Abstract

A study was conducted on three natural mineral materials referred to as basalt, scoria, and calcined shale. These materials were provided by an industrial mineral producer in British Columbia. The main objectives of this study are, to evaluate the selected materials for treatment of metal contaminated effluents by adsorption, and to assess the possibility of replacing cement with the materials and to evaluate the performance of the cement replaced mortars.

In this research study, adsorption tests were conducted to assess the possibility of removing cationic and anionic metal ions from prepared and sampled oil refinery, and mine water effluents. Results of these tests indicate that the calcined shale material was an efficient adsorbent removing more than 99.8% of the copper from the effluent. Basalt material is a natural adsorbent that is highly capable of removing more than 99.9% molybdenum and arsenic ions and performs better than activated carbon. The treated effluents meet the regulatory limits of the Canadian Fisheries Act. The adsorption process when supplements the high density sludge (HDS) treatment, presents a reliable treatment process in removing metal ions in mine water to the regulatory limits. In particular, post treatment should serve to reduce fluctuations in the effluent discharge level.

The materials are assessed as natural pozzolans according to ASTM C618 “Standard specifications for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete”. Results indicate that the materials comply with the standard specifications. Naturally calcined shale is a highly desirable natural pozzolan
in which the calcination process to enhance the physical properties of the pozzolan occurs naturally requiring no energy consumption. Over time, natural pozzolan mortars gained higher compressive strength than that of fly ash and control mortars, making them suitable for mass concrete applications where early high strength is not required and low heat of hydration is favorable.

Further testing is required to evaluate the kinetics of the metal adsorption processes and to assess the possibility of regenerating the adsorbent bed.

Additional testing is recommended to evaluate the performance of the metal loaded adsorbents as pozzolans for long term storage. Leaching tests need to be conducted in order to assess the leachability of adsorbed metal ions.
Table of Contents

Abstract .................................................................................................................. ii

Table of Contents ................................................................................................. iv

List of Tables .......................................................................................................... viii

List of Figures ......................................................................................................... x

Nomenclature ......................................................................................................... xii

Acknowledgements ................................................................................................. xiv

Chapter 1  Introduction ............................................................................................. 1

1.1  Industrial Minerals ............................................................................................. 1

1.2  Studied Materials .............................................................................................. 2

1.3  Applications ........................................................................................................ 3

  1.3.1  History of the Material Use ........................................................................ 3

  1.3.2  Potential Applications and Previous Studies .............................................. 5

  1.3.3  Physical and Chemical Properties of Materials .......................................... 7

1.4  Objectives ........................................................................................................... 8

Chapter 2  Materials Characterization ...................................................................... 10

2.1  Mine Location .................................................................................................... 10

2.2  Geology .............................................................................................................. 11

2.3  Sample Composition ......................................................................................... 12
3.1 Introduction ................................................................................................................................. 15

3.2 Acid Rock Drainage ....................................................................................................................... 16
  3.2.1 Acid Rock Drainage Chemistry .............................................................................................. 16
  3.2.2 Treatment Methods for Acid Rock Drainage ......................................................................... 18
    3.2.2.1 Lime Treatment ................................................................................................................ 19
  3.2.3 Supplementary Treatment Methods ....................................................................................... 22
    3.2.3.1 Lime Pretreatment Process ............................................................................................. 22
    3.2.3.2 Lime Post-treatment Process ............................................................................................ 23
    3.2.3.3 Adsorbents ....................................................................................................................... 23
      3.2.3.3.1 Adsorption Models ..................................................................................................... 25
  3.2.4 Copper and Zinc Ions Chemistry ............................................................................................ 28

3.2.5 Procedures .................................................................................................................................. 29
  3.2.5.1 Adsorption Tests ................................................................................................................ 29
  3.2.5.2 Scoping Tests ..................................................................................................................... 29
  3.2.5.3 Loading Capacity Tests ...................................................................................................... 30
  3.2.5.4 Britannia ARD Treatment ................................................................................................. 31

3.2.6 Results and Discussions ......................................................................................................... 32
  3.2.6.1 Scoping Tests ..................................................................................................................... 33
  3.2.6.2 Loading Capacity ............................................................................................................... 37
  3.2.6.3 Adsorption Isotherm Models ............................................................................................. 39
  3.2.6.4 Britannia ARD Treatment ................................................................................................. 43

3.2.7 Conclusions and Recommendations ....................................................................................... 46

3.3 Alkaline/Neutral Rock Drainage ................................................................................................. 48
  3.3.1 Alkaline/Neutral Rock Drainage Chemistry ......................................................................... 48
  3.3.2 Treatment Methods for Alkaline Rock Drainage ................................................................... 48
    3.3.2.1 Iron Coprecipitation ........................................................................................................ 49
    3.3.2.2 Anion Exchange .............................................................................................................. 50
    3.3.2.3 Adsorption ...................................................................................................................... 50
4.1.3.1 Pozzolanic Reactions................................................................. 81

4.2 Procedures .................................................................................. 85
  4.2.1 Materials .............................................................................. 85
  4.2.2 Chemical Characterizations .................................................. 85
  4.2.3 Physical Characterizations ..................................................... 86
  4.2.4 Preparing Mortar for Flowability Test ................................... 87
  4.2.5 Determination of Flow .......................................................... 88
  4.2.6 Moulding Test Specimens ...................................................... 89
  4.2.7 Specimens Storage ................................................................. 89
  4.2.8 Determination of Strength Activity Index .............................. 90

4.3 Results and Discussions ................................................................ 91
  4.3.1 Chemical Properties ............................................................... 91
  4.3.2 Physical Properties ................................................................. 92
    4.3.2.1 Fineness and Specific Surface Area ................................. 92
    4.3.2.2 Flowability ................................................................. 93
    4.3.2.3 Strength Activity Index ............................................... 95

4.4 Conclusions ................................................................................. 101

Chapter 5 Conclusions and Recommendations ..................................... 104

Chapter 6 References ......................................................................... 108

Appendix A: Material Characterization .................................................. 118

Appendix B: Water Treatment ............................................................. 124

Appendix C: Supplementary Cementing Materials ............................. 130
List of Tables

Table 1-1: Top three non-metallic mineral products for Canada in 2202 (Natural Resources Canada, Preliminary Estimates) ................................................................. 2
Table 1-2 Existing applications of the materials .................................................................................................................................................................................. 4
Table 2-1 Result of whole rock analysis for major element oxides, loss on-ignition, and total sulfur ........................................................................ 12
Table 2-2 Results of quantitative phase analysis in percentage for major minerals 13
Table 3-1: Britannia mine water major ion concentrations ............................................................. 16
Table 3-2: Theoretical minimum solubility of copper and zinc ions ........................................ 28
Table 3-3 Copper and zinc removal scoping test conditions ......................................................... 30
Table 3-4 Copper an zinc removal loading capacity test conditions ........................................ 30
Table 3-5 Specific surface area of the adsorbents ..................................................................... 32
Table 3-6 Analyzed reference solutions at pH 4 ......................................................................... 32
Table 3-7 Copper and zinc removal using Sh and Ac ................................................................. 35
Table 3-8 Langmuir and Freundlich isotherm constants for metal ion adsorption .............. 41
Table 3-9: Copper concentration in treated water ................................................................. 44
Table 3-10: Metal ion concentrations in reference solutions at pH 4 ....................................... 56
Table 3-11: Arsenic and Molybdenum removal scoping test conditions .............................. 57
Table 3-12: Arsenic and molybdenum removal loading capacity test conditions .......... 57
Table 3-13: Highest adsorption capabilities in comparison with Ac ................................. 59
Table 3-14: Summary of test processes for boron removal .............................................. 67
Table 3-15 Natural sorption capability of sorbents for boron removal ................................. 70
Table 3-16 Sorption of boron on acid activated minerals .................................................. 71
Table 3-17 Sorption of boron on amine activated sorbents ............................................... 71
Table 3-18 Boron precipitation with amine followed by filtration (tests 9 and 10) .............. 73
Table 3-19 Boron removal using ion flotation (test 11) ....................................................... 73
Table 3-20 Result of SX test for boron removal (test 12) ....................................................... 73
Table 4-1 Quantities of materials for making nine test specimens ................................... 88
Table 4-2: Chemical requirements for natural pozzolan by ASTM and values for studied SCMs ........................................................................................................ 91
Table 4-3 Specific surface area of the SCMs

Table 4-4 Maximum compressive strength of the mortars in MPa

Table A1-6-1 Results of whole rock analysis

Table A-6-2 Results of quantitative phase analysis (wt. %)

Table B-6-3: Preliminary results of metal ion removal

Table B-6-4 Results of loading capacity tests

Table C-6-5: Maximum force applied (in KN) to 20% replaced SCM and control specimens in compressive strength test

Table C-6-6: Maximum force applied (in KN) to 30% replaced SCM specimens in compressive strength test

Table C-6-7 Maximum force applied (in KN) to 40% replaced SCM specimens in compressive strength test
List of Figures

Figure 1-1: Value of non-metallic mineral products (source: Natural Resources Canada Statistics) .......................................................................................................................................................... 1

Figure 2-1 Rietveld refinement plot for black scoria (Sc) .......................................................................................................................................................... 14

Figure 3-1: Thermodynamic stability of metal ion hydroxides and sulfides .......................................................................................................................... 21

Figure 3-2 Copper concentration in treated solution at pH 4 ........................................................................................................................................ 34

Figure 3-3 Zinc concentration in treated solution at pH 4 ........................................................................................................................................ 34

Figure 3-4 Copper ion removal onto Sh at room temperature at pH 4 ........................................................................................................................ 37

Figure 3-5 Zinc ion removal onto Sh at room temperature at pH 4 ........................................................................................................................ 38

Figure 3-6 Langmuir equilibrium isotherm of copper adsorbed onto Sh at pH 4 ........................................................................................................ 39

Figure 3-7 Langmuir equilibrium isotherm of zinc adsorbed onto Sh at pH 4 ........................................................................................................ 40

Figure 3-8 Langmuir and Freundlich equations applied to the copper adsorption onto Sh at pH4 .................................................................................. 42

Figure 3-9 Langmuir and Freundlich equations applied to the zinc adsorption onto Sh at pH 4 .................................................................................. 42

Figure 3-10 Investigated two scenarios for treating ARD ........................................................................................................................................ 44

