many harmful metals are removed, such as zinc, cadmium and selenium, beneficial metals are also removed, such as calcium and magnesium. RO membranes are non-selective with regard to the removal of metals; they generally reject ionized divalent metals. Note that the actual rejection rate of metals depends on the type of RO membrane used (make and model), system design and operating conditions.

The pressure utilized during reverse osmosis depends on the Total Dissolved Solids (TDS) concentration, with typical pressures ranging from 300 to 1,200 psi to create flows of clean water from high TDS influent concentrations through the membrane. Depending on the contaminants in the feed water, high TDS concentrations in the process water would reduce the effectiveness of a reverse osmosis system (i.e. a reduction in volume of treated water produced).

Gypsum levels may be near saturation in process water. High gypsum saturation levels in reverse osmosis feed streams means the membranes are highly likely to foul or clog, resulting in unreliable performance. However, in some reverse osmosis processes, fouling is controlled by the addition of anti-scaling chemicals and by operating in acidic conditions.

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A brine waste stream would result from the reverse osmosis units. This would require an encapsulated disposal area which would need to hold both precipitation sludge and brine.

Reverse osmosis systems are in place at other mines and other industrial facilities, and are used to treat wastewaters with low metal loadings. While reverse osmosis may be technically feasible, high TDS levels in the influent and adverse climatic conditions present challenges for successful design and operation. In addition, large volumes of brine would need to be disposed of over the long-term.

Furthermore, reverse osmosis must be preceded by a pre-treatment system whose objective is to remove as much of the fouling materials from the raw water stream as possible, such as total suspended solids (TSS). The pre-treatment system must also include a filtration step, either granular filtration or membrane ultra-filtration.

High dissolved metal concentrations (i.e. 10s to 100s mg/L) in the feed water can also cause a rapid fouling of the membrane surface due to metal oxide precipitation. To prevent this, metal concentrations can be reduced ahead of the reverse osmosis system by lime precipitation. Alternatively, the reverse osmosis plant could also be operated under acidic condition, ensuring the dissolved metals are in their ionic form.

Generally, reverse osmosis is used as a final polishing step, separating the dissolved metals from the process water, and producing a treated effluent that is generally very low in TDS and metals that can be discharged directly to the environment and/or re-used in the process.

## (ii) Nanofiltration

Nanofiltration is a membrane system similar to reverse osmosis except the membrane has a larger particle size cutoff; up to 0.005 micron compared to less than 0.002 micron for reverse osmosis. Typical pressures for nanofiltration applications range from 50 to 200 psi. Nanofiltration removes bacteria, and some viruses from water as well as most organic matter and some natural minerals. Nanofiltration, however, does not remove dissolved salts to the same high efficiency as reverse osmosis, solids rejection being 85 to 95% efficient compared to reverse osmosis at 99% rejection.

## (iii) Electrodialysis

Electrodialysis is another membrane treatment technology where electricity is used as the driving force for separation instead of pressure. An electrical current is used to move ions through a series of selective membranes. The consecutive

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membranes concentrate the ions in a waste stream. Electrodialysis reversal is a modification of the process that switches charges during operation to promote cleaning. This technology is applicable for treatment of high TDS water because it is less susceptible to plugging and is easily cleaned. The downside of this process is the high energy use and the volumes of concentrated wastes requiring disposal (typically more volume that reverse osmosis). In addition, there are no examples of the use of electrodialysis at mining operations. Electrodialysis is therefore not considered a viable option for Prairie Creek.

## Activated Carbon Adsorption

Activated carbon is an effective adsorbent and removes many organic and metal contaminants from drinking water. With the column technique, the contaminated solution flows through the carbon and dissolved metals are adsorbed. The loaded carbon can be disposed of and replaced with fresh carbon, or stripped and regenerated for re-use. Adsorption capacity of activated carbon depends on:

- Physical and chemical characteristics of adsorbent (i.e. filtration media);
- Physical and chemical characteristics of adsorbate (i.e. contaminants to be adsorbed on the media);
- Concentration of the adsorbate in liquid solution;
- Characteristics of the liquid phase (pH, temperature, etc.);
- Retention time

As can be anticipated, most of the dissolved metals will be adsorbed but the loading capacity is very limited. This would make this process extremely impractical and expensive to operate on a large industrial scale. Some of the metals are removed to very low concentrations (sub ppb) but others will remain a concern. Due to the limited loading capacity, activated carbon treatment could be considered as a polishing step that follows a primary metal removal system.

## Ion Exchange

lon exchange (IX) technology is well suited to remove dissolved heavy metals and sulphate from a water stream that is close to saturation with gypsum. Feed water is first pumped through a cation loading stage where cations like calcium (Ca<sup>2+</sup>) and metals are removed from the feed water through adsorption onto a strong acid cation resin (i.e. resin that is selective to positively charged ions) and replaced generally by hydrogen ions (H+) or sodium (Na+). After this stage, the water is pumped through an anion loading stage where anions like sulphate (SO4<sup>2-</sup>) are removed through adsorption onto a weak base anion resin (i.e. resin that is selective to negatively charged ions) and replaced by hydroxide ions (OH-). In

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cases where sulphate concentrations are not high, only a strong acid cation resin step can be used to selectively remove the dissolved metals from the effluent stream. Note that there are many types of IX resins available on the market and can be chosen to be highly selective in the removal of a specific metal ions, or non-selective where removal of all positively or negatively charged ions occurs.

Typically, ion exchange treatment can be conducted in either a column system or a fluidized bed where the contaminated solution is contacted with the resin. When contaminant breakthrough occurs, the resin can be regenerated using a dilute sulphuric acid and lime solution.

Provided the ion exchange system is properly sized for the effluent to be treated, and the right resins with the required selectivity are chosen, low metals and sulphate concentrations can be achieved. The volume of regeneration waste produced typically varies between 5 to 10% of the total daily volume treated. The exact volume will depend on the type of resins used and the sizing of the column.

The regeneration waste from cationic and anionic ion exchange units are often mixed together in order to produce a neutral solution. In a mine application, this regeneration waste must be disposed of since it contains a high concentration of dissolved metals and sulphate. Thus, gypsum and metal hydroxide sludge must be removed from the regeneration waste by clarification, and can be co-disposed of in the tailings.

## Biological Treatment

Biological treatment processes can be used if the treatment of sulphate is desirable via a process called biological sulphate reduction. The process takes place under anaerobic conditions and requires the addition of a carbon source, such as ethanol or acetic acid. Under these conditions, sulphate reducing bacteria (SRB) can reduce the sulphate to elemental sulphur. Furthermore, successful sulphate reduction is generally accompanied by an increase in pH due to the production of alkalinity. If the alkalinity levels are sufficiently high, and the pH is at the right value, certain metals can precipitate out.

Though this technology sounds promising, biological treatment of mine effluent has only had limited success in commercial applications. The main concerns with biological treatment of mill effluent in a cold climate are the following:

• An additional carbon source has to be added to the stream. Thus, a large volume of ethanol or acetic acid has to be stored on site.

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- Under cold water conditions, biological activity exponentially reduces. Thus, no treatment is possible during cold water conditions unless the water is heated.
- Inconsistent results and difficult control.

For this reason, a biological process for mine effluent is not considered as a Best Available Technology for Prairie Creek.

## **Barium Hydroxide**

Also for sulphate treatment, barium salts are very effective in removing sulphate from the wastewater stream due to the high insolubility of barite (BaSO<sub>4</sub>). Barium salts that are commonly used for sulphate removal by precipitation of barium sulphate include barium hydroxide, Ba(OH)<sub>2</sub>, barium carbonate, BaCO<sub>3</sub> and barium sulphide, BaS. The precipitation of barium sulphate occurs according to the following reactions:

 $\begin{array}{l} BaCO_{3 (S)} + H_2SO_4 \twoheadrightarrow BaSO_{4 (S)} + H_2CO_3 \\ Ba(OH)_{2 (S)} + H_2SO_4 \twoheadrightarrow BaSO_{4 (S)} + 2H_2O \\ BaS_{(S)} + H_2SO_4 \twoheadrightarrow BaSO_{4 (S)} + H_2S_{(q)} \end{array}$ 

Barium hydroxide and barium sulphide are very effective in removing sulphate over the entire pH range; however, barium carbonate is only effective in a specific pH range. Studies have shown that barium hydroxide removal can reduce the concentration of sulphate to below 200 mg/L. Due to the high cost of barium, further treatment of precipitated barium sulphate might be possible in order to recycle the barium. Also, barium hydroxide is not very effective in removing heavy metals; therefore, this process can only be used in conjunction with another technology, such as lime treatment.

## > Hydroxide Precipitation

The removal of dissolved metals from acid mine drainage is traditionally carried out by hydroxide precipitation. In this treatment scheme, an alkali precipitating agent is generally added to the effluent to raise the pH of the effluent and precipitate the dissolved metals as metal hydroxides (Me(OH)x). The alkali typically used in the mining industry is hydrated lime (Ca(OH)2). Sodium hydroxide (NaOH) can also be used, but it is generally used when the metal concentrations in the effluents are low. Therefore, this approach may not be appropriate for Prairie Creek mill water.

Following the addition of the alkali, the metal hydroxide has to be separated from the treated effluent. At certain mine sites, lime is added at the inlet of a large tailing pond and the metal hydroxide sludge is allowed to settle in the pond. At

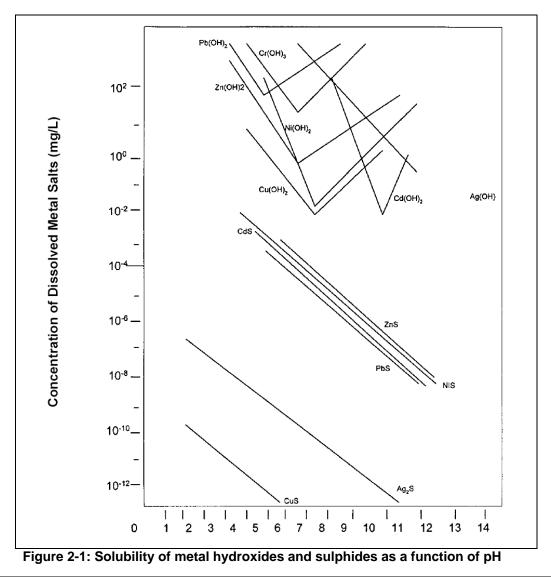
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other mine sites, the settling takes place in a clarifier with the addition of a flocculant to aid the settling process.

#### Treatment performance

With hydroxide precipitation, metals such as copper, cadmium, iron, lead, nickel and zinc can be removed as metal hydroxide precipitates. However, the treatment performance of hydroxide precipitation depends greatly on the operating pH selected and the desired metals to be removed. As shown in Figure 2.1, the minimum solubility of different metal hydroxides varies with pH.



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The typical treatment performance that can be achieved using hydroxide precipitation is as follows:

- Copper: 0.3 mg/L
- Iron: 3 mg/L
- Lead: 0.2 mg/L
- Nickel: 0.5 mg/L
- Zinc: 0.5 mg/L

Hydroxide precipitation, however, does not reduce sulphate concentrations or total dissolved solids (TDS). For example, when treating acid mine drainage, the concentration of sulphate in the treated effluent is generally close to saturation (1500 to 2000 mg/L of SO4) when the sulphate concentration in the feed water is very high (i.e. > 3000 mg/L)

Hydroxide precipitation generates metal hydroxide sludge. If the process water contains high concentration of sulphates, gypsum will also be formed.

When the treatment is carried out within a tailings pond, the metal hydroxide and gypsum sludge settle and accumulate in the pond. When the treatment is carried out in a clarifier, the sludge is typically dewatered using a belt filter or filter press and disposed off in the tailings. The filtrate is recycled either back to the tailings pond or ahead of the clarifier.

## > Sulphide Precipitation

Sulphide precipitation works under the same basic principle as hydroxide precipitation. A precipitating agent, in this case sodium sulphide (Na<sub>2</sub>S), is added to precipitate the metals as a metal sulphide (MeS).

As shown in Figure 2.1, sulphide precipitation is generally used when low metal concentrations are required in the treated effluent. Low metal concentrations can also be achieved over a wider range of pH than hydroxide precipitation. Similar to hydroxide precipitation, TDS is not removed, nor are sulphates.