Figure 3-11 Eh-pH diagram of aqueous arsenic species in the system As–O2–H2O at 25°C and 1 bar total pressure .................................................................................................................................................. 52

Figure 3-12 Eh-pH diagram for part of the system Mo-S-O-H. Source: Brookins (1978) ........................................................................................................................................ 55

Figure 3-13 Molybdenum concentrations in treated solution at pH 4 and 8 ........................................................................................................ 58

Figure 3-14 Arsenic concentration in treated effluent at pH 4 and 8 ....................................................................................................................... 59

Figure 4-1 Rietveld refinement plot for black scoria (Sc) ........................................................................................................................................ 83

Diagram 4-2 Flow sheet of mortar making for compressive strength test ........................................................................................................ 87

Figure 4-3 Order of Tamping in Moulding Test Specimens ........................................................................................................................................ 89

Figure 4-4 Flow of control and 20% SCM mortars. The flow for all mortars exceeded the required 110mm. ........................................................................................................................................ 94

Figure 4-5 Flow of additional cement replacement ........................................................................................................................................ 94

Figure 4-6 Strength activity index of test specimens based on 28 day control specimen. ........................................................................................................................................ 96

Figure 4-7 Trend of the strength activity index based on 28 day control specimen .......................................................................................... 98

Figure 4-8 Relative compressive strength of SCM to control specimens at 7 days ........................................................................................ 99
Figure 4-9 Relative compressive strength of SCM to control specimens at 28 days..... 100
Figure A-6-1 Map of Quesnel, BC, Canada........................................................................... 118
Figure A-6-2 Rietveld refinement plot for sample “Calcined Shale”................................. 121
Figure A-6-3 Rietveld refinement plot for sample “Black Scoria”........................................ 122
Figure A-6-4 Rietveld refinement plot for sample “Red Basalt”........................................... 123
Figure B-6-5 Copper concentration in treated solution at pH 8........................................ 127
Figure B-6-6 Zinc concentration in treated solution at pH 8 .............................................. 128
Figure B-6-7 Freundlich equilibrium isotherm of copper adsorbed onto Sh.................... 128
Figure B-6-8 Freundlich equilibrium isotherm of zinc adsorbed onto Sh......................... 129
## Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>$Sc$</td>
<td>Black scoria</td>
</tr>
<tr>
<td>$Sc;c$</td>
<td>Coarse black scoria</td>
</tr>
<tr>
<td>$Sc;f$</td>
<td>Fine black scoria</td>
</tr>
<tr>
<td>$Sh$</td>
<td>Calcined shale</td>
</tr>
<tr>
<td>$Sh;c$</td>
<td>Coarse calcined shale</td>
</tr>
<tr>
<td>$Sh;f$</td>
<td>Fine calcined shale</td>
</tr>
<tr>
<td>$Ba$</td>
<td>Red basalt</td>
</tr>
<tr>
<td>$Ba;c$</td>
<td>Coarse red basalt</td>
</tr>
<tr>
<td>$Ba;f$</td>
<td>Fine red basalt</td>
</tr>
<tr>
<td>$Ac$</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>$Fa$</td>
<td>Fly ash</td>
</tr>
<tr>
<td>SCM</td>
<td>Supplementary cementing material</td>
</tr>
<tr>
<td>$w/cm$</td>
<td>Water to cementations material ratio</td>
</tr>
<tr>
<td>C</td>
<td>CaO</td>
</tr>
<tr>
<td>S</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>A</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>H</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>$C_3S$</td>
<td>Tricalcium silicate</td>
</tr>
<tr>
<td>$C_2S$</td>
<td>Dicalcium silicate</td>
</tr>
<tr>
<td>$C_3S_2H_8$</td>
<td>calcium silicate hydrate</td>
</tr>
<tr>
<td>N</td>
<td>Normal</td>
</tr>
</tbody>
</table>
M  Molar
DAH  Dodecylamine hydrochloride
HDTMA  Hexadecyltrimethylammonium
\(c_0\)  initial metal ion concentration, (ppm)
\(c_e\)  equilibrium concentration of metal ion in solution, (ppm)
m  mass of adsorbent used, (g)
\(q_e\)  equilibrium solid - liquid metal ion concentration (mg/g)
\(Q_0\)  Langmuir monomolecular layer capacity (mg/g)
x  mass of metal ion adsorbed onto adsorbent (mg)
LOI  Loss on ignition
XRD  X-ray diffraction
Acknowledgements

I would like to express my sincere gratitude to my supervisor, Dr. Bern Klein for his invaluable supervision, support and encouragement, and my advisors, Dr. Marek Pawlik, Dr. George Oprea, and Dr. Marcello Veiga for their collaboration through the course of this work. I am very grateful to Mr. Brian Wear, President of Canada Pumice Corp., and the Natural Science and Engineering Research Council of Canada (NSERC) for the financial support leading to completion of this thesis.

I would also like to express my gratitude to Dr. Mory Ghomshei, Carmen Oprea, Dr. Nemy Banthia, Sally Finora, and Frank Schmidiger for their kind guidance and helpful assistance through my study.

I would like to sincerely thank my wife for her love and support and finally I would like to dedicate my deepest gratitude to my parents for all their sacrifice, love, and unwavering support and it is to them that I dedicate this work.
Chapter 1 Introduction

1.1 Industrial Minerals

Industrial minerals is a growing sector in the Canadian mining industry. The value of non-metallic mineral production increased from $5.4 billion in 1995 to $7.6 billion in 2001 (Natural Resources Canada). As illustrated in Figure 1-1, the steady growth of this sector suggests that the value of this sector may exceed that of metallic minerals by 2005 (Klein 2003).

Figure 1-1: Value of non-metallic mineral products (source: Natural Resources Canada Statistics)
Table 1-1 shows the top three valuable non-metallic products in Canada in 2002, in which, cement encounters the second valuable product after potash.

**Table 1-1: Top three non-metallic mineral products for Canada in 2002 (Natural Resources Canada, Preliminary Estimates)**

<table>
<thead>
<tr>
<th>Product</th>
<th>Value (Millions $)</th>
<th>Tonnes (thousands)</th>
<th>Average (Value $/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potash</td>
<td>1598</td>
<td>8189</td>
<td>195</td>
</tr>
<tr>
<td>Cement</td>
<td>1387</td>
<td>13201</td>
<td>105</td>
</tr>
<tr>
<td>Sand and gravel</td>
<td>1047</td>
<td>229535</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Sustainable production of industrial minerals requires that a diverse range of products be processed. Processing the industrial minerals adds value to the products, for instance, crushing limestone aggregate can produce agricultural lime stone which increases its value from $5/t to as much as $30/t (Klein 2003).

### 1.2 Studied Materials

Industrial minerals generally referred to naturally occurring minerals and rocks that are of economic value. The definition excludes metallic ores, gemstones, and manufactured products; however, the boundaries are undefined. Industrial minerals include manufactured products such as cement and lime as well as mixtures of different minerals that comprise “materials” with specific characteristics (Donald et al, 1994).

The materials used for this study are mixtures of different minerals that are of economic value and therefore they are referred to as “materials” through this study.
In this study these materials were evaluated for applications in water treatment and as pozzolanic cement. Two volcanic tuff materials were evaluated including vesicular basalt and a scoria which were formed after volcanic eruption. The materials are fine, porous, and low density. The other material is a soft sedimentary rock with clay size particles. The material is naturally calcined in the geothermal area and therefore porous.

1.3 Applications

This research evaluated two potential areas of application for the materials including water treatment and as cement replacements. The performance of the materials was compared with other materials that have been used commercially for these areas of applications. The potential areas of applications were identified based on:

- History of the material use
- Potential applications and previous studies
- Physical and chemical properties of the materials

1.3.1 History of the Material Use

These materials from the company are presently being used for a wide range of applications including lightweight construction aggregate, horticulture/agriculture, landscaping groundcover, water filtration, recreational and playing fields, winter road abrasive, and many bagged retail products for the consumer market. Existing applications of the materials are listed below (Amec Ltd. technical report 2000). This study was conducted to evaluate other potential applications.
The current applications indicate unique physical and chemical properties of the materials. For instance, colorful rigid rocks are suitable for landscaping. The volcanic rocks are resistant to high temperatures and can be used as barbecue rocks. The low density volcanic rocks have applications as lightweight aggregates. The materials are also beneficial in horticulture and agriculture as a replacement for traditional soil amendment, growing mediums, and filtration mediums. Table 1-2 summarizes the existing applications of the materials.

<table>
<thead>
<tr>
<th>Vesicular basalt and scoria</th>
<th>Calcined shale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Landscaping</td>
<td>Landscaping</td>
</tr>
<tr>
<td>Lightweight aggregate</td>
<td>Lightweight aggregate</td>
</tr>
<tr>
<td>Sports field</td>
<td>Sports field</td>
</tr>
<tr>
<td>Anti slip</td>
<td>Filtration medium</td>
</tr>
<tr>
<td>Horticulture</td>
<td>Odor adsorbent</td>
</tr>
<tr>
<td>Construction back fill</td>
<td></td>
</tr>
<tr>
<td>Barbecue rocks</td>
<td></td>
</tr>
</tbody>
</table>
1.3.2 Potential Applications and Previous Studies

Volcanic tuffs and clays have successful applications in treating waters containing metal ions and also in concrete manufacturing as cement replacements.

In a number of studies volcanic tuffs were used to remove inorganic substances and ammonium. These studies show volcanic tuffs are capable of removing metal ions to different concentrations. Results of a study by Drews et al. (1990), showed the volcanic tuffs were not able to remove arsenic, and selenium from water, however, copper, zinc, lead, and aluminum were partly removed from the solution. The efficiency of metal ion removal was affected mainly by pH and the concentration of sorbent. Total exchange capacity of a volcanic tuff tested for copper ion removal was measured at 1.3 mgCu\(^{2+}/g\) tuff. In this test the volcanic tuff material was regenerated using sodium chloride (Pode et al, 1996)

Studies on sedimentary rocks containing solid organic material show successful applications in water treatment especially in metal ion removal (Shevchenko et al, 2003). Al-Asheh et al. (2001) studied the sorption of copper and zinc ions onto oil shale and concluded that the sorbent is suitable for copper and zinc removal, especially the latter. The metal ion removal is favorable by increasing the sorbent concentration, pH and temperature. The equilibrium was achieved after 24 hours and the Freundlich model best described the isotherm adsorption. A patented study by Japan Agency of Industrial
Science and Technology demonstrated the possibility of removing over 87% Cr, Mo, and V using 1g oil shale adsorbent/0.1L contaminated solution (JP 57135040).

Volcanic tuffs have proven successful applications when used as a cement replacement. The pozzolanic reaction of the supplementary cementing materials in concrete leads to higher compressive strength over time. Liebig et al. (1998) evaluated the performance of volcanic tuffs and the effect of the calcination on mortars. The compressive strength of the specimens increased due to the pozzolanic activity; however, heating had different effect on the properties of the mortars.

Naturally calcined shale is also proven to enhance the properties of the concrete. Barger et al. (2001) studied the performance of calcined shale on different concrete properties and concluded that calcination modifies the crystalline structure of shale to an amorphous phase. The amorphous phase participates in pozzolanic reactions and enhances properties of the hardened concrete including higher sulfate resistance and lower permeability (Rodrigues-Camacho et al, 2002).

The calcined shale material, used for the study, had successful applications as a natural pozzolan in mass local concrete projects including construction of a dam (Wear 2003).
1.3.3 Physical and Chemical Properties of Materials

Materials for water treatment and cement replacement require unique properties.

Sorbent materials require following physical and chemical properties (Bennie et al., 2002):

- Adsorption or ion exchange capability
- High surface area
- High pore volume
- Rigid physical structure
- Non-toxic leachable substances

The materials tested for this study have shown metal ion removal capabilities. They are porous and consequently have large surface area. Preliminary sorption tests showed the materials were able to keep their solid structure during the treatment tests. It is very important that the sorbent be free of any toxic substances that could leach out to the treated solution during the sorption process. When an ion adsorbs onto the surface of an clay adsorbent, a similar charge ion desorbs and enters the solution in an ion exchange process. It is important to consider the concentration of the exchanged ion in treated solution since it may exceed the allowable limits. For instance, in an ion exchange process where arsenic exchanges with sodium ions of an adsorbent, excess sodium in treated solution could be considered as contamination.

Having high surface area is also an asset for a pozzolanic material. Physical and chemical requirements of natural pozzolans for use as supplementary cementing materials are
determined by standard agencies including American Society for Testing and Materials (ASTM) Canadian Standards Association (CSA). The materials for this study were tested based on standards for chemical and physical properties.

1.4 Objectives

This study was conducted in two separate but related areas including for metal ion removal and as supplementary cementing materials. The industrial minerals tested for the study were characterized and the economical aspects of introducing new products were investigated.

The main objectives of this study are:

- To evaluate the selected materials for removal of dissolved metal ions by adsorption.
- To evaluate the selected materials for use as supplementary cementing materials.

The water treatment study was aimed at evaluating the selected industrial minerals for adsorption of ions including:

- Acid rock drainage for the removal of copper and zinc.
- Acid rock drainage for the removal of copper and zinc in combination with lime treatment.
- Alkaline/neutral rock drainage for the removal of arsenic and molybdenum.
- Oil refinery effluent for the removal of boron.
The cement replacing study was aimed at assessing the selected minerals for use as supplementary cementing materials with the following objectives:

- To comply with standard specifications for use as a mineral admixture in Portland cement concrete.
- To evaluate the physical performance of the replaced cement mortar and compare to commercially available activated carbon.
Chapter 2 Materials Characterization

The following natural materials were selected for evaluation with respect to water treatment and pozzolanic cement applications:

1. Red to grey vesicular basalt (*Ba*)
2. Black to dark grey scoria (*Sc*)
3. Pink to tan calcined shale (*Sh*)
4. Zeolite (*Ze*)

Natural clinoptilolite zeolite (*Ze*) material which used as a reference for the study was received from Western Industrial Clay Minerals (www.wicp.com).

For removal of metal ions, these materials were compared to commercially available activated carbon which was purchased from Fisher Scientific (www.fishersci.com). The materials were used to replace cement and the performance was compared to pozzolanic fly ash, purchased from Lafarge (www.lafarge.com).

2.1 Mine Location

The first two materials, *Ba* and *Sc*, are mined from the Nazko cone which is a volcanic cone located approximately 100 km west of Quesnel, BC near the Nazko Valley (see map in Appendix A). The proven reserve is in excess of 45 million tones (Machibroda 2004).
The third material is mined from a deposit west of Quesnel, BC from a deposit known as Red Bluff. Studies on the deposit show that the shale has been naturally calcined in the geothermal area some 10,000 years ago. Steam currently venting on the property provides the fact that the geothermal area is active (Wear 2003).

2.2 Geology

The volcanic rocks in this study are categorized as vesicular basalt and scoria which were formed around 7000 years ago (Geological Survey of Canada). When the volcanic lava or magma cooled after eruption the red vesicular basalt (Ba) was formed. The rock is fine grained, porous, and low density and contains holes which were formed due to the gas bubbles in the lava. The black scoria (Sc) material is a glassy lava rock of basaltic to andesitic composition which was ejected from a vent during explosive eruption. The rock is low density and porous due to the escape of volcanic gases during eruption. The grain size is smaller in Sc compared to Ba indicating faster lava cooling rate during the rock formation (Chapin et al, 1979).

The tan color naturally calcined shale (Sc) is a type of sedimentary soft, layered rock which was formed when clay-size particles were deposited in relatively calm, muddy waters. Over a long period of time these particles became compacted to form a shale rock (Friedman et al, 1978).

Most shale rocks are grey to brown color. Calcination of shale rock causes the rock structure to shrink to half of its original size leading to a soft and porous texture (Friedman et al, 1978). The generally grey to brown color of shale could have changed to
tan color mainly due to loosing the black-colored organic materials and gaining the red color from iron oxide. The Quesnel deposit is mostly a light orange, yellow and tan color.

2.3 Sample Composition

Table 2-1 shows the results of a whole rock analysis indicating the grades of the main rock forming elements. Sc and Ba volcanic rocks are alumina silicates that are rich in iron oxides. In case of Sh, the major formation is alumina silicates.

<table>
<thead>
<tr>
<th>Elements</th>
<th>%SiO₂</th>
<th>%Al₂O₃</th>
<th>%Fe₂O₃</th>
<th>%MgO</th>
<th>%CaO</th>
<th>%Na₂O</th>
<th>%LOI</th>
<th>%S*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sh</td>
<td>48.78</td>
<td>23.77</td>
<td>2.92</td>
<td>0.79</td>
<td>0.68</td>
<td>0.39</td>
<td>8.6</td>
<td>0.11</td>
</tr>
<tr>
<td>Sc</td>
<td>43.11</td>
<td>14.22</td>
<td>15.11</td>
<td>8.26</td>
<td>9.45</td>
<td>3.54</td>
<td>&lt;.1</td>
<td>0.07</td>
</tr>
<tr>
<td>Ba</td>
<td>41.91</td>
<td>13.52</td>
<td>15.37</td>
<td>8.61</td>
<td>9.07</td>
<td>3.49</td>
<td>1.3</td>
<td>0.09</td>
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</tbody>
</table>

* %S= % total sulfur

The results of quantitative phase analysis by Rietveld refinement are given in Table 2-2. These amounts represent the relative amounts of crystalline phases normalized to 100%. The procedure and Rietveld refinement plots for the samples are shown in Appendix A1 (plots at Figure A-6-2 Figure A-6-4). Calcined shale is mainly composed of muscovite, quartz, and feldspar minerals. These minerals resisted decomposition when naturally calcined. Black scoria is rich in forsterite and augite minerals and contains amorphous phases as indicated in the X-ray diffraction diagram (XRD) illustrated in Figure 2-1. Red basalt is high in augite and plagioclase minerals.
### Table 2-2 Results of quantitative phase analysis in percentage for major minerals

<table>
<thead>
<tr>
<th></th>
<th>Ideal Formula</th>
<th>Sh</th>
<th>Sc</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>25</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Cristobalite</td>
<td>SiO₂</td>
<td>4.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-feldspar</td>
<td>KAlSi₃O₈</td>
<td>18.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plagioclase</td>
<td>NaAlSi₃O₈ – CaAl₂Si₂O₈</td>
<td>3.8</td>
<td>2.6</td>
<td>30.5</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₂AlSi₃O₁₀(OH)₂</td>
<td>42.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td>(Mg,Fe²⁺)₅Al(Si₃Al)O₁₀(OH)₈</td>
<td>4.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Augite</td>
<td>(Ca,Na)Mg₂Fe₂⁺Al₂(Ti)(Si₃Al)₂O₆</td>
<td>23.7</td>
<td>34.7</td>
<td></td>
</tr>
<tr>
<td>Enstatite</td>
<td>Mg₂Si₂O₆</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forsterite</td>
<td>Mg₂SiO₄</td>
<td>55.7</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>α-Fe₂O₃</td>
<td>0.9</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>8.1</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Nepheline</td>
<td>(Na,K)AlSiO₄</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The hump in the XRD plot shown in Figure 2-1 for Sc indicates presence of amorphous phases. This glassy amorphous phase may participate in pozzolanic reaction which will be discussed in Chapter 5.
Figure 2-1 Rietveld refinement plot for black scoria (Sc)

The hump at 28° is the indication of the amorphous phase
Chapter 3 Water Treatment

3.1 Introduction

Removal of metal ions from effluents represents a significant technical challenge. As a consequence several industries are faced with issues relating to removal of contaminant cations and anions from solution. Mine waters, potable waters, and refinery effluents can be contaminated by the dissolved ions and pose an acute risk to the environment.

Environmental effects or pollution associated with mines nearly always have to do with an acidic or alkaline drainage with elevated concentrations of heavy metals in nearby waters and soils. Mine waters can be highly acidic or alkaline, depending on the complex interactions of hydraulic, chemical, and biological processes occurring. It can be held responsible for devastating watercourses and maybe highly visible, defacing the rivers (e.g. Britannia Mine, Canada) presenting an acute challenge to many countries (King 1995). Examples of the ion contaminations in low or high pH are excess amount of iron, copper, zinc, arsenic, and molybdenum ions in solution. Discharge of the oil refinery effluents, in particular, can be challenging where high concentration of boron contaminant is present.