Sulphide precipitation generates metal sulphide sludge and can be disposed of in a similar fashion to hydroxide sludge. Precipitates are fine and pose challenges to settling, generally requiring either a higher dosage of flocculant, higher flocculation contact time and/or a larger settling area (i.e. larger clarifier).

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# 3.0 TREATMENT OPTIONS

Based on the assumed process effluent stream to be treated at Prairie Creek, and the objective of meeting the most stringent requirements for discharge into a natural body of water, one or a combination of the treatment technologies noted above can be used to meet this objective.

The following section presents several suggested treatment options. These are based on a combination of the technologies, or unit processes, that were presented in Section 2. For each option, a list of advantages and disadvantages is presented based on the following criteria:

- Treated effluent quality with regard to dissolved metals and total dissolved solids
- Complexity of the residual management system
- Operation complexity
- Maintenance complexity
- Maturity of the technology proposed

For this review, the treatment options are based on the following assumptions:

- 1. The concentrations of dissolved metals in the process water are less than 10 mg/L.
- Each treatment option will be designed to produce a treated effluent that will meet or exceed the following <u>minimum</u> monthly average effluent criteria (note: the values indicated are typical regulatory values required by some provinces):
  - Arsenic: 0.2 mg/L
  - Copper: 0.3 mg/L
  - Iron: 3.0 mg/L
  - Lead: 0.2 mg/L
  - Nickel: 0.5 mg/L
  - Zinc: 0.5 mg/L
  - TSS: 15 mg/L (TSS = Total suspended solids)
  - pH: 6 to 9.5

## Base Case – Sulphide / Lime Treatment

The base case option is the previously proposed treatment system which consists of sulphide precipitation followed by lime precipitation. The metal sulphide and

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hydroxide precipitates are separated from the treated water by clarification. The following figure presents a block diagram of this option.

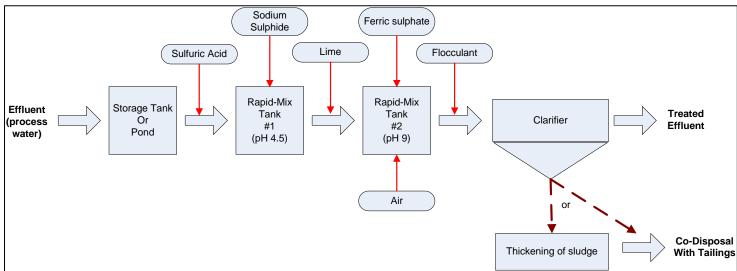


Figure 3-1: Base Case – Sulphide / Lime Treatment Followed by Clarification

## Advantages

- The dissolved metal concentrations in the treated effluent are expected to be much lower than the assumed discharge criteria since the solubility of metal sulphides is much lower than for metal hydroxide precipitates.
- The TSS criterion will be met when the clarifier is operating normally.
- The only residual to manage is the metal hydroxide and sulphide precipitate. The sludge from the clarifier can be managed by co-disposal with the tailings. This is generally done in most mines.
- Lime precipitation is a proven technology.

## **Disadvantages**

- Sulphate concentrations are expected to be at saturation levels (i.e. approx. 2000 mg/L).
- TDS will not change in this process.
- The chemicals that need to be added and managed are hazardous (acid and sulphide).
- Risk management required for hydrogen sulphide gas emissions from the use of sodium sulphide.
- Potential risk of residual sulphide in the treated effluent.
- Risk of scaling in the rapid-mix tanks and the clarifier due to precipitation of calcium sulphate (gypsum) and hydroxide sludge (only applicable if sulphate is present in the feed water).

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- Full scale mining installations may not exist that use both sulphide and lime precipitation in series.
- Fineness of the sulphide precipitate makes settling difficult.

## Option 1 – Lime Treatment & Reverse Osmosis (RO) / Nanofiltration (NF)

Option 1 consists of a two stage treatment process. The 1st stage involves lime precipitation of the dissolved metals followed by separation of the metal hydroxide sludge. The 2nd stage involves the polishing of the treated effluent to remove residual dissolved metals and reduce the total dissolved solids by reverse The following figure presents a block diagram of this osmosis/nanofiltration. option.

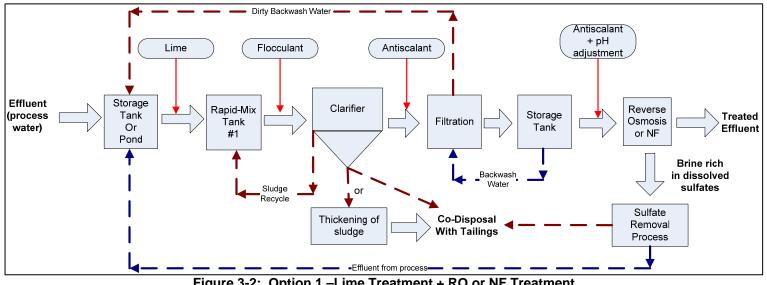


Figure 3-2: Option 1 – Lime Treatment + RO or NF Treatment

## Advantages

- The dissolved metal concentrations after the 1<sup>st</sup> stage lime precipitation are expected to meet the assumed discharge criteria with regard to dissolved metals. Sulphate concentrations will be at saturation.
- The treated effluent quality after the RO/NF process is expected to be of a much higher quality. The metal concentrations will be much lower than the assumed discharge criteria. Sulphate and total dissolved solids will also be reduced.
- The TSS criterion will be met when the clarifier is operating normally, and TSS will be non-existent after the RO/NF unit.
- The residual to manage from the 1<sup>st</sup> stage of the process consists of metal hydroxide sludge. The sludge from the clarifier can be managed by co-disposal with the tailings.

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- Lime precipitation is a proven technology.
- Cold water temperatures do not impact treatment performance of lime precipitation.
- Relatively simple operation.

#### **Disadvantages**

- More sludge is generated with lime precipitation.
- Hydroxide precipitate left in lime precipitation effluent could resolubilize with solution pH reduction.
- Risk that the metal hydroxide sludge can resolubilize if the pH in the tailings is reduced.
- High risk of scaling the RO/NF membranes if the anti-scalant is not dosed in sufficient concentration and/or the pH is not adjusted properly. Worst case, irreversible scaling of the membrane.
- Risk of fouling due to metal oxide precipitation on the membrane surface.
- Frequent cleaning of the RO/NF membranes will be required to remove the precipitates on the membrane (minimum once a month).
- Membranes need to be replaced typically after five years of operation.
- Though RO/NF is a proven technology in municipal and process water applications, the use of RO/NF for the treatment of mill effluent is new. There are only a handful of full scale mining installations that use RO/NF.
- RO/NF produces a waste stream that is equal at best to 25% of the total flow for treatment, and can be higher depending on the feed effluent quality (up to 50% in some cases).
- The concentrated effluent produced (i.e. brine waste) by RO will be primarily high in dissolved metals and sulphates (if present in high concentration in the feed effluent). The brine stream must be treated to remove the dissolved metals and sulphates as insoluble precipitates that can be safely co-disposed with the tailings.

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## Option 2 – Sulphide Treatment & Reverse Osmosis (RO) / Nanofiltration (NF)

Option 2 is similar to option 1, except that the 1st stage of treatment involves sulphide precipitation of the dissolved metals followed by separation of metal sulphide sludge. The following figure presents a block diagram of this option.

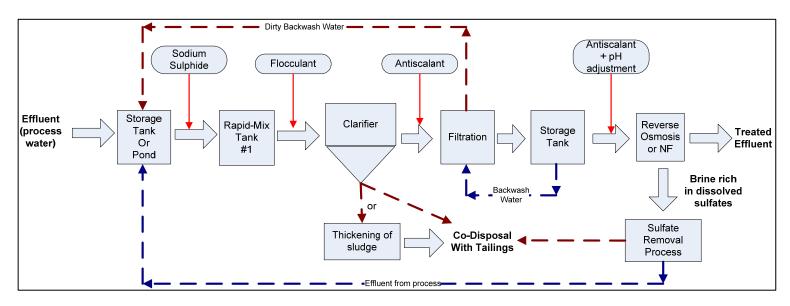


Figure 3-3: Option 2 – Sulphide Treatment + RO or NF Treatment

The advantages and disadvantages listed for option 1 with regard to the RO/NF system are the same for option 2. Additional advantages/disadvantages with sulphide treatment are presented below:

<u>Advantages</u>

- Dissolved metal concentrations after the 1<sup>st</sup> stage sulphide precipitation are expected to exceed the assumed discharge criteria with regard to dissolved metals. Sulphate concentrations will be at saturation.
- The residual to manage from the 1<sup>st</sup> stage of the process consists of metal sulphide sludge. The sludge from the clarifier can be managed by co-disposal with the tailings.
- Sulphide precipitation is a proven technology.
- Cold water temperatures do not impact on treatment performance.
- pH of the water has very little impact on the process, and much less acid is needed for pH adjustment
- Metal sulphide sludge is more stable over a larger range of pH than metal hydroxide sludge.
- Relatively simple operation.

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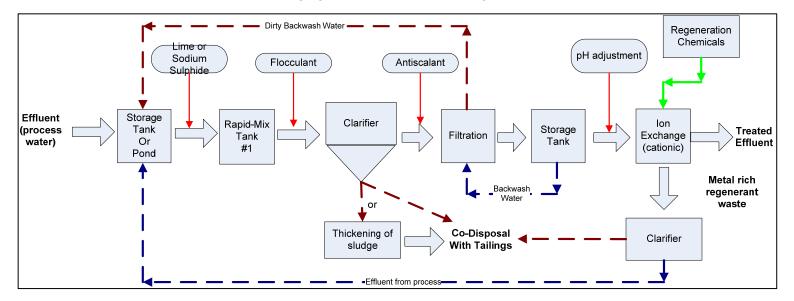
 Any residual sulphide particles remaining in the effluent from the 1<sup>st</sup> stage of the process will be filtered out by the downstream filtration step and the reverse osmosis step.

#### **Disadvantages**

- Risk management for hydrogen sulphide gas emissions.
- Potential for residual sulphide in the treatment effluent.
- Higher capital and operating costs than hydroxide precipitation.
- Fineness of the sulphide precipitate makes settling difficult.

## **Option 3 – Lime/Sulphide Treatment & Ion Exchange (IX)**

Option 3 consists of using a lime or sulphide precipitation step to remove the dissolved metals. The 2nd stage of the process involves using an ion exchange system as a polishing step to remove the residual metals in the effluent. If required, sulphate can also be removed from solution using IX. The ion exchange system consists of a cationic ion exchange to remove residual metals from solution. The following figure presents a block diagram of this option.



#### Figure 3-4: Option 3 – Lime or Sulphide Treatment + Ion Exchange Treatment

The advantages/disadvantages for the lime/sulphide treatment system are described in options 1 and 2, respectively. Additional advantages/disadvantages with the ion exchange system, used specifically for the removal of residual metals, are presented below:

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#### Advantages

- Produces an effluent with low dissolved metal concentrations. Also reduces TDS in the treated effluent.
- IX polishing will minimize sulphate generation caused from sulphide overdosing for maximum metal removal in the precipitation step.
- If required, an anionic ion exchange unit can be added to the process stream to remove sulphates.
- Relatively simple operation.
- Performance not impacted by cold water temperatures.
- The volume of regeneration waste produced is lower than the waste produced by reverse osmosis.
- After regeneration, the acidic waste stream can be neutralized with the addition of lime to precipitate the dissolved metal as metal hydroxide.

#### Disadvantages

- Depending on the residual dissolved metal loadings, the volume of resins required can be large (i.e. large IX vessel, or multiple vessels required).
- Once the resins are saturated, regeneration of the cationic resins will be required.
- Few full-scale installations in operation.
- Regeneration waste has to be managed on site.

## **Option 4 – Reverse Osmosis Treatment**

Option 4 consists of removing the dissolved metals, as well as reducing the TDS in the effluent, using reverse osmosis as the primary metal removal stage. Prior to treatment, the raw water is treated to remove colloidal and suspended solids using coagulation/flocculation/clarification and filtration processes. The following figure presents a block diagram of this option.