This part of the study is aimed at understanding the chemistry and formation of the mentioned contaminants with a review of common treatment methods to propose and evaluate a treatment technique.
3.2 Acid Rock Drainage

Acidic drainage is a persistent environmental problem at many active and abandoned metal and coal mine sites. Acid rock drainage (ARD) is mainly caused by mining activities. An outstanding example is ARD from Britannia Mine which is located near Squamish, BC, Canada. Britannia Mine is one of the largest metal pollution sources in North America. Although the mine is inactive, high flow rate of ARD is still discharging to Howe Sound. The table below shows the major ion concentrations of the mine water with an average flow of 500 m$^3$/h. (O’Hearn et al, 2000)

Table 3-1: Britannia mine water major ion concentrations

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Regulations *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (mg/L)</td>
<td>23</td>
<td>0.3</td>
</tr>
<tr>
<td>Zinc (mg/L)</td>
<td>26</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>1530</td>
<td></td>
</tr>
</tbody>
</table>

* Mean metal mining regulations.

3.2.1 Acid Rock Drainage Chemistry

Acid rock drainage (ARD) is formed naturally when a reduced state rock exposes to water and oxygen. Mining activities, in particular, allow the introduction of oxygen into deep geological environment and thus oxidation of these minerals. The most common type of these minerals is sulfides.

Sulfide oxidation produces acidification of the surface water resulting in high dissolved metal concentrations (Chapman et al, 1983; Ferguson and Erikson 1988). The oxidation process is a complex cycle of reactions. The most ubiquitous metal sulfide is pyrite that
may exist in association with other elements such as copper, zinc, arsenic, and molybdenum (Spears et al, 1994). This oxidation process occurs in undisturbed rock but at a slow rate and the water is able to buffer the generated acid. Mining activities increase the exposed surface area of these sulfur bearing rocks allowing for excess acid generation beyond the water’s natural buffering capabilities.

The reaction below shows the general formation process: (Nordstrom et al, 2000).

\[
2\text{FeS}_2 (s) + 7\text{O}_2 (aq) + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{+2} + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad [3.1]
\]

Further oxidation of ferrous iron to ferric iron occurs when sufficient oxygen is dissolved in the water or when the water is exposed to adequate atmospheric oxygen.

\[
2\text{Fe}^{+2} + \frac{1}{2} \text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{+3} + \text{H}_2\text{O} \quad [3.2]
\]

Some acidity is consumed in this reaction, however, the stage is set for further hydrogen ion release and therefore more acidic that will surpass these benefits. Ferric iron can either precipitate producing red-orange color ferric hydroxide or it can react directly with pyrite to produce more ferrous iron and acidity.

\[
2\text{Fe}^{+3} + 6\text{H}_2\text{O} \leftrightarrow 2\text{Fe(OH)} (s) + 6\text{H}^+ \quad [3.3]
\]

\[
14\text{Fe}^{+3} + \text{FeS}_2 (s) + 8\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 15\text{Fe}^{+2} + 16\text{H}^+ \quad [3.4]
\]

When ferrous iron is produced as a result of equation 3.4 with sufficient dissolved oxygen, the cycle of equations 3.2 and 3.3 will continue (Younger et al., 2002). Without
dissolved oxygen, equation 3.4 continues to elevate level of ferrous iron in the drainage (Younger et al., 2002).

The oxidation reactions is catalyzed by the action of acidophilic sulfide oxidizing bacteria, in particular, *Thiobacillus ferrooxidans*, which thrives in the pH range of 1.5 to 3.0 (McGinness et al, 1993).

The oxidation of sulfide minerals to release heavy metals is the fundamental reaction of acid rock drainage formation. The pH level of the mine water decreases by the acidity generated in the reactions. If produced acidity exceeds the alkali available in the system, the net drainage is in acidic state.

### 3.2.2 Treatment Methods for Acid Rock Drainage

Several treatment methods are proposed for ARD treatment. By far the most common application for reducing acidity and adding alkalinity is lime. This process, however, faces limitations that will be discussed.

There are two types of treatment techniques for ARD, active and passive treatment, that can be utilized based on the volume of the effluent, type, and concentrations of the present contaminants.

Active treatments follow the pattern of an ordinary waste water plant and require ongoing inputs of artificial energy and/or chemical reagents. The most prominent active treatment
technique is oxidation, dosing with alkali, and sedimentation (ODAS). Other active treatments include sulfidization, biosedimentation, sorption and ion exchange, and membrane processes including filtration and reverse osmosis (Younger, et al, 2002).

Passive treatments utilize naturally occurring geochemical and biological processes in order to improve the quality of the contaminated waters with minimal operation and maintenance requirements. The pH of mine drainage is raised when the water mixes with alkaline water or through direct contact with carbonate rocks. The removal of metal contaminants is then effected through the precipitation of hydroxides, oxyhydroxides and sulphides. Reactions in wetlands occur under aerobic or anaerobic environment depending on the oxygen content, water and soil chemistry (Hedin et at, 1994).

3.2.2.1 Lime Treatment

In the lime treatment process, one of the most used active processes, metal ions in solution form hydroxides when reacted with lime. Precipitated metal hydroxide and gypsum (CaSO₄) are extremely difficult to filter. In the process of sludge formation, flocculants help to form large particles with high settling rates. The treated water is discharged from a clarifier and the sludge is stored. In the high density sludge (HDS) process, sludge from the clarifier recycles to the process to provide nucleation sites for new precipitate formation (Kuyucak 1998).

Limestone (calcium carbonate) increases the pH of water by consuming hydrogen ions and adding alkalinity (Younget al., 2002).
\[
CaCO_3 + 2H^+ \leftrightarrow Ca^{+2} + H_2O + CO_2 \quad [3.5]
\]

\[
CaCO_3 + H_2CO_3 \leftrightarrow Ca^{+2} + 2HCO_3^- \quad [3.6]
\]

Other commonly used alkaline agents are hydrated lime, soda ash, caustic soda, and ammonia (Comp, 2002).

The process, however, faces problems in treatment and sludge disposal. Although the process is straightforward, not all metal ions can be precipitated to the required levels at a given pH. As shown in Figure 3-1, thermodynamically, metal ions have different solubility behavior by pH. Other challenges are related to sludge and include:

- Large volume sludge that is extremely difficult to filter
- Stability of the contaminated sludge over time
Figure 3-1: Thermodynamic stability of metal ion hydroxides and sulfides

Source: EPA 625/8-80-003
3.2.3 Supplementary Treatment Methods

Lime treatment, in some cases, is inadequate of removing all the contaminant metal ions in the drainage to the required levels. The complex chemistry of mine water and different thermodynamic behavior of metal ions versus pH (shown in Fig 3-1) make precipitation of all metal ions challenging. A pilot scale HDS treatment conducted on Britannia mine water was unable to remove copper ion adequately. Supplementing this process with an adsorption process to meet all the metal ion requirements brings significant advantages to the treatment system. Treatment by adsorption can either follow a HDS process or be conducted prior to HDS treatment.

3.2.3.1 Lime Pretreatment Process

The advantages of having the adsorption process after HDS treatment are:

- It leaves the option of running the adsorption process whenever needed. As shown in Error! Reference source not found.. In certain times when the concentration of copper exceeds the maximum allowed, conducting the additional process is mandatory.
- Since most of metal ions are precipitated in the sludge, less adsorbent is needed and consequently the operating cost of supplementary adsorption process will be low.

The disadvantages include:

- High capital cost
• High volume sludge

3.2.3.2 Lime Post-treatment Process

Having the adsorption process prior to the lime treatment has the following advantages:

• Less lime is needed for the lime treatment process since a portion of the metal ions are removed in the adsorption process.
• Less flocculants are needed since less precipitate is formed.
• The adsorbent can be regenerated to reduce the cost of supplying the adsorbent.

The disadvantages include:

• The capital and maintenance cost of the adsorption process.

3.2.3.3 Adsorbents

Adsorption is a process where the removed material is distributed over the surface of the adsorbing material. The adsorption isotherm relates the concentration of a chemical in solution to its concentration on a surface. Generally, the greater the concentration of a chemical in solution, the greater its concentration bound to the surface. The actual concentration on the surface depends on the chemical involved and with what else it is competing for space on the surface. It has been observed that there is always a preference for the binding of some ions over others but it is normal in nature for a wide variety of
ions to be adsorbed at once. This competition for binding sites means that the amount of ion adsorbed always is sensitive to the concentration of other ions present (Dabrowski et al, 2001).

Activated carbon (Ac) is the most common adsorbent made by heat treatment of carbonaceous material like coal, coconut shell, and wood under controlled condition. This treatment results in an open structure with a high surface area that allows liquid to penetrate. Performance of activated carbon is based on its physical and adsorption properties. The most effective application of Ac is at removing metal ions and organic compounds such as proteins and hormones. An example of water treatment using activated carbon would be purifying the drinking water to remove taste and odor. As with any treatment system, however, it cannot remove all possible drinking water contaminants. Testing requires identifying the extent to which the contaminant removal is feasible (Lorenzen et al, 1995).

A number of studies have demonstrated successfully removal of copper and zinc ions from solution by adsorption (Drews et al, 1990; Pode et al, 1996; Shevchenko et al, 2003; Al-Asheh et al, 2001).

Although activated carbons are the most common used adsorbents in the removal of the metal ions from solution due to their large surface area, they still present some disadvantages in which they are flammable, and more expensive to produce compared to natural industrial mineral adsorbents. The solution in which the adsorption takes place
also affects the sorption process. Concentration and molecule size of the adsorbates, pH, and temperature of the solution are important factors that affect the process (Bennie et al, 2002).

An advantage of Ac over other natural adsorbent materials like volcanic tuffs and clays is excessive specific surface area. A disadvantage is higher cost due to the heat treatment process involved.

3.2.3.3.1 Adsorption Models

Sorption models allow calculating useful coefficients from the experimental points and quantifying the affinity of the ions for the sorbent. Many adsorption models have been developed to describe adsorption characteristics and to predict the adsorption quantity of several systems. In ion exchange, free metal ions are adsorbed when surface protons are displaced. The energy for adsorption reaction is provided by specific chemical bonding (Benfield et al, 1982). In the ion solvent interaction model, adsorption is described in terms of the competition between the free energy changes. Adsorption energy includes electrostatic, specific chemical reaction, and solvation (James and Healy, 1972). In the Langmuir (Langmuir, 1918) and Freundlich (Freundlich 1906) models, adsorption of gas molecules onto metal surfaces is investigated. The concept has found many other successful applications in other sorption processes including metal ion adsorption from solution. The models of Langmuir and Freundlich were selected for this study due to their wide use in adsorption data modeling.
In order to optimize the design of an adsorption system to remove the metal ions from solution, it is important to establish the most appropriate correlations of the equilibrium data for the system. Applicability of the isotherm equations was compared by judging the correlation coefficients ($R$).

The Langmuir equation is the most common used two parameter equation, expressed as (Langmuir, 1918):

$$q_e = \frac{x}{m} = \frac{Q_0 c_e}{1 + b c_e}$$

Where, 

- $c_e$ is equilibrium concentration of metal ion in solution (ppm), 
- $m$ is mass of adsorbent used (g), 
- $q_e$ is equilibrium solid - liquid metal ion concentration (mg/g), 
- $Q_0$ is Langmuir monomolecular layer capacity (mg/g), 
- $x$ is mass of metal ion adsorbed onto adsorbent (mg), 
- $b$ is rate of adsorption to desorption. The equation derivation is described in Appendix B.

This theory was first applied to adsorption of gas molecules onto metal surfaces and found successful application in many other sorption processes as well.

Constant $b$ is a direct measure for the adsorption process intensity and $Q_0$ is a constant related to the occupied area of a monolayer of adsorbate, reflecting the adsorption capacity.

A linear form of the equation is:

$$c_e/q_e = 1/Q_0 b + c_e/Q_0$$
The Freundlich model stipulated that the adsorption of adsorbate is a function of its concentration in the solution (Freundlich, 1906).

The equation is expressed as:

\[ \frac{x}{m} = kc_e^{1/n} \]

Where \( k \) and \( n \) are empirical constants.

A linear form of the equation is:

\[ \log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log c_e \]

Empirical constants \( k \) and \( 1/n \) indicate the level of adsorption related to the bonding energy and the degree of non-linearity between solutions and concentrations, respectively. Value \( k \) indicates the quantity of the adsorbate adsorbed onto the adsorbents for a unit equilibrium concentration. The slope \( 1/n \), above one indicates cooperative adsorption; while below one specify a normal Langmuir isotherm. Values closer to 0 indicate more heterogeneous surface of adsorbent.
3.2.4 Copper and Zinc Ions Chemistry

Copper and zinc usually occur in solutions as single cations (Cu$^{2+}$ and Zn$^{2+}$). The table below shows the minimum solubility of these cations in pure water at 25°C based on Figure 3-1.

<table>
<thead>
<tr>
<th></th>
<th>Hydroxide</th>
<th>Sulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (mg/L)</td>
<td>$2.2 \times 10^{-2}$</td>
<td>$5.8 \times 10^{-18}$</td>
</tr>
<tr>
<td>Zinc (mg/L)</td>
<td>1.1</td>
<td>$2.3 \times 10^{7}$</td>
</tr>
</tbody>
</table>

Acid rock drainage has a pH below 4 and according to Fig 3-1 high amounts of copper and zinc are dissolved in the drainage.

In a lime treatment process for ARD, as the pH level rises, copper and zinc become extremely insoluble and precipitate as hydroxides. These ions, however, can be adsorbed onto the surface of an adsorbent even at low pH. Therefore, this fact brings an advantage to metal ion removal by the adsorption technique.

It should be noted that regulations, however, often limit the pH of treated effluent to a relative neutral range. Therefore for ARD treatment, addition of an alkaline chemical is compulsory to the treated effluent.
3.2.5 Procedures

Copper and zinc solutions were prepared from sulfate solutions in low pH. The concentration of 30 mg/l was selected which is close to the average concentrations of copper and zinc in Britannia mine water (O'Hearn et al, 2000). The solutions contained hydrochloric acid and the pH was adjusted by adding droplets of 5N hydrochloric acid or caustic soda.

In order to characterize the physical properties of the adsorbents, the specific surface area of the adsorbents was determined by BET (Brunauer, Emmett, and Teller) method.

3.2.5.1 Adsorption Tests

In this test, the adsorbent was mixed with the solution containing metal ions and shaken for 24 hours at room temperature to obtain equilibrium state. The pH was adjusted according to the test condition using minimum amounts of 5N hydrochloric acid and caustic soda. The treated solution was filtered using a 0.45μm millipore filter. The solution was analyzed for metal ion concentrations by ICP analysis.

3.2.5.2 Scoping Tests

Sixteen scoping tests were carried out to determine the maximum adsorption capability of Sc, Ba, Sh, and Ac for the removal of copper and zinc from solutions. Adsorption tests were conducted according to section 3.2.5.1 with the conditions shown in Table 3-3.
Table 3-3 Copper and zinc removal scoping test conditions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Name</th>
<th>Concentration g/100mL</th>
<th>Ion</th>
<th>Concentration mg/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sc</td>
<td>10</td>
<td>Cu</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Ba</td>
<td>10</td>
<td>Cu</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Sh</td>
<td>10</td>
<td>Cu</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>Ac</td>
<td>10</td>
<td>Cu</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>Sc</td>
<td>10</td>
<td>Cu</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>Ba</td>
<td>10</td>
<td>Cu</td>
<td>30</td>
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<td>7</td>
<td>Sh</td>
<td>10</td>
<td>Cu</td>
<td>30</td>
<td>8</td>
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<td>8</td>
<td>Ac</td>
<td>10</td>
<td>Cu</td>
<td>30</td>
<td>8</td>
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<tr>
<td>9</td>
<td>Sc</td>
<td>10</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
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<td>10</td>
<td>Ba</td>
<td>10</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
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<td>11</td>
<td>Sh</td>
<td>10</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
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<td>12</td>
<td>Ac</td>
<td>10</td>
<td>Zn</td>
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<td>13</td>
<td>Sc</td>
<td>10</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>14</td>
<td>Ba</td>
<td>10</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>15</td>
<td>Sh</td>
<td>10</td>
<td>Zn</td>
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<td>4</td>
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<tr>
<td>16</td>
<td>Ac</td>
<td>10</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
</tr>
</tbody>
</table>

3.2.5.3 Loading Capacity Tests

Based on the scoping tests, loading capacity tests were conducted to obtain loading capacity and adsorption isotherm data for copper and zinc ions onto calcined shale.

Adsorption tests 17 to 24 were conducted according to section 3.2.5.1 with conditions outlined in Table 3-4.

Table 3-4 Copper and zinc removal loading capacity test conditions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Name</th>
<th>Concentration g/100mL</th>
<th>Ion</th>
<th>Concentration mg/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>Sh</td>
<td>0.01</td>
<td>Cu</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>18</td>
<td>Sh</td>
<td>0.5</td>
<td>Cu</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>19</td>
<td>Sh</td>
<td>1</td>
<td>Cu</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>20</td>
<td>Sh</td>
<td>2</td>
<td>Cu</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>21</td>
<td>Sh</td>
<td>0.01</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>22</td>
<td>Sh</td>
<td>0.5</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>23</td>
<td>Sh</td>
<td>1</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>24</td>
<td>Sh</td>
<td>2</td>
<td>Zn</td>
<td>30</td>
<td>4</td>
</tr>
</tbody>
</table>
3.2.5.4 Britannia ARD Treatment

In order to supplement the lime treatment technique in removing metal ions from ARD, two possible scenarios of treating Britannia ARD were considered for evaluation. The first scenario involved adsorption followed by lime treatment process and the second scenario involved lime treatment followed by adsorption and is referred to as post-treatment.

For pretreatment, Britannia mine water was first treated in a continuous HDS treatment process. A sample of the discharged water was filtered at 0.45 μm and treated using the batch adsorption test described in section 3.2.5.1 with 2g Sh/100 ml as adsorbent.

For post treatment, sample of Britannia mine water was filtered and treated in a batch adsorption process using 2g Sh/100 ml according to section 3.2.5.1. Lime was then added to the treated water until a pH of 9.25 was reached. The treated solution was filtered at 0.45μm and a sample was sent for ICP analysis to determine copper concentration.
3.2.6 Results and Discussions

Surface area of the adsorbents was measured by the BET and results are shown in Table 3-5.

Table 3-5 Specific surface area of the adsorbents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>1.49</td>
</tr>
<tr>
<td>Ba</td>
<td>2.51</td>
</tr>
<tr>
<td>Sh</td>
<td>43.02</td>
</tr>
<tr>
<td>Ac</td>
<td>837.65</td>
</tr>
</tbody>
</table>

As shown in the table, commercially activated carbon had a significantly higher specific surface area than the natural materials tested. Since the adsorption takes place on the surface of the adsorbent, the Ac should have a much higher loading capacity than the tested natural material. Among the natural materials, the Sh had a higher specific surface area than the volcanic tuff materials.

The prepared solutions of copper and zinc with 30 mg/L were analyzed for metal ion concentrations and the results are shown in Table 3-6. These concentrations were used as reference concentrations in further calculations.

Table 3-6 Analyzed reference solutions at pH 4

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>Metal Ion</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Copper</td>
<td>27.8</td>
</tr>
<tr>
<td>2</td>
<td>Zinc</td>
<td>31.4</td>
</tr>
</tbody>
</table>
3.2.6.1 Scoping Tests

Scoping tests 1 to 16 were conducted in order to obtain the adsorption capacity of adsorbents for removing metal ions from solutions. Since copper and zinc form metal hydroxides at high pH, only low pH tests were considered.