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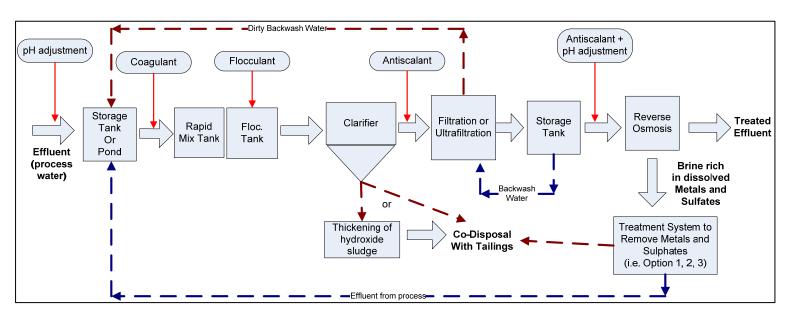


Figure 3-5: Option 4 – Reverse Osmosis Treatment

## Advantages

- Produces a treated effluent with very low metal, sulphate and TDS concentrations.
- Relatively simple operation.
- Fouling can be controlled to a certain degree with the use of anti-scalants and/or by operating at acidic pH.

#### **Disadvantages**

- Reverse osmosis is best suited to low influent metal loadings. If metal loads are too high, metal oxide precipitation can occur which can ultimately lead to fouling issues on the membrane.
- Under high metal loads, it is better to use the RO unit as a polishing step following metal precipitation using lime or sulphide.
- Treatment throughput is impacted by cold water. Thus, under cold water conditions, a lower treatment flow will occur or the unit will operate at a higher feed pressure to maintain the desired treated water flow.
- The hydroxide sludge from the pre-treatment stage is very dilute, typically around 4%. Additional sludge management is required.
- Frequent cleaning required ensuring the membrane does not scale or foul with metal oxides and/or gypsum.
- The RO process produces a waste stream that is equal at best to 25% of the total flow to be treated, and can be higher depending on the feed effluent quality (up to 50% in some cases).

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The concentrated effluent produced (i.e. brine waste) by the RO will be primarily high in dissolved metals and sulphates (if present in high concentration in the feed effluent). The brine stream must be treated to remove the dissolved metals and sulphates as insoluble precipitates that can be safely co-disposed with the tailings, similar to options 1 to 3..

## **Option 5 – Ion Exchange Treatment**

Option 5 consists of removing dissolved metals and sulphates, as well as reducing the TDS in the effluent, using ion exchange. The ion exchange will consist of a strong cationic column to remove the metals. This can be followed by a strong anionic column to remove sulphate. Regeneration takes place using sulphuric acid and sodium hydroxide. Prior to treatment by ion exchange, the raw water is treated to remove suspended solids from the effluent. The following figure presents a block diagram of this option.

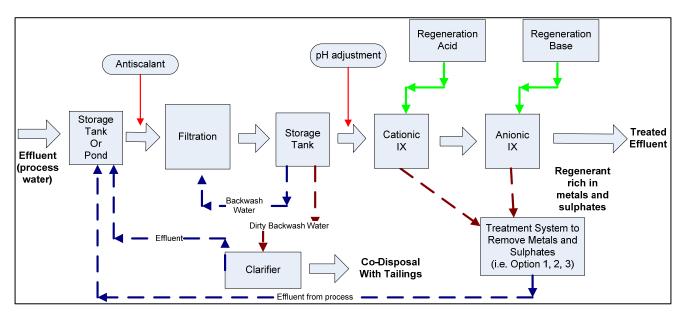


Figure 3-6: Option 5 – Ion Exchange Treatment

## Advantages:

- Treated water quality should meet and exceed the assumed design criteria.
- Proven technology.
- Simple operation.
- Performance not impacted by cold water temperatures.
- 100% of the flow is treated.

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#### Disadvantages:

- Will remove other cations/anions in the water, such as calcium and magnesium, thus increasing the frequency of resin regenerations.
- Depending on the metal and sulphate loads to be treated, the size of the ion exchange units can be very large.
- Acid and base regeneration chemicals are required.
- Complex regeneration procedures.
- High maintenance cost associated with the replacement of spent, non-regenerable ion exchange resins.
- The regeneration waste will require further treatment. Processes such as options 1, 2 and 3 could be used to treat the regeneration waste.

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## 4.0 ORDER OF MAGNITUDE CAPITAL/OPERATING COSTS

To provide an order of magnitude cost estimate (+/- 50%) associated with the water treatment technologies described herein, historical data from budget pricing of treatment equipment systems has been used. It should be noted that the application of the equipment was not the same as for that reviewed for Prairie Creek, but provides a good general idea of the capital cost of the equipment required.

The costs associated with the technologies listed were estimated from the project database records of SNC-Lavalin Montreal, as well as documented literature present in the public domain. These costs were up-dated and revised as shown in Table 4.1. Note that the order of magnitude capital costs includes both direct cost (equipment, instrumentation and controls, building, etc.) and indirect cost (engineering and supervision, construction, etc.) components.

Costs have been updated to present day 2011 figures at a 3% annual inflation rate, however no account has been taken with respect to the costs of transportation within Northwest Territories.

For illustration purposes, operating costs are reflected in \$/m3 of treated process water effluent for each of the treatment options, and are presented as higher or lower than the base case treatment system.

As mentioned above, the costs provided in Table 4.1 are very generic and provide an order of magnitude estimate of treatment costs. Treatment costs will be highly dependent on a number of site-specific factors, and the effluent quality and flows to be treated.

The following assumptions were also made:

- Design basis of the plant: 34 m<sup>3</sup>/hr
- For options using lime or sulphide precipitation, the clarification steps will take place in a circular metallic clarifier
- Disposal of sludge from the clarifier will be carried out by co-disposal with tailings without additional thickening.
- To estimate the cost for the residual treatment required for RO or IX, a lime precipitation unit will be used to treat the waste. The cost of a lime precipitation unit was pro-rated based on the volume of waste to be treated.
- For RO used as a polishing step after lime or sulphide precipitation, 25% of the total flow is wasted as brine.

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- For RO used as the primary treatment step, 40% of the total flow is wasted as brine.
- For IX, the volume of regeneration waste produced on a daily basis is equal to 10% of the daily flow treated and that the waste will be treated over a 12 hour shift.

#### Table 4-1: Order of Magnitude Capital Cost (+/-50%) and Operating Cost Estimates for Representative Treatment Technologies

Options	Description	 ital Cost 000's)	Operating Cost (\$/m3/treated)
Base Case	Sulphide/Lime Treatment & Clarification	\$ 1,990	\$ 1.03
Option 1	Lime Treatment/Clarification & Reverse Osmosis. Residual Treatment using Lime Precipitation	\$ 3,430	+
Option 2	Sulphide Treatment/Clarification & Reverse Osmosis. Residual Treatment using Lime Precipitation	\$ 3,590	++
Option 3	Lime or Sulphide Treatment/Clarification & Ion Exchange. Residual Treatment using Lime Precipitation	\$ 3,190	+
Option 4	Reverse Osmosis Treatment (including pre- treatment by clarification/filtration). Residual Treatment using Lime Precipitation	\$ 3,750	+++
Option 5	Ion Exchange Treatment (including pre- treatment by clarification/filtration). Residual Treatment using Lime Precipitation	\$ 3,400	++

Notes:

1. Costing rating: + cost slightly higher than the base case, ++ cost higher than the base case, +++ cost much higher than the base case

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# 5.0 DISCUSSION

## Treatment Effectiveness

The expected performance of the technologies presented in Section 2 of this report is summarized in Table 5.1. The efficiencies shown in Table 5.1 are based on judgement and the assumptions given in the footnotes. Although treatment efficiency will depend on a number of factors, including the specific composition of the process water effluent, Table 5.1 gives a reasonable estimate of typical treatment system performance.

Treatment Technologies	TDS	Hg	Ag	Pb	Cu	Zn	As	Se	Cd	Sb
Membrane Filtration	***	***	***	***	***	***	**	***	***	-
Activated Carbon Adsorption	*	***	***	**	**	**	**	-	**	**
lon Exchange	**	**	**	***	**	**	*	**	***	**
Biological (anaerobic) reduction	-	-	-	-	-	-	-	-	-	-
Barium Hydroxide	-	-	-	-	-	-	-	-	-	-
Hydroxide Precipitation (lime)	-	**	**	**	**	**	**	**	**	**
Sulphide Precipitation	-	**	**	***	***	***	**	**	**	**

Notes:

- 1. Legend: TDS: Total Dissolved Solids, Hg: Mercury, Ag: Silver, Pb: Lead, Cu: Copper, Zn: Zinc, As: Arsenic, Se: Selenium, Cd: Cadmium, Sb: Antimony.
- 2. Treatment effectiveness: \*: limited, \*\*: good, \*\*\*: excellent.
- 3. Membrane filtration requires extensive influent pre-treatment to remove solids.
- 4. Assumes pH control and chemical control will remove metals to technology limits where dissolved metals are above MMER.
- 5. Assumes that metals are mostly present as dissolved contaminants.
- 6. Removal efficiency will be highly effluent dependent, but typical performance is provided.

Based on the summary presented in Table 5.1, the following observations can be made:

• Biological anaerobic reduction and barium hydroxide treatments are specifically designed to remove sulphates and have very little impact on the removal of dissolved metals.

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- Hydroxide (lime) precipitation provides effective dissolved metals removal. This is the treatment option used in many mine sites to remove heavy metals from an effluent stream.
- Sulphide precipitation provides a greater removal of dissolved metals than hydroxide precipitation due to the lower solubility of the metal sulphides.
- Both hydroxide and sulphide precipitation do not have an impact on TDS.
- Membrane filtration (i.e. reverse osmosis) and ion exchange can have superior dissolved metals removal, and will also reduce TDS.
- Activated carbon is also effective in removing certain heavy metals. However, this treatment technology can only retain a limited amount of metals before the media has to be changed. For this reason, activated carbon is generally used as a polishing step for the removal of dissolved metals.
- The removal of selenium and antimony may be enhanced by coprecipitation with a coagulant, such as ferric sulphate or ferric chloride.

Consequently, the treatment technologies that are considered to be potentially viable for dissolved metals removal from Prairie Creek process water are hydroxide precipitation, sulphide precipitation, reverse osmosis and ion exchange. Section 3 and 4 of this report presented different combinations of these unit processes.

## Hydroxide/sulphide precipitation + RO/IX polishing steps

The base case and options 1 to 3 use hydroxide and/or sulphide precipitation as an initial treatment step. The removal of dissolved metals from an effluent stream using lime or sulphide precipitation is generally practiced at many mine sites. The metals are precipitated as metal hydroxide or metal sulphide sludge which is typically co-disposed with the tailings. Thus, no additional residual management is required. The clarified water is then discharged directly to the receiving water stream. To enhance the treatment efficiency, the clarified water can also be sent to a polishing filtration step to remove any residual suspended solids prior to discharge.

The minimum concentration of metals that can be removed with this process is limited by the minimum solubilities of the hydroxide metals in water, as shown in Figure 2-1. Furthermore, the pH of the precipitation reaction also favours the removal of certain metals over others, especially when lime precipitation is used. Thus, the hydroxide/sulphide precipitation process can remove most of the heavy metals present in the process water and meet the typical discharge criteria presented in section 3. However, if the treated effluent is required to meet more

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stringent discharge criteria, a polishing step is needed to remove any residual dissolved metals. This can be accomplished using either reverse osmosis (RO) or ion exchange (IX). The main advantage of using RO or IX is that a consistent treated effluent will be produced. Furthermore, since metal loadings to the RO/IX are significantly lower than the initial loads, the size and complexity of the equipment is greatly reduced. However, there are certain disadvantages to note:

- RO treatment continuously produces a brine flow generally equal to 25% of the total flow treated. This brine stream can either be returned ahead of the lime/sulphide precipitation system or treated by a separate system. It may be possible to reduce the volume of brine produced by treating the brine with another RO unit (i.e. 2<sup>nd</sup> pass RO treatment). However, fouling of the membrane elements becomes a critical operating issue and can lead to frequent membrane cleaning.
- With IX, after a given amount of time, the resins will need to be regenerated in order to remove the dissolved metals that were adsorbed onto the resins, and allow re-use in the process. The regenerant will then have to be treated to precipitate the metals.
- The volume of regeneration waste produced by an IX system is typically much lower than an RO system.
- Another concern is the risk of fouling of the RO membrane with metal oxides, resulting in frequent cleaning of the membrane elements, and in a worst case, replacement of the membrane elements.

## **RO or IX Treatment**

RO generally has an excellent rejection rate of dissolved heavy metals, specifically when the metals are in their ionic form. With IX, the resins can be selected to selectively remove specific metals or remove all heavy metals. However, there are certain disadvantages to note:

- Both RO and IX require a pre-treatment step to remove all suspended solids that could foul the units.
- Due to the high metal loads in the untreated effluent, the volume of resins required for the IX will be much larger. The frequency of resin regeneration will also be high.
- There will be fouling of the RO membrane by metal oxides due to the high concentration in the untreated effluent. Furthermore, to manage the fouling caused by the metal oxides, the RO would have to be designed with a lower recovery, resulting in a higher continuous brine flow that will need to be treated.

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• RO continuously produces a relatively high volume of brine for disposal. IX regeneration produces a waste brine episodically, and of a much smaller volume.

The advantages of RO and IX are comparable. However, waste brine management is a significant disadvantage with RO. Further, there is no known industrial scale RO plant successfully treating the type of water expected to b produced at Prairie Creek. Therefore, only IX is recommended for further consideration.

## Treatment Options to Consider for the Next Phase

Considering that the concentration of dissolved metals in the process effluent stream can be very high and highly variable, direct treatment by ion exchange is not recommended. It is prudent to have a lime or sulphide precipitation step first to remove as much of the dissolved metals as possible, followed by a filtration step to remove any residual solids in the treated effluent. IX could also be used as a polishing step to ensure that the treated effluent will consistently meet discharge criteria. The precipitation process is more robust when dealing with high metal loads and a variable feed.

For the treatment of heavy metals by sulphide and/or lime, the base case treatment should be considered and optimized based on different operating pH. Furthermore, the following treatment should also be investigated in the laboratory:

- Evaluation of lime precipitation only at different operating pH;
- Evaluation of sulphide precipitation only at different operating pH;
- Addition of sodium sulphate and ferric sulphate at raw water pH, followed by lime precipitation.
- For all treatment options, add a filtration step downstream using different filter sizes to emulate a disk filter (10 micron), a multimedia filter (1 micron) and ultrafiltration (0.1 micron) and compare results to the non-filtered samples.

For the polishing step, ion exchange should be investigated further. The treated effluent produced from the precipitation test can then be treated by ion exchange. Contact with ion exchange resin vendors should be made to obtain samples of resins for testing. Testing should also be conducted using ion exchange to remove sulphate and nitrogen species from the influent stream in case these parameters are present in concentrations that warrant removal, and the concentrations cannot be controlled by other means (e.g. water storage, treated water discharge strategy).

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# 6.0 **RECOMMENDATIONS**

For the next step of the project, the following bench scale tests should be carried out on a synthetic process effluent:

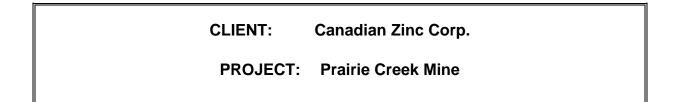
- Optimization of the base case treatment process (i.e. operating pH, reagent required).
- Evaluating the treatment performance of a lime only precipitation process at different pH conditions.
- Evaluating the treatment performance of a sulphide only precipitation process at different pH conditions.
- Evaluate whether the precipitate formed during lime and sulphide treatment can resolubilize at neutral pH (7) and acidic pH (5).
- Addition of sodium sulphate and ferric sulphate at raw water pH, followed by lime precipitation.
- For all treatment options, add a filtration step downstream using different filter sizes to emulate a disk filter (10 micron), a multimedia filter (1 micron) and ultrafiltration (0.1 micron) and compare results to the non-filtered samples.
- Bench test the treatment of the treated effluent from the lime/sulphide precipitation tests using one or two different ion exchange resins for metals removal and sulphate/nitrogen species removal. An ion exchange vendor should be contacted to obtain samples for testing.

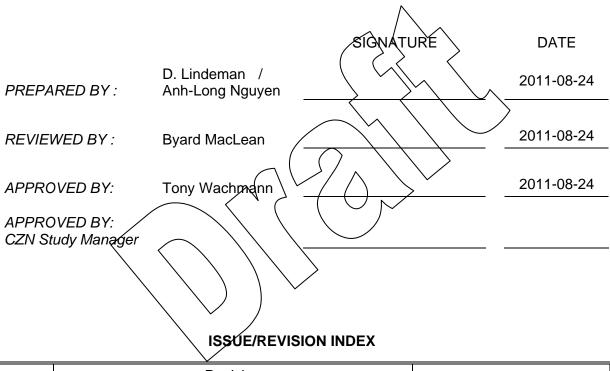
The results from these bench scale tests will provide treatment performance with regard to dissolved metal removal based on different treatment scenarios and operating conditions.

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# **APPENDIX A – SNC DRAFT REPORT DATED 2011-08-24**

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Issue			Revis			
Code	Rev.	Prep.	Rev.	App.	Date	Revision Details
	No.	By	By	By		
RR	PA	DL	BM		2011-07-28	Issued for comments
RR	PB	ALN/DL	BM		2011-08-03	Issued for comments
<u>RD</u>	<u>00</u>	<u>ALN/DL</u>	<u>BM</u>		<u>2011-08-24</u>	Issued for comments

Issue Codes: RC = Released for Construction, RD = Released for Design, RF = Released for Fabrication, RI = Released for Information, RP = Released for Purchase, RQ = Released for Quotation, RR = Released for Review and Comments.

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# 1.0 INTRODUCTION

SNC-Lavalin was requested to undertake a desk-based review of process water treatment alternatives by Canadian Zinc Corporation, based on water expected to be produced from <u>the</u> Mill at their Prairie Creek Mine.

## 1.1 Location

The Prairie Creek Mine site is located in the southern Mackenzie Mountains in the south-west corner of the Northwest Territories. The mine site facilities are situated on the eastern side of and adjacent to Prairie Creek, about 43 km upstream from its confluence with the South Nahanni River.

## 1.2 Background to Process Water Treatment Review

The water treatment plant at Prairie Creek is intended for the treatment of mine underground water and a portion of process plant effluent water.

Early bench-scale treatment testing of representative water samples for metals removal and subsequent optimization of reagent and settling characteristics performed by SGS-CEMI in 2006 led to the development of the currently proposed water treatment processes for the two water streams to be produced during operations. The proposed treatment processes include hydrated lime for mine water, and a combination of sulphide/lime/iron III treatment for process water.

Data reported in 2010 by SGS-CEMI confirmed the required treatment processes to remove metals from both waters and optimized the processes.

The currently proposed process water treatment scheme consists of first adding sulphuric acid to lower the pH to 4.5. Sodium sulphide is added at this time to react with the dissolved metals to form insoluble metal sulphides, which are stable throughout the remainder of the treatment process. The sodium sulphide treated process water then proceeds to a rapid mix in-line mixer where hydrated lime is added to adjust the pH from 4.5 to 9.0. The precipitated solids are maintained in suspension. Iron III Sulphate is then added to promote settling of the metals. Compressed air is added into this reactor to ensure full oxidation of all ions in solution. Flocculant is added to help unite smaller particles, and the solution flows into a clarifier where settled solids and treated decant water are separated.

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## 1.3 Scope of "Process Water Screening Review"

The purpose of this study is to perform a 'process water screening review' of base metal and heavy metal removal technologies which can be used successfully to produce an effluent meeting the most stringent requirements for discharge to the environment. Sulphate and total dissolved solids (TDS) removal were a secondary consideration for this study. The purpose is neither to review the correct selection of the treatment scheme for process water, nor to criticipue the design of the water treatment facility presently proposed for the Prairie Creek Mine Site.

The process water treatment option review will include the current treatment technology proposed for Prairie Creek; several membrane processes; treatment with barium hydroxide; ion exchange, and biological treatment alternatives. "Screening" criteria that were assumed included full-scale plant reliability; waste product disposal, consistent and reproducible effluent quality, order of magnitude capital and operating costs, and suitability to laboratory level bench-scale testing (since a full-scale plant would not be built if satisfactory results could not be generated on a bench-scale).

# 1.4 Current recommended Water Treatment Process

Selective laboratory tests on simulated mill water effluent and their subsequent engineering review have defined the best practical available technology to remove metals from the waste water at Prairie Creek. The use of sulphide/lime precipitation can be considered the 'base case' for this review.

The success of metal precipitation processes whether using sulphide or lime, depends to a large extent on other water quality parameters such as alkalinity and suspended solids in the treated water streams. It should be noted that metal hydroxide and sulphide precipitates are generally very fine and require additional steps of coagulation and flocculation coupled with high performance clarification to obtain very low levels of total metals in the treated effluent.

# 1.5 Explosive Management and Ammonia/Nitrate in Mine Water

CZN is planning to use emulsion explosives for 100% of their blasting needs. This is because of the level of nitrogen residues that would occur if ANFO is used. Use of emulsions would not avoid theses residues, but with appropriate handling, hole charging and excess product management, emulsion losses and thus residues are expected to be low.

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Mine water is to be pumped from underground to a large storage pond on surface, where the water will be stored for several months before either being recycled to the Mill or sent to the Water Treatment Plant. The several month residence time is expected to allow the low concentrations of nitrogen residues from blasting to oxidize and degrade.

Therefore, these factors, together with CZN's water treatment and discharge plan which will reduce or avoid discharge in the winter and during periods of low creek flow, means that water treatment to reduce nitrogen species concentrations may not be necessary.

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## 2.0 SUMMARY OF TREATMENT TECHNOLOGIES

This review is an evaluation of prescribed techniques and industrially-accepted operations to determine their performance in the removal of metals and reduction of dissolved solids content.

The 'case by case' consideration of each treatment approach is performed using 'Best Professional Judgment' standards to meet the purpose of the study.

## > Membrane Processes

### (i) Reverse Osmosis

Reverse osmosis (RO) units force water through a semi-permeable membrane under pressure, leaving contaminants behind. Reverse osmosis assemblies can treat approximately three times more water than they discharge. 75% of the water fed to the RO becomes treated water, while 25% becomes a waste brine flow. However, the actual recovery of the system (i.e. treated flow over total flow fed to the unit), will vary greatly based on the feed water quality. Reverse osmosis removes turbidity, microbes and virtually all dissolved substances. However, while many harmful metals are removed, such as zinc, cadmium and selenium, beneficial metals are also removed, such as calcium and magnesium. RO membranes are non-selective with regard to the removal of metals; they generally reject ionized divalent metals. Note that the actual rejection rate of metals depends on the type of RO membrane used (make and model), system design and operating conditions.

The pressure utilized during reverse osmosis depends on the Total Dissolved Solids (TDS) concentration, with typical pressures ranging from 300 to 1,200 psi to create flows of clean water from high TDS influent concentrations through the membrane. Depending on the contaminants in the feed water, high TDS concentrations in the process water would reduce the effectiveness of a reverse osmosis system (i.e. a reduction in volume of treated water produced).

Gypsum levels may be near saturation in process water. High gypsum saturation levels in reverse osmosis feed streams means the membranes are highly likely to foul or clog, resulting in unreliable performance. However, in some reverse osmosis processes, fouling is controlled by the addition of anti-scaling chemicals and by operating in acidic conditions.

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A brine waste stream would result from the reverse osmosis units. This would require an encapsulated disposal area which would need to hold both precipitation sludge and brine.

Reverse osmosis systems are in place at other mines and other industrial facilities, and are used to treat wastewaters with low metal loadings. While reverse osmosis may be technically feasible, high TDS levels in the influent and adverse climatic conditions present challenges for successful design and operation. In addition, large volumes of brine would need to be disposed of over the long-term.