The amount of metal ion removed was calculated by the difference of the initial and the equilibrium concentrations as follows:

\[
\text{Removal, } \% = \frac{(c_0 - c_e)}{c_0} \times 100
\]

Where,

\[c_0 = \text{initial metal ion concentration, (ppm)}\]
\[c_e = \text{equilibrium concentration of metal ion in solution, (ppm)}\]

Results of the scoping test are shown in Figure 3-2 and Figure 3-3. Among Sc, Ba, and Sh adsorbents, Sh had the highest capability for copper and zinc removal and therefore was selected for further testing. Table 3-7 shows the result of the highest metal ion adsorption onto Sh and Ac at pH 4. Results of the tests at pH 8 are shown in Appendix B.
Figure 3-2 Copper concentration in treated solution at pH 4

Figure 3-3 Zinc concentration in treated solution at pH 4
<table>
<thead>
<tr>
<th>Test No</th>
<th>Adsorbent</th>
<th>Adsorbate Ion</th>
<th>Initial Concentration (mg/L)</th>
<th>Final Concentration (µg/L)</th>
<th>Removal (%)</th>
<th>Limit* (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Sh</td>
<td>Cu</td>
<td>30</td>
<td>35.9</td>
<td>99.88</td>
<td>300</td>
</tr>
<tr>
<td>8</td>
<td>Ac</td>
<td>Cu</td>
<td>30</td>
<td>11.0</td>
<td>99.96</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Sh</td>
<td>Zn</td>
<td>30</td>
<td>5542</td>
<td>81.53</td>
<td>200</td>
</tr>
<tr>
<td>12</td>
<td>Ac</td>
<td>Zn</td>
<td>30</td>
<td>131.8</td>
<td>99.56</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-7 Copper and zinc removal using Sh and Ac

* Source: Mean metal mining regulations, Fisheries Act, Canada Gazette part II, Vol. III, No5, monthly mean values

The presence of the counter ions affects the adsorption process. In copper and zinc treatment tests the counter ion was chloride due to the availability of copper and zinc chloride at the time of testing. In Britannia mine, the counter ion present is sulfate and therefore different ion-ion interactions could affect the process. This effect is proven to be negligible. In an adsorption study using natural zeolite to remove nickel cations, the capacity of the adsorbent to remove nickel was 2% higher in presence of sulfate than chloride ions (Papachristou et al, 1993).

As shown in Table 3-7, for copper removal, both adsorbents were capable of treating copper containing solution to the required level defined by Canadian Fisheries Act. For zinc removal, however, only treated solutions by Ac met the regulation requirements.

Chemical properties (see Table 2-1) of the materials indicate that Sh has significantly higher loss on ignition (LOI). If the 8.6% LOI can be related to the organic content of the
material, it can be speculated that the adsorption of copper and zinc at low pH occurs chemically on the organic component of this material.

Ac was shown to be the strongest adsorbent which removed more than 99% of copper and zinc in the solution.
3.2.6.2 Loading Capacity

The adsorption isotherms were used to determine the adsorption capacity and the nature of metal ions adsorption onto the adsorbents. Adsorption of copper and zinc ions onto Sh was investigated conducting tests 33-40. Two widely used isotherm adsorption models (i.e. Langmuir and Freundlich) were used to describe adsorption characteristics.

Figure 3-4 and Figure 3-5 illustrate the results of copper and zinc removal with different adsorbent dosage, respectively. For the 30 mg/L metal ion solution, it can be observed that nearly complete copper ion removal can be achieved using 40 g/L (4 g/100mL) of Sh. The graph reaches plateau at 20 g/L of adsorbent and therefore this concentration is considered as the optimum amount of adsorbent to remove 30 mg/L of copper. Also, 20 g/L (2 g/100ml) Sh removes 86% of zinc ion and can be considered as the optimum amount of adsorbent to remove 30 mg/L zinc.

![Copper ion removal onto Sh at room temperature at pH 4](image)
Results of test 3, 19, and 20 were used to obtain the Langmuir and Freundlich isotherm modeling data for copper adsorption onto Sh. Low concentrations of adsorbent used in tests 17 and 18 made the modeling equation very sensitive to low range variation of equilibrium concentrations. Therefore, they were not considered in data modeling for copper ion removal.

Test 21 also uses a very low amount of adsorbent for zinc adsorption which made the data modeling sensitive. As can be observed in Figure 3-5, although test 11 uses a higher amount of adsorbents than test 24, less zinc removal was achieved, causing significant error in data modeling. Therefore, for zinc adsorption onto Sh only results from tests 22, 23, and 24 were considered.
3.2.6.3 Adsorption Isotherm Models

Figure 3-6 and Figure 3-7 show the Langmuir analysis of the copper and zinc ion isotherm data, respectively. The Langmuir isotherm appears to fit the data reasonably well, as reflected by the correlation coefficient ($R$) in the range of 0.999. The values of loading capacity ($Q_0$) and constant $b$ were calculated from the slope and the intercept of the graphs and are presented in Table 3-8. Figure 3-8 and Figure 3-9 shows the isotherm fits of copper and zinc to the measured adsorption capacity data, respectively.

![Graph showing Langmuir equilibrium isotherm of copper adsorbed onto Sh at pH 4](image)

**Figure 3-6 Langmuir equilibrium isotherm of copper adsorbed onto Sh at pH 4**
Figure 3-7 Langmuir equilibrium isotherm of zinc adsorbed onto Sh at pH 4

Values for the Freundlich Model constants are obtained from the linear form of the equation and are presented in Table 3-8.

By comparing the results of the correlation coefficients the Langmuir model presents a better fit than the Freundlich model (see Freundlich equilibrium fit in Appendix B). Results from Freundlich isotherm indicate that the adsorption is taking place on a highly heterogeneous surface as $1/n$ values close to zero were obtained. The monomolecular capacity of copper and zinc adsorption according to the Langmuir model are 2.21 and 1.91 mg/g respectively. Higher $k$ values for copper adsorption in the Freundlich model confirms that higher adsorption of copper onto Sh has occurred.
Table 3-8 Langmuir and Freundlich isotherm constants for metal ion adsorption

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$Q_0$ (mg/g)</th>
<th>b (L/mg)</th>
<th>R</th>
<th>$k$ (L/g)</th>
<th>1/n</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>2.21</td>
<td>3.35</td>
<td>1.00</td>
<td>1.21</td>
<td>0.39</td>
<td>0.96</td>
</tr>
<tr>
<td>Zinc</td>
<td>1.91</td>
<td>1.25</td>
<td>0.99</td>
<td>1.11</td>
<td>0.18</td>
<td>0.72</td>
</tr>
</tbody>
</table>

The loading capacity of 2.2 mg/g for copper and 1.9 mg/g for zinc suggests the maximum capacity of 14 and 16 g/L for $Sh$ to remove 30 mg/L of copper and zinc, respectively. The model shows the optimum concentrations can be less than 20 g/L as suggested earlier in section 3.2.6.2.

Figure 3-8 and Figure 3-9 show the equilibrium adsorption of copper and zinc on the shale is characterized by a long flat and nearly horizontal branch. This type of isotherm may be interpreted from the assumption that the adsorbed layer is only one molecule thick or that the surface is saturated with the adsorbate (copper or zinc) and that the plateau region of the isotherm corresponds to the completion of its mono layer. However, it should be noted that the extension of the simple mechanism developed for adsorption on an open external surface of a micro porous adsorbent represents a very long extrapolation.
Figure 3-8 Langmuir and Freundlich equations applied to the copper adsorption onto Sh at pH4

Figure 3-9 Langmuir and Freundlich equations applied to the zinc adsorption onto Sh at pH 4
3.2.6.4 Britannia ARD Treatment

Results of a continuous high density sludge (HDS) treatment on Britannia mine water show that the average level of total and dissolved copper in the discharge of the HDS plant was 231 and 137 \( \mu g/L \) which are close to the 300 \( \mu g/L \) maximum allowed limit. In some operating days, the concentration of dissolved copper in the discharge exceeds the 300 \( \mu g/L \) limit. Therefore, this treatment process requires modification or supplementing with other treatment processes.

The original water sample from Britannia mine water containing 11.9 mg/l dissolved copper has been treated in two scenarios. In the first scenario, HDS treatment reduced the dissolved copper in the mine water to 171 \( \mu g/L \). When treated by the adsorption process by \( Sh \) at high pH, 72% of the copper was removed and the dissolved copper level lowered to 48 \( \mu g/L \).

Results from the second scenario indicated that adsorption before the HDS treatment can remove about half of the dissolved copper in the mine water at pH 4.5. The copper concentration of the treated solution reached 6.2 mg/L and the lime addition reduced the copper content to 125 \( \mu g/L \). This content is similar to the copper concentrations from HDS treatment discharge alone.
The difference in these scenarios is that adsorption process is taking place at alkaline and acidic pH in scenario 1 and 2, respectively. The results of the tests show that the lime treatment if conducted alone or after the adsorption process, reduces the level of dissolved copper in Britannia mine water to about 130 µg/L. Therefore, there is no apparent improvement using scenario 2. As indicated earlier (Fig 3-10), the copper concentration in HDS treatment plants may exceed the 300 µg/L limit in normal fluctuations. This suggests that the chemistry of the copper compound in the mine water is complex and has higher solubility than copper hydroxide and does not precipitate to the
target level. For scenario 1, the adsorption process was able to remove the dissolved copper in the lime treatment discharge to below 50 μg/L.

This suggests that supplementing the lime treatment technique with the subsequent adsorption process ensures metal removal to below the regulatory limits.
3.2.7 Conclusions and Recommendations

From the results of the literature review and the study, the following conclusions can be made:

- Adsorption process using Ac and Sh as adsorbents is capable of lowering dissolved copper concentration from 30 mg/L to below 50 µg/L which meets the regulatory limits of the Canadian Fisheries Act.

- It can be speculated that the adsorption of copper and zinc onto Sh in low pH occurs chemically on the organic content of this material.

- Ac was an efficient adsorbent removing more than 99% of the copper and zinc from the effluent.

- The Langmuir model gives the best fit for the copper and zinc adsorption.

- The loading capacities for the Sh for the removal of copper and zinc according to the Langmuir model are 2.21 and 1.91 mg/g, respectively. For these loading capacities 14g/L and 16 g/L of Sh are needed to remove 30 mg/L of copper and zinc, respectively.

- The HDS treatment process when supplemented by the adsorption process with shale, presents a reliable treatment process in removing metal ions in mine water to the regulatory limits. In particular, post treatment should serve to reduce fluctuations in the effluent discharge level.
Based on the results and conclusions of the presented study the following future work is recommended:

- Further testing is required to indicate the loading capacity of $Sh$ for removing 300 $\mu$g/L of mine water previously treated by the HDS process.

- Further testing is required to determine the kinetics of adsorption.

- Further testing is required to evaluate the supplemented treatment process for Britannia mine in a continuous process.

- Further testing is recommended to assess the possibility of regenerating the adsorbent bed.

- Leaching tests need to be conducted according to British Columbia Special Waste Extraction Procedure (BC SWEP) in order to assess the leachability of adsorbed metal ions.