Furthermore, reverse osmosis must be preceded by a pre-treatment system whose objective is to remove as much of the fouling materials from the raw water stream as possible, such as total suspended solids (TSS). The pre-treatment system must also include a filtration step, either granular filtration or membrane ultra-filtration.

High dissolved metal concentrations (i.e. 10s to 100s mg/L) in the feed water can also cause a rapid fouling of the membrane surface due to metal oxide precipitation. To prevent this, metal concentrations can be reduced ahead of the reverse osmosis system by lime precipitation. Alternatively, the reverse osmosis plant could also be operated under acidic condition, ensuring the dissolved metals are in their ionic form.

Generally, reverse osmosis is used as a final polishing step, separating the dissolved metals from the process water, and producing a treated effluent that is generally very low in TDS and metals that can be discharged directly to the environment and/or re-used in the process.

## (ii) Nanofiltration

Nanofiltration is a membrane system similar to reverse osmosis except the membrane has a larger particle size cutoff; up to 0.005 micron compared to less than 0.002 micron for reverse osmosis. Typical pressures for nanofiltration applications range from 50 to 200 psi. Nanofiltration removes bacteria, and some viruses from water as well as most organic matter and some natural minerals. Nanofiltration, however, does not remove dissolved salts to the same high efficiency as reverse osmosis, solids rejection being 85 to 95% efficient compared to reverse osmosis at 99% rejection.

## (iii) Electrodialysis

Electrodialysis is another membrane treatment technology where electricity is used as the driving force for separation instead of pressure. An electrical current is used to move ions through a series of selective membranes. The consecutive

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membranes concentrate the ions in a waste stream. Electrodialysis reversal is a modification of the process that switches charges during operation to promote cleaning. This technology is applicable for treatment of high TDS water because it is less susceptible to plugging and is easily cleaned. The downside of this process is the high energy use and the volumes of concentrated wastes requiring disposal (typically more volume that reverse osmosis). In addition, there are no examples of the use of electrodialysis at mining operations. Electrodialysis is therefore not considered a viable option for Prairie Creek.

## Activated Carbon Adsorption

Activated carbon is an effective adsorbent and removes many organic and metal contaminants from drinking water. With the column technique, the contaminated solution flows through the carbon and dissolved metals are adsorbed. The loaded carbon can be disposed of and replaced with fresh carbon, or stripped and regenerated for re-use. Adsorption capacity of activated carbon depends on:

- Physical and chemical characteristics of adsorbent (i.e. filtration media);
- Physical and chemical characteristics of adsorbate (i.e. contaminants to be adsorbed on the media);
- Concentration of the adsorbate in liquid solution;
- Characteristics of the liquid phase (pH, temperature, etc.);
- Retention time

As can be anticipated, most of the dissolved metals will be adsorbed but the loading capacity is very limited. This would make this process extremely impractical and expensive to operate on a large industrial scale. Some of the metals are removed to very low concentrations (sub ppb) but others will remain a concern. Activated carbon treatment should be discounted based on the above observations. Due to the limited loading capacity, activated carbon treatment cwould be considered as a polishing step that follows a primary metal removal system.

## > Ion Exchange

Ion exchange (IX) technology is well suited to remove dissolved heavy metals and sulphate from a water stream that is close to saturation with gypsum. Feed water is first pumped through a cation loading stage where cations like calcium ( $Ca^{2+}$ ) and metals are removed from the feed water through adsorption onto a strong acid cation resin (i.e. resin that is selective to positively charged ions) and replaced generally by hydrogen ions (H+) or sodium (Na+). After this stage, the water is pumped through an anion loading stage where anions like sulphate (SO4<sup>2-</sup>) are

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removed through adsorption onto a weak base anion resin (i.e. resin that is selective to negatively charged ions) and replaced by hydroxide ions (OH-). In cases where sulphate concentrations are not high, only a strong acid cation resin step can be used to selectively remove the dissolved metals from the effluent stream. Note that there are many types of IX resins available on the market and can be chosen to be highly selective in the removal of a specific metal ions, or non-selective where removal of all positively or negatively charged ions occurs.

Typically, ion exchange treatment can be conducted in either a column system or a fluidized bed where the contaminated solution is contacted with the resin. When contaminant breakthrough occurs, the resin can be regenerated using a dilute sulphuric acid and lime solution.

Provided the ion exchange system is properly sized for the effluent to be treated, and the right resins with the required selectivity are chosen, low metals and sulphate concentrations can be achieved. <u>The volume of regeneration waste produced typically varies between 5 to 10% of the total daily volume treated. The exact volume will depend on the type of resins used and the sizing of the column.</u>

The regeneration waste from cationic and anionic ion exchange units are often mixed together in order to produce a neutral solution. In a mine application, this regeneration waste must be disposed of since it contains a high concentration of dissolved metals and sulphate. Thus, gypsum and metal hydroxide sludge must be removed from the regeneration waste by clarification, and can be co-disposed of in the tailings.

## > Biological Treatment

Biological treatment processes can be used if the treatment of sulphate is desirable via a process called biological sulphate reduction. The process takes place under anaerobic conditions and requires the addition of a carbon source, such as ethanol or acetic acid. Under these conditions, sulphate reducing bacteria (SRB) can reduce the sulphate to elemental sulphur. Furthermore, successful sulphate reduction is generally accompanied by an increase in pH due to the production of alkalinity. If the alkalinity levels are sufficiently high, and the pH is at the right value, certain metals can precipitate out.

Though this technology sounds promising, biological treatment of mine effluent has only had limited success in commercial applications. The main concerns with biological treatment of mill effluent in a cold climate are the following:

• An additional carbon source has to be added to the stream. Thus, a large volume of ethanol or acetic acid has to be stored on site.

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- Under cold water conditions, biological activity exponentially reduces. Thus, no treatment is possible during cold water conditions unless the water is heated.
- Inconsistent results and difficult control.

For this reason, a biological process for mine effluent is not considered as a Best Available Technology for Prairie Creek.

## > Barium Hydroxide

Also for sulphate treatment, barium salts are very effective in removing sulphate from the wastewater stream due to the high insolubility of barite (BaSO<sub>4</sub>). Barium salts that are commonly used for sulphate (removal by precipitation of barium sulphate include barium hydroxide, Ba(OH)<sub>2</sub>, barium carbonate, BaCO<sub>3</sub> and barium sulphide, BaS. The precipitation of barium sulphate occurs according to the following reactions:

 $BaCO_{3}(S) + H_2SO_4 \rightarrow BaSO_4(S)$  $Ba(OH)_{2(S)} + H_2 O_4 \Rightarrow BaSO_4 + 2H_2 C_2$ BaS  $_{(S)}$  +  $H_2$ SO  $\downarrow$  +  $H_2$ S

Barium hydroxide and barium sulphide are very effective in removing sulphate over the entire pH range; however, barium carbonate is only effective in a specific pH range. Studies have shown that barium hydroxide removal can reduce the concentration of sulphate to below 200 mg/L. Due to the high cost of barium, further treatment of precipitated barium sulphate might be possible in order to recycle the barium. Also, barium hydroxide is not very effective in removing heavy metals; therefore, this process can only be used in conjunction with another technology, such as line treatment.

## > Hydroxide Precipitation

The removal of dissolved metals from acid mine drainage is traditionally carried out by hydroxide precipitation. In this treatment scheme, an alkali precipitating agent is generally added to the effluent to raise the pH of the effluent and precipitate the dissolved metals as metal hydroxides (Me(OH)x). The alkali typically used in the mining industry is hydrated lime (Ca(OH)2). Sodium hydroxide (NaOH) can also be used, but it is generally used when the metal concentrations in the effluents are low. Therefore, this approach may not be appropriate for Prairie Creek mill water.

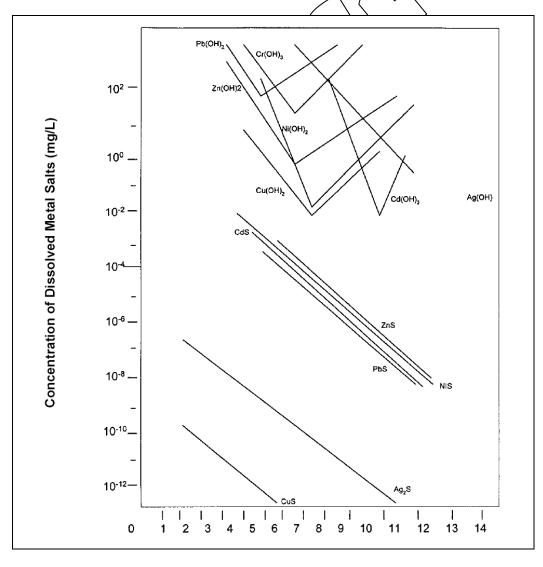
Following the addition of the alkali, the metal hydroxide has to be separated from the treated effluent. At certain mine sites, lime is added at the inlet of a large tailing pond and the metal hydroxide sludge is allowed to settle in the pond. At

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other mine sites, the settling takes place in a clarifier with the addition of a flocculant to aid the settling process.

#### Treatment performance

With hydroxide precipitation, metals such as copper, cadmium, iron, lead, nickel and zinc can be removed as metal hydroxide precipitates. However, With regard to metal removal, the treatment performance of hydroxide precipitation depends greatly on the operating pH selected and the desired metals to be removed. As shown in Figure 2.1, the minimum solubility of different metal hydroxides varies with pH.



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### Figure 2-1: Solubility of metal hydroxides and sulphides as a function of pH

The typical treatment performance that can be achieved using hydroxide precipitation is as follows:

- Copper: 0.3 mg/L
- Iron: 3 mg/L
- Lead: 0.2 mg/L
- Nickel: 0.5 mg/L
- Zinc: 0.5 mg/L

Hydroxide precipitation, however, does not reduce sulphate concentrations or total dissolved solids (TDS). For example, when treating acid mine drainage, the concentration of sulphate in the treated effluent is generally close to saturation (1500 to 2000 mg/L of SO4) when the sulphate concentration in the feed water is very high (i.e. > 3000 mg/L)

Hydroxide precipitation generates metal hydroxide sludge. If the process water contains high concentration of sulphates, gypsum will also be formed.

When the treatment is carried out within a tailings pond, the metal hydroxide and gypsum sludge settle and accumulate in the pond. When the treatment is carried out in a clarifier, the sludge is typically dewatered using a belt filter or filter press and disposed off in the tailings. The filtrate is recycled either back to the tailings pond or ahead of the clarifier.

## Sulphide Precipitation

Sulphide precipitation works under the same basic principle as hydroxide precipitation. A precipitating agent, in this case sodium sulphide (Na<sub>2</sub>S), is added to precipitate the metals as a metal sulphide (MeS).

As shown in Figure 2.1, sulphide precipitation is generally used when low metal concentrations are required in the treated effluent. Low metal concentrations can also be achieved over a wider range of pH than hydroxide precipitation. Similar to hydroxide precipitation, TDS is not removed, nor are sulphates.

Sulphide precipitation generates metal sulphide sludge and can be disposed of in a similar fashion to hydroxide sludge. Precipitates are fine and pose challenges to settling, generally requiring either a higher dosage of flocculant, higher flocculation contact time and/or a larger settling area (i.e. larger clarifier).

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## 3.0 TREATMENT OPTIONS

Based on the assumed process effluent stream to be treated at Prairie Creek, and the objective of meeting the most stringent requirements for discharge into a natural body of water, one or a combination of the treatment technologies noted above can be used to meet this objective.

The following section presents several suggested treatment options. These are based on a combination of the technologies, or unit processes, that were presented in Section 2. For each option, a list of advartages and disadvantages is presented based on the following criteria:

- Treated effluent quality with regard to dissolved metals and total dissolved solids
- Complexity of the residual management system `
- Operation complexity
- Maintenance complexity
- Maturity of the technology proposed

For this review, the treatment options are based on the following assumptions:

- 1. The concentrations of dissolved metals in the process water are less than 10 mg/L.
- Each treatment option will be designed to produce a treated effluent that will meet or exceed the following <u>minimum</u> monthly average effluent criteria (note: the values indicated are typical regulatory values required by some provinces):
  - Arsenic: 0.2 mg/L
  - Copper: V 0.3 mg/L
  - Iron: 3.0 mg/L
  - Lead: 0.2 mg/L
  - Nickel: 0.5 mg/L
  - Zinc: 0.5 mg/L
  - TSS: 15 mg/L (TSS = Total suspended solids)
  - pH: 6 to 9.5

### Base Case – Sulphide / Lime Treatment

The base case option is the previously proposed treatment system which consists of sulphide precipitation followed by lime precipitation. The metal sulphide and

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hydroxide precipitates are separated from the treated water by clarification. The following figure presents a block diagram of this option.

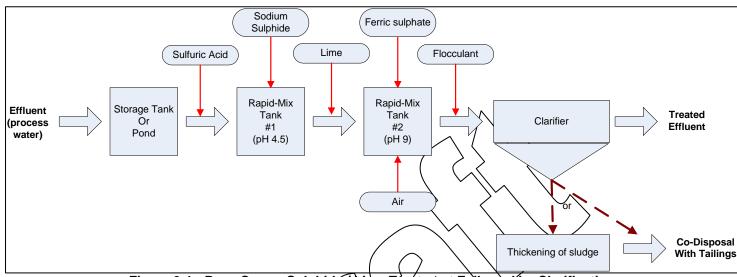


Figure 3-1: Base Case - Sulphide / Lime Freatment Followed by Clarification

### Advantages

- The dissolved metal concentrations in the treated effluent are expected to be much lower than the assumed discharge criteria since the solubility of metal sulphides is much lower than for metal hydroxide precipitates.
- The TSS criterion will be met when the clarifier is operating normally.
- The only residual to manage is the metal hydroxide and sulphide precipitate. The sludge from the clarifier can be managed by co-disposal with the tailings. This is generally done in most mines.
- Lime precipitation is a proven technology.

## **Disadvantages**

- Sulphate concentrations are expected to be at saturation levels (i.e. approx. 2000 mg/L).
- TDS will not change in this process.
- The chemicals that need to be added and managed are hazardous (acid and sulphide).
- Risk management required for hydrogen sulphide gas emissions from the use of sodium sulphide.
- Potential risk of residual sulphide in the treated effluent.
- Risk of scaling in the rapid-mix tanks and the clarifier due to precipitation of calcium sulphate (gypsum) and hydroxide sludge (only applicable if sulphate is present in the feed water).

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- Full scale mining installations may not exist that use both sulphide and lime precipitation in series.
- Fineness of the sulphide precipitate makes settling difficult.

## Option 1 – Lime Treatment & Reverse Osmosis (RO) / Nanofiltration (NF)

Option 1 consists of a two stage treatment process. The 1st stage involves lime precipitation of the dissolved metals followed by separation of the metal hydroxide sludge. The 2nd stage involves the polishing of the/treated effluent to remove residual dissolved metals and reduce the total dissolved solids by reverse The following figure presents a block diagram of this osmosis/nanofiltration. option.

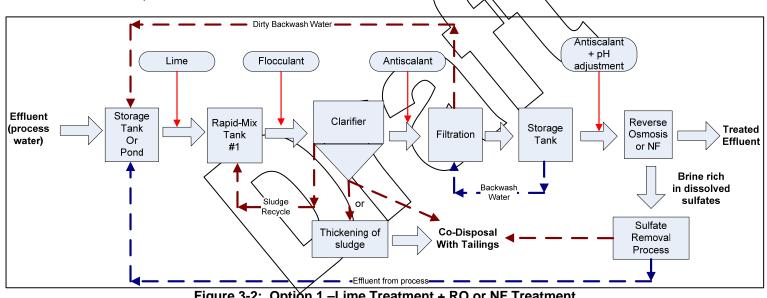


Figure 3-2: Option 1 – Lime Treatment + RO or NF Treatment

## Advantages

- The dissolved metal concentrations after the 1<sup>st</sup> stage lime precipitation are expected to meet the assumed discharge criteria with regard to dissolved metals. Sulphate concentrations will be at saturation.
- The treated effluent quality after the RO/NF process is expected to be of a much higher quality. The metal concentrations will be much lower than the assumed discharge criteria. Sulphate and total dissolved solids will also be reduced.
- The TSS criterion will be met when the clarifier is operating normally, and TSS will be non-existent after the RO/NF unit.
- The residual to manage from the 1<sup>st</sup> stage of the process consists of metal hydroxide sludge. The sludge from the clarifier can be managed by co-disposal with the tailings.

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- Lime precipitation is a proven technology.
- Cold water temperatures do not impact treatment performance of lime precipitation.
- Relatively simple operation.

#### <u>Disadvantages</u>

- More sludge is generated with lime precipitation.
- Hydroxide precipitate left in lime precipitation effluent could resolubilize with solution pH reduction.
- Risk that the metal hydroxide sludge can resolubilize if the pH in the tailings is reduced.
- High risk of scaling the RO/NF membranes if the anti-scalant is not dosed in sufficient concentration and/or the pH is not adjusted properly. Worst case, irreversible scaling of the membrane.
- Risk of fouling due to metal oxide precipitation on the membrane sufface.
- Frequent cleaning of the RO/NF membranes will be required to remove the precipitates on the membrane (minimum once a month).
- Membranes need to be replaced typically after five years of operation.
- Though RO/NF is a proven technology in municipal and process water applications, the use of RO/NF for the treatment of mill effluent is new. There are only a handful of <u>full</u> scale mining installations that use RO/NF.
- RO/NF produces a waste stream that is equal at best to 25% of the total flow for treatment, and can be higher depending on the feed effluent quality (up to 50% in some cases).
- The concentrated effluent produced (i.e. brine waste) by RO will be primarily high in dissolved metals and sulphates (if present in high concentration in the feed effluent). The brine stream must be treated to remove the dissolved metals and sulphates as insoluble precipitates that can be safely co-disposed with the tailings.

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### Option 2 – Sulphide Treatment & Reverse Osmosis (RO) / Nanofiltration (NF)

Option 2 is similar to option 1, except that the 1st stage of treatment involves sulphide precipitation of the dissolved metals followed by separation of metal sulphide sludge. The following figure presents a block diagram of this option.

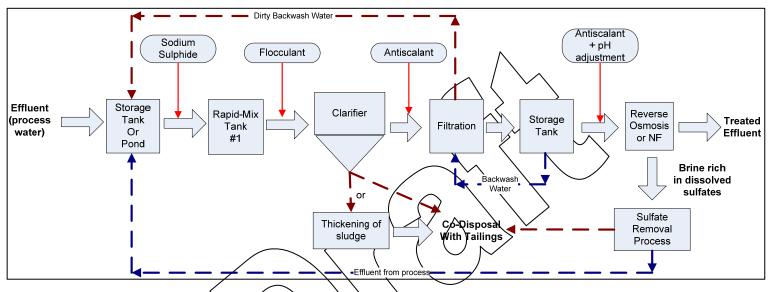


Figure 3-3: Option 2 - Sulphide Treatment + RO or NF Treatment

The advantages and disadvantages listed for option 1 with regard to the RO/NF system are the same for option 2. Additional advantages/disadvantages with sulphide treatment are presented below:

### <u>Advantages</u>

- Dissolved metal concentrations after the 1<sup>st</sup> stage sulphide precipitation are expected to exceed the assumed discharge criteria with regard to dissolved metals. Sulphate concentrations will be at saturation.
- The residual to manage from the 1<sup>st</sup> stage of the process consists of metal sulphide sludge. The sludge from the clarifier can be managed by co-disposal with the tailings.
- Sulphide precipitation is a proven technology.
- Cold water temperatures do not impact on treatment performance.
- pH of the water has very little impact on the process, and much less acid is needed for pH adjustment
- Metal sulphide sludge is more stable over a larger range of pH than metal hydroxide sludge.
- Relatively simple operation.

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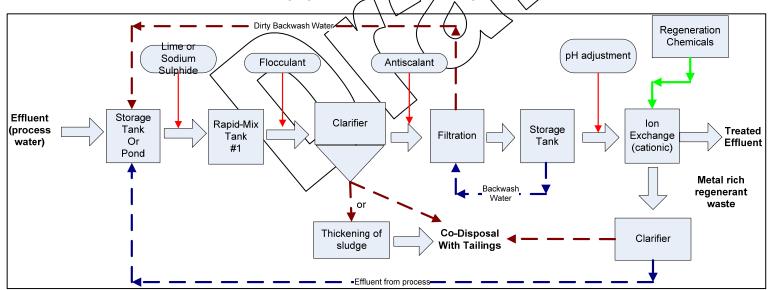
 Any residual sulphide particles remaining in the effluent from the 1<sup>st</sup> stage of the process will be filtered out by the downstream filtration step and the reverse osmosis step.

### **Disadvantages**

- Risk management for hydrogen sulphide gas emissions.
- Potential for residual sulphide in the treatment effluent.
- Higher capital and operating costs than hydroxide precipitation.
- Fineness of the sulphide precipitate makes settling difficult.

## Option 3 – Lime/Sulphide Treatment & Ion Exchange (IX)

Option 3 consists of using a lime or sulphide precipitation step to remove the dissolved metals. The 2nd stage of the process involves using an ion exchange system as a polishing step to remove the residual metals in the effluent. If required, sulphate can also be removed from solution using IX. The ion exchange system consists of a cationic ion exchange to remove residual metals from solution. The following figure presents a block diagram of this option.



#### Figure 3-4: Option 3 – Lime or Sulphide Treatment + Ion Exchange Treatment

The advantages/disadvantages for the lime/sulphide treatment system are described in options 1 and 2, respectively. Additional advantages/disadvantages with the ion exchange system, used specifically for the removal of residual metals, are presented below:

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### Advantages

- Produces an effluent with low dissolved metal concentrations. Also reduces TDS in the treated effluent.
- IX polishing will minimize sulphate generation caused from sulphide overdosing for maximum metal removal in the precipitation step.
- If required, an anionic ion exchange unit can be added to the process stream to remove sulphates.
- Relatively simple operation.
- Performance not impacted by cold water temperatures.
- The volume of regeneration waste produced is lower than the waste produced by reverse osmosis.
- After regeneration, the acidic waste stream can be neutralized with the addition of lime to precipitate the dissolved metal as metal hydroxide.

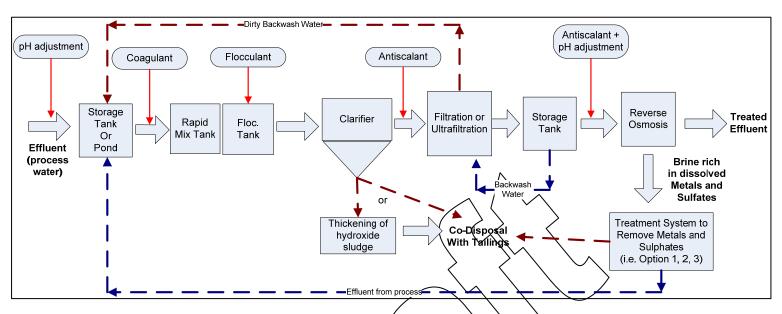
### Disadvantages

- Depending on the residual dissolved metal loadings, the volume of resins required can be large (i.e. large IX vessel, or multiple vessels required).
- Once the resins are saturated, regeneration of the cationic resins will be required.
- Few full-scale installations in operation.
- Regeneration waste has to be managed on s(te.

## Option 4 - Reverse Osmosis Treatment

Option 4 consists of removing the dissolved metals, as well as reducing the TDS in the effluent, using reverse osmosis as the primary metal removal stage. Prior to treatment, the raw water is treated to remove colloidal and suspended solids using coagulation/flocculation/clarification and filtration processes. The following figure presents a block diagram of this option.

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### Advantages

- Produces a treated effluent with very low metal, sulphate and TDS concentrations.
- Relatively simple operation.
- Fouling can be controlled to a certain degree with the use of anti-scalants and/or by operating at acidic pH.