- Further testing is recommended to evaluate the performance of the metal loaded adsorbents as pozzolans for long term storage.
3.3 Alkaline/Neutral Rock Drainage

3.3.1 Alkaline/Neutral Rock Drainage Chemistry

Alkaline rock drainage is formed in the systems where bacterially catalyzed sulfate reduction occurs, resulting in metal sulfides and/or hydrogen sulfide and alkalinity (Younger et al., 1994). The pH of such systems can be elevated to around 8. The drainage is associated with low concentrations of toxic metals and considerable amount of hydrogen sulfides (Younger et al., 1994). The alkalinity may also arise from buffering reactions, where an overall alkaline drainage is generated.

Common contaminants in alkaline drainage are arsenic and molybdenum which can occur in both alkaline and acidic solutions. Brenda Mines in British Columbia faces alkaline mine drainage with about 3 mg/L molybdenum concentration (Brown 1989).

3.3.2 Treatment Methods for Alkaline Rock Drainage

Arsenic and molybdenum are two anionic contaminants which are present naturally or as a result of mining activities in the environment. Unlike copper and zinc which have low solubility in hydroxide state, arsenic and molybdenum are highly soluble in alkaline drainage. Consequently, removal of these ions in drainage requires treatment methods other than lime precipitation. Common contemporary treatment methods for removal of these ions are described below.
3.3.2.1 Iron Coprecipitation

Ferrihydrite is an iron oxy-hydroxide with large surface area, strong adsorptive properties, and high adsorptive capacity. At relatively high concentrations of iron(III) and arsenic(V) and at low pH, coprecipitation results in the formation of iron(III) ferric arsenate, FeAsO$_4$ 2H$_2$O (Robins et al, 1987). When arsenic(V) concentration is low, the product is a poorly crystalline iron oxy-hydroxide which incorporates the vast majority of the arsenic impurity (Riveros et al, 2001).

A number of studies investigated removal of arsenic by iron compounds. In a study by Bohro and Merkl (1993), it was observed that more than 95% of As(V) were removed from a solution initially containing 300 ppb As(V) with 0.09 mmol/L Fe(III). Removal of As(III) was shown to be more difficult than As(V), where only 50 to 60% of As(III) was removed at the same conditions (Bissen et al, 2003).

In order to treat Brenda Mines alkaline drainage, ferric sulphate is added to the alkaline mine drainage and the pH is controlled to 4.5 by adding sulfuric acid. A flocculant is added to improve solid/liquid separation in the clarifier. A sand filter is also used to remove all residual Mo from the effluent to meet the regulations limit. This plant treats an alkaline mine drainage with about 3 mg/L of Mo to a final discharge of 0.03 mg/L (Aube et al., 2000).
3.3.2.2 Anion Exchange

Strongly basic anion-exchanger resins are capable of removing anions from the solution. The reactions below show the process in which arsenic(V) ion is exchanged for chloride ion in the resin.

\[
\text{R-Cl + H}_2\text{AsO}_4^- \rightarrow \text{R-H}_2\text{AsO}_4 + \text{Cl}^- \quad [3.7]
\]

\[
2\text{R-Cl + HAsO}_4^{2-} \rightarrow \text{R}_2\text{-HAsO}_4 + 2\text{Cl}^- \quad [3.8]
\]

The arsenic impregnated resin is regenerated by contacting with high concentrations of chloride anion. Sodium chloride and hydrochloric acid are the two sources of chloride that can be used for resin regeneration.

\[
\text{RH}_2\text{AsO}_4^- + \text{Cl}^- \rightarrow \text{RCl} + \text{H}_2\text{AsO}_4^- \quad [3.9]
\]

It was observed than more than 99% of arsenic was removed by the strong anionic resins from an initial solution concentration of 600 ppb. The resin was regenerated by sodium chloride or hydrochloric acid (Korngold et al, 2001).

3.3.2.3 Adsorption

Adsorption process is described in detail in section 3.2.3.3. In a study by Jiang (2001), it was observed that 96% of arsenic can be removed from solution by activated carbon in a concentration range of 21 to 1100 ppm. Other studies showed that activated carbon can remove As(V) but not As(III). The uptake capacity of As(V), however, was low, reaching 20 mg/g on activated carbon (Jubinka et al, 1992).
3.3.3 Arsenic Ion Chemistry

Arsenic is sensitive to mobilization at the pH values typically found in groundwaters (pH 6.5–8.5) and under both oxidizing and reducing conditions. Arsenic occurs in the environment in several oxidation states (-3, 0, +3 and +5) but in solution arsenic forms oxyanions of arsenate As(V) and arsenite As(III) under oxidized and reduced conditions, respectively (Sadiq et al., 1997). Arsenite is more mobile and toxic (Webb et al., 1966).

Arsenic is found in different forms in sulfide mineral deposits and dissolves in the ARD due to oxidation reactions. Unlike other toxic trace elements such as copper and zinc, arsenic becomes increasingly soluble as the pH increases. (Dzombak et al., 1990). The highest reported arsenic concentration of 850,000 ppm is from an acid seep in the Richmond mine at Iron Mountain, California (Nordstrom et al., 1999).

In a HDS process, arsenic coprecipitates with iron and forms ferric arsenate (FeAsO₄), the stable form of arsenic, in the sludge and is removed from the solution (Lawrence et al., 1999).

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. As Figure 3-11 shows, under oxidizing conditions, H₂AsO₄⁻ is dominant at low pH (less than about pH 6.9), while at higher pH, HAsO₄²⁻ is dominant. In extremely acidic and alkaline conditions H₃AsO₄⁻ and AsO₄³⁻ may be present respectively. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H₃AsO₃⁰ will predominate (Brookins et al., 1988; Yan et al., 2000).
Figure 3-11 Eh-pH diagram of aqueous arsenic species in the system As–O₂–H₂O at 25°C and 1 bar total pressure

Source: Brookins et al, (1988)
3.3.4 Molybdenum Ion Chemistry

Molybdenum, in its general chemistry is very different from the common toxic heavy metals such as cadmium, lead, and mercury. It is ingested, transported, and excreted as an anion $[\text{MoO}_4]^{2-}$ which is structurally similar to phosphate and sulfate. Molybdenum has a number of stable oxidation states. In its compounds, molybdenum exhibits all oxidation states from 2- to 6+. The most common oxidation numbers are +6 and +4. In oxidation states 3+ to 6+ molybdenum forms a large number of complexes with oxygen and nitrogen donor ligands and with the halogens. The relative stabilities of different oxidation states with respect to oxidation and reduction depend on their environments (Mitchell et al, 1990).

The Redox potential (Eh) and pH of molybdenum is shown in Figure 3-12 (Brookins 1978). The molybdate species in aqueous solutions depend on the Mo concentration and the pH. At molybdenum concentrations greater than $10^{-3}$ moles/L and pH higher than 6, the predominant species is the $[\text{MoO}_4]^{2-}$ ion. By decreasing the pH, polymerisation condensation occurs and at pH 5-6 the ion $[\text{Mo}_7\text{O}_{24}]^{6-}$ and at pH 3-5 the ion $[\text{Mo}_8\text{O}_{26}]^{4-}$ are formed. At pH 5, MoO$_3$ precipitates and in more acidic solutions the $[\text{MoO}_2]^{2+}$ ion is formed. At concentrations below $10^{-3}$ moles/L, monomeric species are formed (Aveston et al., 1964). Treatment tests in this study were conducted in pH 4 and 8, where in high oxidation state, molybdenum occurs as HMoO$_4$.
Molybdate is less soluble under reducing conditions compared to arsenic. Molybdenum is also commonly found in solution as the molybdate oxyanion ($\text{MoO}_4^{2-}$), exhibiting similar behavior to arsenate (Roy et al, 1986).
Figure 3-12 Eh-pH diagram for part of the system Mo-S-O-H. Source: Brookins (1978)
3.3.5 Procedures

Molybdenum solution was prepared from molybdic anhydride. Corresponding quantity of arsenic trioxide was dissolved in hydrochloric acid and distilled water to prepare the arsenic solution. The concentrations of As and Mo in prepared solution were analyzed and results are shown in the table below. These values were used for further calculations.

Table 3-10: Metal ion concentrations in reference solutions at pH 4

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>Metal Ion</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Molybdenum</td>
<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>Arsenic</td>
<td>6.4</td>
</tr>
</tbody>
</table>

3.3.5.1 Adsorption Tests

In the same procedure as 3.2.5.1, the adsorbent was mixed with the solution containing metal ions and shaken for 24 hours at room temperature. The pH was adjusted to meet test conditions using hydrochloric acid and caustic soda. The treated solution was filtered with a 0.45 millipore filter to remove particles and analyzed for final ion concentrations using ICP analysis.

3.3.5.2 Scoping Tests

Scoping tests 25-40 were conducted to evaluate the maximum adsorption capacity of Sc, Ba, Sh, and Ac for the removal of arsenic and molybdenum in the prepared solutions. Adsorption tests were conducted according to section 3.3.5.1 with the conditions shown in the Table 3-12.
Table 3-11: Arsenic and Molybdenum removal scoping test conditions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Name</th>
<th>Concentration g/100mL</th>
<th>Ion</th>
<th>Concentration mg/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Sc</td>
<td>10</td>
<td>Mo</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>26</td>
<td>Ba</td>
<td>10</td>
<td>Mo</td>
<td>3</td>
<td>4</td>
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<tr>
<td>27</td>
<td>Sh</td>
<td>10</td>
<td>Mo</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>28</td>
<td>Ac</td>
<td>10</td>
<td>Mo</td>
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<td>32</td>
<td>Ac</td>
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<td>Mo</td>
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</tr>
<tr>
<td>33</td>
<td>Sc</td>
<td>10</td>
<td>As</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>34</td>
<td>Ba</td>
<td>10</td>
<td>As</td>
<td>6</td>
<td>4</td>
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<td>35</td>
<td>Sh</td>
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<td>As</td>
<td>6</td>
<td>4</td>
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<td>36</td>
<td>Ac</td>
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<td>38</td>
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<td>As</td>
<td>6</td>
<td>8</td>
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<tr>
<td>39</td>
<td>Sh</td>
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<td>8</td>
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<tr>
<td>40</td>
<td>Ac</td>
<td>10</td>
<td>As</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>

3.3.5.3 Loading Capacity Tests

Based on the scoping tests, loading capacity tests were conducted to obtain loading capacity and adsorption isotherm data for arsenic and molybdenum ions onto Ba.