### **Disadvantages**

- Reverse osmosis is best suited to low influent metal loadings. If metal loads are too high, metal oxide precipitation can occur which can ultimately lead to fouling issues on the membrane.
- Under high metal loads, it is better to use the RO unit as a polishing step following metal precipitation using lime or sulphide.
- Treatment throughput is impacted by cold water. Thus, under cold water conditions, a lower treatment flow will occur or the unit will operate at a higher feed pressure to maintain the desired treated water flow.
- The hydroxide sludge from the pre-treatment stage is very dilute, typically around 4%. Additional sludge management is required.
- Frequent cleaning required ensuring the membrane does not scale or foul with metal oxides and/or gypsum.
- The RO process produces a waste stream that is equal at best to 25% of the total flow to be treated, and can be higher depending on the feed effluent quality (up to 50% in some cases).

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The concentrated effluent produced (i.e. brine waste) by the RO will be primarily high in dissolved metals and sulphates (if present in high concentration in the feed effluent). The brine stream must be treated to remove the dissolved metals and sulphates as insoluble precipitates that can be safely co-disposed with the tailings, similar to options 1 to 3. Additional treatments similar to options 1 to 3 are required to separate metals and sulphates from the concentrated stream.

## **Option 5 – Ion Exchange Treatment**

Option 5 consists of removing dissolved metals and subhates, as well as reducing the TDS in the effluent, using ion exchange. The ion exchange will consist of a strong cationic column to remove the metals. This can be followed by a strong anionic column to remove sulphate. Regeneration takes place using sulphuric acid and sodium hydroxide. Prior to treatment by ion exchange, the raw water is treated to remove suspended solids from the effluent. The toflowing figure presents a block diagram of this option.

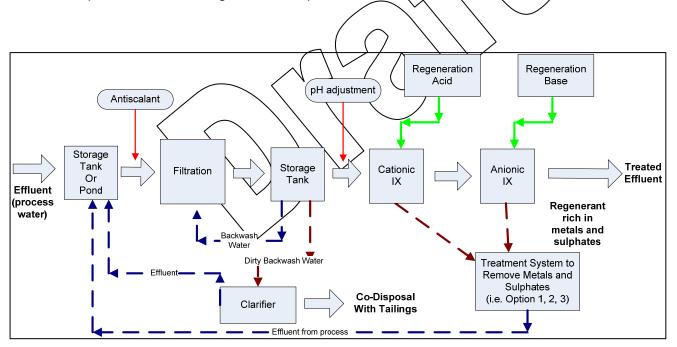


Figure 3-6: Option 5 – Ion Exchange Treatment

### <u>Advantages:</u>

- Treated water quality should meet and exceed the assumed design criteria.
- Proven technology.
- Simple operation.
- Performance not impacted by cold water temperatures.

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• 100% of the flow is treated.

Disadvantages:

- Will remove other cations/anions in the water, such as calcium and magnesium, thus increasing the frequency of resin regenerations.
- Depending on the metal and sulphate loads to be treated, the size of the ion exchange units can be very large.
- Acid and base regeneration chemicals are required.
- Complex regeneration procedures.
- High maintenance cost associated with the replacement of spent, nonregenerable ion exchange resins.
- The regeneration waste will require further treatment. Processes such as options 1, 2 and 3 could be used to treat the regeneration waste.

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## 4.0 ORDER OF MAGNITUDE CAPITAL/OPERATING COSTS

To provide an order of magnitude cost estimate (+/- 50%) associated with the water treatment technologies described herein, historical data from budget pricing of treatment equipment systems has been used. It should be noted that the application of the equipment was not the same as for that reviewed for Prairie Creek, but provides a good general idea of the capital cost of the equipment required.

The costs associated with the technologies listed were estimated from the project database records of SNC-Lavalin Montreal, as well as documented literature present in the public domain. These costs were up dated and revised as shown in Table 4.1. Note that the order of magnitude capital costs includes both direct cost (equipment, instrumentation and controls, building, etc.) and indirect cost (engineering and supervision, construction, etc.) components.

Costs have been updated to present day 2011 figures at a 3% annual inflation rate, however no account has been taken with respect to the costs of transportation within Northwest Territories.

For illustration purposes, operating costs are reflected in \$/m3 of treated process water effluent for each of the treatment options, and are presented as higher or lower than the base case treatment system.

As mentioned above, the costs provided in Table 4.1 are very generic and provide an order of magnitude estimate of treatment costs. Treatment costs will be highly dependent on a number of site specific factors, and the effluent quality and flows to be treated.

The following assumptions were also made:

- Design basis of the plant: 34 m<sup>3</sup>/hr
- For options using lime or sulphide precipitation, the clarification steps will take place in a circular metallic clarifier
- Disposal of sludge from the clarifier will be carried out by co-disposal with tailings without additional thickening.
- To estimate the cost for the residual treatment required for RO or IX, a lime precipitation unit will be used to treat the waste. The cost of a lime precipitation unit was pro-rated based on the volume of waste to be treated.
- For RO used as a polishing step after lime or sulphide precipitation, 25% of the total flow is wasted as brine.

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- For RO used as the primary treatment step, 40% of the total flow is wasted as brine.
- For IX, the volume of regeneration waste produced on a daily basis is equal to 10% of the daily flow treated and that the waste will be treated over a 12 hour shift.

#### Table 4-1: Order of Magnitude Capital Cost (+/-50%) and Operating Cost Estimates for Representative Treatment Technologies

		$\wedge$	-	
Options	Description		ital Cost 000's)	Operating Cost (\$/m3/treated)
Base Case	Sulphide/Lime Treatment & Clarification	\$	1,990	\$ 1.03
Option 1	Lime Treatment/Clarification & Reverse Osmosis. Residual Treatment using Lime Precipitation	\$	3,430	+
Option 2	Sulphide Treatment/Clarification & Reverse Osmosis. Residual Treatment using Line Precipitation	\$	3,590	++
Option 3	Lime or Sulphide Treatment/Clarification & Ion Exchange. Residual Treatment using Lime Precipitation	<b>\$</b>	3,190	+
Option 4	Reverse Osmosis Treatment (including pre- treatment by clarification/filtration). Residual Treatment using Lime Precipitation	\$	3,750	+++
Option 5	Ion Exchange Treatment (including pre- treatment by clarification/filtration). Residual Treatment using Lime Precipitation	\$	3,400	++

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#### 5.0 DISCUSSION

### Treatment Effectiveness

The expected performance of the technologies presented in Section 2 of this report is summarized in Table 5.1. The efficiencies shown in Table 5.1 are based on judgement and the assumptions given in the footnotes. Although treatment efficiency will depend on a number of factors, including the specific composition of the process water effluent, Table 5.1 gives a reasonable estimate of typical treatment system performance.

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						$\sim$	$\overline{\ }$	<u></u>		
Treatment Technologies	TDS	Hg	Ag	Pb	Cu <	Zn	As∽	Se	Cd	Sb
Membrane Filtration	***	***	***	***	***	***	**	***	***	-
Activated Carbon Adsorption	*	***	***	**	**	**	**	-	**	**
Ion Exchange	**	**	**(	***	**	**	*	**	***	**
Biological (anaerobic) reduction	-⁄	X - X	<b>~-</b> /	$(\epsilon)$		> -	-	-	-	-
Barium Hydroxide		-	- \	-	)-	-	-	-	-	-
Hydroxide Precipitation (lime)	<u>``</u> `	** `	**	**	**	**	**	**	**	**
Sulphide Precipitation	`	**	**	***	***	***	**	**	**	**
	$\backslash$	$ \rangle$								

Table 5-1: Treatment Effectiveness of Wa	Vater Treatment Technologies
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Notes:

1. Legend: TDS: Total Dissolved Solids, Hg: Mercury, Ag: Silver, Pb: Lead, Cu: Copper, Zn: Zinc, As: Arsenic, Se: Selenium, Cd. Cadmium, Sb: Antimony.

- Treatment effectiveness: \* fimited, \*\*: good, \*\*\*: excellent.
   Membrane filtration requires extensive influent pre-treatment to remove solids.
- 4. Assumes pH control and chemical control will remove metals to technology limits where dissolved metals are above MMER.
- 5. Assumes that metals are mostly present as dissolved contaminants.
- 6. Removal efficiency will be highly effluent dependent, but typical performance is provided.

Based on the summary presented in Table 5.1, the following observations can be made:

Biological anaerobic reduction and barium hydroxide treatments are specifically designed to remove sulphates and have very little impact on the removal of dissolved metals.

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- Hydroxide (lime) precipitation provides effective dissolved metals removal. This is the treatment option used in many mine sites to remove heavy metals from an effluent stream.
- Sulphide precipitation provides a greater removal of dissolved metals than hydroxide precipitation due to the lower solubility of the metal sulphides.
- Both hydroxide and sulphide precipitation do not have an impact on TDS.
- Membrane filtration (i.e. reverse osmosis) and ion exchange can have superior dissolved metals removal, and will also reduce TDS.
- Activated carbon is also effective in removing certain heavy metals. However, this treatment technology can only retain a limited amount of metals before the media has to be changed. For this reason, activated carbon is generally not-used as <u>a treatmentpolishing</u> step for the removal of dissolved metals.
- The removal of selenium and antimony may be enhanced by coprecipitation with a coagulant, such as terric sulphate or terric chloride.

Consequently, the treatment technologies that are considered to be potentially viable for dissolved metals removal from Prairie Creek process water are hydroxide precipitation, sulphide precipitation, reverse osmosis and ion exchange. Section 3 and 4 of this report presented different combinations of these unit processes.

## Hydroxide/sulphide precipitation + RO/IX polishing steps

The base case and options 1 to 8 use hydroxide and/or sulphide precipitation as an initial treatment step. The removal of dissolved metals from an effluent stream using lime or sulphide precipitation is generally practiced at many mine sites. The metals are precipitated as metal hydroxide or metal sulphide sludge which is typically co-disposed with the tailings. Thus, no additional residual management is required. <u>The clarified water is then discharged directly to the receiving water</u> stream. To enhance the treatment efficiency, the clarified water can also be sent to a polishing filtration step to remove any residual suspended solids prior to discharge.

However, tThe minimum concentration of metals that can be removed with this process is limited by the minimum solubilities of the hydroxide metals in water, as shown in Figure 2-1. Furthermore, the pH of the precipitation reaction also favours the removal of certain metals over others, especially when lime precipitation is used. Thus, the hydroxide/sulphide precipitation process can remove most of the heavy metals present in the process water and meet the typical discharge criteria presented in section 3.

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Thus,<u>However</u>, if the treated effluent is required to meet the mostmore stringent discharge criteria, a polishing step is needed to remove any residual dissolved metals. This can be accomplished using either reverse osmosis (RO) or ion exchange (IX). The main advantage of using RO or IX is that a consistent treated effluent will be produced. Furthermore, since metal loadings to the RO/IX are significantly lower than the initial loads, the size and complexity of the equipment is greatly reduced. However, there are certain disadvantages to note:

- RO treatment continuously produces a brine flow generally equal to 25% of the total flow treated. This brine stream can either be returned ahead of the lime/sulphide precipitation system or treated by a separate system. It may be possible to reduce the volume of brine produced by treating the brine with another RO unit (i.e. 2<sup>nd</sup> pass RO treatment). However, fouling of the membrane elements becomes a critical operating issue and can lead to frequent membrane cleaning.
- With IX, after a given amount of time, the resins will need to be regenerated in order to remove the dissolved metals that were adsorbed onto the resins, and allow re-use in the process. The regenerant will then have to be treated to precipitate the metals.
- The volume of regeneration waste produced by an IX system is typically much lower than an RO system.
- Another concern is the risk of fouling of the RO membrane with metal exides, resulting in frequent cleaning of the membrane elements, and in a worst case, replacement of the membrane elements.

## **RO or IX Treatment**

RO generally has an excellent rejection rate of dissolved heavy metals, specifically when the metals are in their ionic form. With IX, the resins can be selected to selectively remove specific metals or remove all heavy metals. However, there are certain disadvantages to note:

- Both RO and IX require a pre-treatment step to remove all suspended solids that could foul the units.
- Due to the high metal loads in the untreated effluent, the volume of resins required for the IX will be much larger. The frequency of resin regeneration will also be high.
- There will be fouling of the RO membrane by metal oxides due to the high concentration in the untreated effluent. Furthermore, to manage the fouling caused by the metal oxides, the RO would have to be designed with a lower recovery, resulting in a higher continuous brine flow that will need to be treated.

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 RO continuously produces a relatively high volume of brine for disposal. IX regeneration produces a waste brine episodically, and of a much smaller volume.

The advantages of RO and IX are comparable. However, waste brine management is a significant disadvantage with RO. <u>Further, there is no known industrial scale RO plant</u> <u>successfully treating the type of water expected to b produced at Prairie Creek.</u> Therefore, only IX is recommended for further consideration.

## Treatment Options to Consider for the Next Phase

Considering that the concentration of dissolved metals in the process effluent stream can be very high and highly variable, direct treatment by ion exchange is not recommended. It is prudent to have a lime or sulphide precipitation step first to remove as much of the dissolved metals as possible, followed by a filtration step to remove any residual solids in the treated effluent -followed by an IX could also be used as a polishing step if required to ensure that the treated effluent will consistently meet discharge criteria. The precipitation process is more robust when dealing with high metal loaps and a variable feed.

For the treatment of heavy metals by sulphide and/or lime, the base case treatment should be considered and optimized based on different operating pH. Furthermore, the following treatment should also be investigated in the laboratory:

- Evaluation of lime precipitation only at different operating pH;
- Evaluation of sulphide precipitation only at different operating pH;
- Addition of sodium sulphate and ferric sulphate at raw water pH, followed by lime precipitation.
- For all treatment options, add a filtration step downstream using different filter sizes to emulate a disk filter (10 micron), a multimedia filter (1 micron) and ultrafiltration (0.1 micron) and compare results to the non-filtered samples.

For the polishing step, ion exchange should be investigated further. The treated effluent produced from the precipitation test can then be treated by ion exchange. Contact with ion exchange resin vendors should be made to obtain samples of resins for testing. <u>Testing should also be conducted using ion exchange to remove sulphate and nitrogen species from the influent stream in case these parameters are present in concentrations that warrant removal, and the concentrations cannot be controlled by other means (e.g. water storage, treated water discharge strategy).</u>

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## 6.0 **RECOMMENDATIONS**

For the next step of the project, the following bench scale tests should be carried out <u>ontreating</u> a synthetic process effluent:

- Optimization of the base case treatment process (i.e. operating pH, reagent required).
- Evaluating the treatment performance of a lime only precipitation process at different pH conditions.
- Evaluating the treatment performance of a sulphide only precipitation process at different pH conditions.
- Evaluate whether the precipitate formed during lime and sulphide treatment can resolubilize at neutral pH (7) and acidic pH ( $\mathfrak{S}$ ).
- Addition of sodium sulphate and terric sulphate at raw water pH, followed by lime precipitation.
- For all treatment options, add a filtration step downstream using different filter sizes to emulate a disk filter (10 micron), a multimedia filter (1 micron) and ultrafiltration (0.1 micron) and compare results to the non-filtered samples.
- Bench test the treatment of the treated effluent from the lime/sulphide precipitation tests using one or two different ion exchange resins for metals removal and sulphate/nitrogen species removal. An ion exchange vendor should be contacted to obtain samples for testing.

The results from these bench scale tests will provide treatment performance with regard to dissolved metal removal based on different treatment scenarios and operating conditions.

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# APPENDIX B – COMMENTS FROM WATER ENGINEERING TECHNOLOGIES INC.

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Water Engineering Technologies, Inc.

# MEMORANDUM

To:	John Brodie	Date:	August 9, 2011
From:	Scott Benowitz		
Cc:			
Subject:	Review of Prairie Creek Water Treatment Scre	ening R	eport

This memo provides a review of SNC-Lavalin *Engineering Specification Process Water Treatment "Desk-Based" Screening Review of Water Treatment Applications*, dated August 3, 2011 (SNC Report). This review focuses on the assumptions used, selection of treatment processes used in the screening, conclusions, and recommendations contained in the SNC Report.

Also included is a review of the Canadian Zinc *Water Treatment, Water Storage, and SSWQO's Prairie Creek Mine* (no date, CZN Report) Review of this document focused on the constituents evaluated and the assumptions used for the treated water quality of the mine and mill water.

## Summary

The SNC Report presents some very good general information on various types of water treatment processes, most of which could be suitable for handling the project's water treatment requirements. Comments are provided that address many aspects of the information contained in the report. Three aspects of the report stand out, and are summarized as follows:

- a. The minimum monthly constituent concentration that a screened treatment process has to meet are similar or equal to the Metal Mining Effluent Regulations (MMER) concentration limits. These limits are at least one to two orders of magnitude higher than what is being evaluated in the CZN Report. So there is bit of disconnect between the two reports. The value of the SNC Report could be improved if the screened treatment technologies have to meet the effluent limits anticipated by this project.
- b. The SNC Report does not address inorganic nitrogen in the form of ammonia-N, nitrate-N, or nitrite-N. As inorganic nitrogen is addressed in the CZN Report, it seems appropriate that inorganic nitrogen be addressed in the SNC Report.
- c. The SNC Report does not address filtration downstream of a lime or lime/sulfide precipitation process. This is a noticeable omission, as filtration can further reduce total metal concentrations achieved from the chemical precipitation process. The screening process needs to include filtration for further consideration. Types of filters that should be included are multi-media and membrane (ultra) filters.

The CZN Report provides predictions of receiving water quality in Prairie Creek under various water storage and treatment scenarios. Review comments focused on what assumptions were used for the untreated mine water and mill water, as they are not provided in this document or the treatability study.

## **Comments Specific to the SNC Report**

It is noted that the purpose of the SNC Report "... is to perform a 'process water screening review' of base metal and heavy metal removal technologies which can be used successfully to produce an effluent meeting the most stringent requirements for discharge to the environment. The purpose is neither to review the correct selection of the treatment scheme for process water, nor to critique the design of the water treatment facility presently proposed for the Prairie Creek Mine Site."

The comments below follow the subject matter in the SNC Report.

- 1. The report does not address inorganic nitrogen in the form of ammonia-N, nitrate-N, or nitrite-N. As inorganic nitrogen is addressed in the CZN Report, it seems appropriate that inorganic nitrogen be addressed in this screening study.
- 2. The report does address sulfate and total dissolved solids (TDS) removal as well as metal removal.
- 3. Activated Carbon Adsorption this treatment technology can be used as a polishing process for dissolved metals that are tied to organics in a waste stream that otherwise will not precipitate as a result of coagulant addition and clarification. This technology is also successfully used to remove mercury from wastewater streams.
- 4. Ion Exchange does not provide an estimate of regenerant unit waste volumes for this process, yet in subsequent sections of the report compares the amount of waste produced to RO.
- 5. Biological Treatment this treatment process has been used successfully for sulfate (down to 200 mg/l) and metal removal at a Zinc Refinery in the Netherlands (see Biological Sulfide Production for Metal Recovery, C.J.N. Buisman, S.H.J. Vellinga, G.H.R. Janssen and H. Dijkman, PAQUES Bio Systems B.V., P.O. Box 52, 8560 AB Balk, Netherlands. Presented at TMS Congress 1999 Fundamentals of Lead and Zinc Extraction and Recycling). BioTeQ has licensed this technology and applied it to a few locations around the world.
- 6. While the SNC Report looks at two different types of coagulants (lime and sodium sulfide) for use in clarification, other coagulants would be appropriate to screen as well. One type is iron salts, such as the ferrous sulfate that is proposed to be used in the mill water treatment process, or ferric chloride. Another type is a chelating agents generally referred to as carbamate, which are available for several water treatment chemical providers. These coagulants would be used in addition to lime and/or sodium sulfide, and enhance the metal removal process. They have been used successfully at many other mine sites for metal removal.
- 7. The minimum monthly constituent concentration that a screened treatment process has to meet are similar or equal to the Metal Mining Effluent Regulations (MMER) concentration limits. These limits are at least one to two orders of magnitude higher than what is being evaluated in the CZN Report. So there is bit of disconnect between the two reports.

The SNC Report constituent list is missing notable constituents applicable to the project, including cadmium, antimony, manganese, selenium, ammonia-N, nitrate+nitrite-N,

sulfate, and TDS. (See Item 1 above.) The concentrations listed in the SNC Report can be met using coagulant addition (lime, or sodium sulfide and lime) and clarification. So there is no advantage to using any other process if these constituent concentrations are used as the benchmark.

The benchmark should more closely reflect those values used by the Province for other mine sites with similar discharge flows, or Canadian Council of Ministers of the Environment (CCME) requirements.

8. The Base Case sulfide/lime treatment process has been used successfully at other miningrelated sites. For instance, the Doe Run Company lead smelter at Glover, MO used this technology to achieve very low metal effluent concentrations (similar to CCME limits).

Using a polishing filter (see Item 12 below) and good process controls can significantly reduce the risk of having fine particulates pass through the clarifier to the discharge. Modifying the coagulant addition process from what is proposed can also improve the particulate size formation (see Item 14a below).

9. For the lime treatment & reverse osmosis (RO) alternative, it is assumed that brine treatment is required prior to sending the regenerant waste to the tails pond for disposal. While this assumption may be valid for some applications, there is no mention why that assumption is made here. For instance, has an assessment been made of how the tailings pond water chemistry would be changed as a result of disposing the brine directly to the tails?

A 25 percent recovery rate for a single-pass RO system is reasonable. If a double-pass RO system is used, the recovery can be increased to 80-85 percent.

RO is becoming more widely used at mining-related sites as regulatory effluent requirements become lower and lower. Examples in the U.S. include the Buckhorn Mine in WA, the Eagle Mine in MI, Barrick's Lead, SD treatment plant, to name a few that have been brought on-line in recent years.

- 10. For the sulfide treatment & RO alternative, the risk of hydrogen sulfide gas emissions can be addressed with proper chemical management. Since the sulfide precipitation is followed by RO, any particulates that pass through the pre-treatment step will be filtered out.
- 11. The RO Option 4 is no different from Options 1 and 2. Not sure why this is listed as a separate option.
- 12. The SNC Report does not address filtration downstream of a lime or lime/sulfide precipitation process. This is a noticeable omission, as filtration can further reduce total metal concentrations achieved from the chemical precipitation process. The screening process needs to include filtration for further consideration. Types of filters that should be included are multi-media and membrane (ultra) filters.
- 13. The SNC Report states that RO waste brine management is a significant disadvantage so it is not recommended for further consideration. I disagree, and recommend that RO still be considered if a treatment requirement greater than sulfide/lime/FeSO4 addition, clarification plus filtration (for filtration, see Item 12 above) is warranted.

The real issue is the amount of water contained in the RO brine or ion exchange (IX) regenerant. The bulk of these liquid wastes are metal and sulfate salts. The RO brine volume can be further concentrated using a second pass RO. The resulting highly concentrated brine can be combined with lime to make gypsum, the same as discussed for the IX brine.

- 14. I recommend that if additional bench tests are performed, the base case treatment process be optimized using a few additional tests:
  - a. Add sodium sulfate and FeSO4 (primarily for arsenic adsorption) at raw water pH and mix; raise pH to ~ 10 or 10.5 using lime and mix; settle and sample.
  - b. Add a filtration step downstream of the optimization study for the base case. Use filter sizes that emulate a disk filter (10 micron), a multi-media filter (~0.x micron), and an ultra-filter (~0.0x micron range) and compare results to non-filtered samples.

## **Comments Specific to the CZN Report**

The comments below relate to Table 3 of the CZN Report.

- 1. As the mill and mine water is to be combined prior to entering the water treatment plant clarifier and become essentially one flow stream, this table should reflect that combined water quality. The combined water chemistry is what will be released to the environment.
- 2. The metal concentrations for the treated mine water, the treated mill water, and the improved treated mill water shown in Table 3 generally reflect conservative concentrations found in the treatability study report *Prairie Creek Water Treatment Testing*, prepared by SGS-CEMI, February, 2010. However, the treatability report does not include mine water and mill water concentrations for ammonia-N, nitrate-N, nitrite-N, sulfate, or TDS. What does CZN expect the concentrations of these constituents to be in the untreated mine water and mill water? It is understood that in the absence of testing data, the CZN Report assumed lower concentrations in the treated water were made using best professional judgment in order to simulate their effect on predicted receiving water concentrations.