Adsorption tests 41 to 48 were conducted according to section 3.3.5.1 with conditions outlined in the Table 3-12.

Table 3-12: Arsenic and molybdenum removal loading capacity test conditions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Name</th>
<th>Concentration g/100mL</th>
<th>Ion</th>
<th>Concentration mg/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>Ba</td>
<td>0.01</td>
<td>Mo</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>42</td>
<td>Ba</td>
<td>0.5</td>
<td>Mo</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>43</td>
<td>Ba</td>
<td>1</td>
<td>Mo</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>44</td>
<td>Ba</td>
<td>2</td>
<td>Mo</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>45</td>
<td>Ba</td>
<td>0.01</td>
<td>As</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>46</td>
<td>Ba</td>
<td>0.5</td>
<td>As</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>47</td>
<td>Ba</td>
<td>1</td>
<td>As</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>48</td>
<td>Ba</td>
<td>2</td>
<td>As</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>
3.3.6 Results and Discussions

Results of the scoping test are shown in Figure 3-13 and Figure 3-14. As results indicate, \(Ba\) had a higher adsorption capacity than the other materials at acidic pH including \(Ac\).

![Figure 3-13 Molybdenum concentrations in treated solution at pH 4 and 8](image)

Figure 3-13 Molybdenum concentrations in treated solution at pH 4 and 8
Figure 3-14 Arsenic concentration in treated effluent at pH 4 and 8

Table 3-13 compares the highest adsorption obtained by Ba in comparison with Ac.

Table 3-13: Highest adsorption capabilities in comparison with Ac

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Adsorbent</th>
<th>Adsorbate Ion</th>
<th>Initial Concentration (mg/L)</th>
<th>Final Concentration (µg/L)</th>
<th>Removal (%)</th>
<th>limit*(µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>Ba</td>
<td>Mo</td>
<td>3</td>
<td>0.8</td>
<td>99.97</td>
<td>73</td>
</tr>
<tr>
<td>20</td>
<td>Ac</td>
<td>Mo</td>
<td>3</td>
<td>41.7</td>
<td>98.67</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Ba</td>
<td>As</td>
<td>6</td>
<td>3.9</td>
<td>99.94</td>
<td>5</td>
</tr>
<tr>
<td>30</td>
<td>Ac</td>
<td>As</td>
<td>6</td>
<td>1784.7</td>
<td>72.25</td>
<td></td>
</tr>
</tbody>
</table>

*Source: Canadian water quality guideline for discharge

As results indicate, more than 99.9% of the molybdenum and arsenic ions were removed and the treated solutions met the requirement of the Canadian water quality guideline for discharge. Among other adsorbents, Ac also reduced the amount of molybdenum in
solution to 42 μg/L which meets the requirement for discharge. However, Acr was incapable of removing arsenic to acceptable levels.

Adsorption of the anions onto the surface of Ba can be chemical, physical, or combination of both. Mineralogy of Ba, shown in Table 2-2, indicates that Ba contains 10.5% hematite (Fe₂O₃). In the adsorption process, it is expected that As and Mo anions chemically adsorb onto Fe surfaces, which is the basis for iron coprecipitation and would explain these results (Lawrence et al, 1999). Comparing the results of cationic and anionic metal ions removal, Ba shows the least affinity for cation adsorption and the highest for anion removal. If adsorption is physical, it can be speculated that Ba has a positive surface area and the anions attract to the surface of the adsorbent by electrostatic forces.

The high affinity of Ba for arsenic and molybdenum removal at low pH, suggests that there may be an advantage on removing these anions from ARD to HDS treatment (Scenario 1). In this process, adsorption is followed by HDS treatment for neutralization of effluent pH and precipitation of other metal ions.

Tests 41 to 48 were conducted to obtain adsorption equilibrium data for molybdenum and arsenic; however, due to the low concentrations of metal ions in solution, laboratory results (shown in Appendix B) were not valid for data modeling.
3.3.7 Conclusions and Recommendations

Based on the results and the discussions, the following conclusions are suggested:

- *Ba* is a natural adsorbent material that is highly capable of removing molybdenum and arsenic ions in solutions. Treated water meets the regulations as outlined in the Canadian water quality guideline for discharge.

- The capability of *Ba* to remove molybdenum and arsenic in low concentrations exceeds that of *Ac*.

- *Ba* can be used in a pretreatment adsorption process for removal of As and Mo from a acid rock drainage effluent.

- Considering the fact that the performance of natural *Ba* is higher and its production cost is cheaper than *Ac*, *Ba* can replace *Ac* in the adsorption processes for removal of these anions.

- It is expected that As and Mo anions chemically adsorb onto the surface of the hematite mineral of *Ba* at low pH.

- Assuming the adsorption of anions occurs physically, *Ba* has a positive surface charge at low pH.

The following future work is recommended based on the results and conclusions of the presented study:
• Further testing is required to determine the kinetics of the adsorption process.

• Further testing is required to determine the adsorption capacity of Ba in treating various concentrations of anions in solution.
3.4 Boron Treatment

3.4.1 Introduction

In this part of the study the industrial materials were evaluated for the removal of boron contaminated oil refinery effluent. The oil refinery effluent contained antifreeze in which borax (260 ppm B) is present to inhibit corrosion. Canadian water quality guideline for protection of aquatic life has limited the discharged boron concentration of up to 5 ppm; therefore 98% boron removal was targeted.

Treatment tests were conducted to characterize the adsorption capacity of the industrial materials for boron removal of the oil refinery effluent. Adsorption processes was enhanced by chemical activations and were characterized by precipitation and flotation tests.

The objectives of treating boron contaminated effluent were:

- To investigate treatment of boron contaminated effluent employing industrial minerals as sorbents.
- To evaluate methods to activate sorbents in order to enhance their anion sorption characteristics.
- To characterize the interaction of cationic surfactant and the anionic boron in the effluent.
3.4.2 Boron Chemistry

The source of boron contamination in oil refinery effluent is antifreeze. Boron is present in antifreeze in form of borax to inhibit corrosion. The borax forms on surfaces containing iron to protect the metal from corrosion. Borax is a highly soluble mineral and dissolves according to the following reaction (Alkan et al, 1991):

$$2\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \leftrightarrow 4\text{Na}^+ + \text{B}_4\text{O}_7^{2-} + \text{HB}_4\text{O}_7^- + \text{OH}^- + 9\text{H}_2\text{O}$$  \[3.10\]

The solubility of borax at 20°C is 0.11 M (41.93 g/L).

3.4.3 Boron Removal Techniques

Several treatment techniques including adsorption and ion flotation were studied and the ways to improve these techniques were investigated.

3.4.3.1 Acid Activated Adsorption

Acid activation has been widely studied as a chemical treatment to increase the surface area and the number of active sites ready for adsorption of industrial minerals like clays and zeolite. The procedure consists of leaching the adsorbents with an inorganic acid to eliminate mineral impurities, disaggregate particles, and dissolve the external layers (Suarez, 1997). By altering the chemical composition and the structure of the mineral, higher surface area and more adsorption sites are created by acid activation.

A number of studies investigated acidic activation of minerals for adsorption. Kerdivarenko et al. (1974) studied activation of bentonite and clay minerals and concluded that the process enlarged the interconnected pores of clays after 1-2 hours.
hydrochloric acid activation. Berak et al. (1982) investigated activation of zeolite using hydrochloric acid which resulted in removing sodium cations from the mineral structure. Another study by Srasra et al (2000) on activation of glauconite mineral by hydrochloric acid showed the porosity and the surface area of the mineral increased with the activation time.

3.4.3.2 Amine Activated Adsorption

Surface activated adsorbents by organic compounds have excellent physical and chemical characteristics for potential treatment of a wide variety of organic and inorganic hazardous wastes. Activated minerals may be economical alternatives to other sorbents for applications in filtration beds or as in-situ permeable barriers to remove ground water contaminants.

Haggerty et al. (1994) investigated sorption of anions onto surface modified zeolite. In this study the zeolite was conditioned with Hexadecyltrimethylammonium (HDTMA) amine. The amine sorbs onto the surface of the zeolite forming a monolayer or “hemimicelle” at the solid-aqueous interface at surfactant concentrations near or below its critical micelle concentration. If the surfactant concentration in solution exceeds the critical micelle concentration, then the hydrophobic tails of the surfactant molecules associate to form a bilayer or “admicelle”. The surface activated zeolite showed strong sorption of inorganic oxyanions (chromate, selenate, and sulfate) from aqueous solution. Three potential sorption mechanisms including sorption due to admicelle formation, chemical reduction of anions to less soluble forms, and/or surface precipitation of oxyanions with HDTMA were discussed. It was concluded that the adsorption
mechanism was most likely surface precipitation of an HDTMA-anion complex. Based on the results of their studies, a zeolite sample was included in this test program.

3.4.3.3 Ion Flotation

In an ion flotation process, the colloidal precipitates are removed from the solution by flotation process (Yalamanchili et al, 1993).

DAH is a cationic amine that ionizes when dissolved in water according to the following equations (Smith and Martel, 1975):

$$RNH_3Cl_{(s)} \leftrightarrow RNH_3^{+}_{(aq)} + Cl^- \quad [3.11]$$

Amine cation reacts with anionic boron species in solution to form amine borate and hydro borate according to the following equations (Gerrard et al, 1961):

$$2RNH^+ + B_4O_7^{2-} \leftrightarrow (RNH_3)_2B_4O_7(s) \quad [3.12]$$

or

$$RNH^+ + HB_4O_7^- \leftrightarrow RNH_3HB_4O_7(s) \quad [3.13]$$

The colloidal precipitates are generally hydrophobic and therefore can be collected in a flotation process.
3.4.4 Procedures

Boron contaminated effluent was subjected to a series of treatment processes. In the first attempt, effluent was treated by different adsorbents to identify the highest capacity adsorbents. These adsorbents were activated chemically in order to enhance their adsorption capabilities. Precipitation and ion flotation tests were carried out to characterize the interaction of boron compound and the surfactant. In the last test, solvent extraction test was carried out to treat the effluent.

3.4.4.1 Adsorption Test

In adsorption tests, the effluent was filtered prior to testing using a 0.45 μm Millipore filter. A 150 ml sample of filtered effluent was treated in a 250 ml Erlenmeyer with 30g of adsorbent at room temperature for 24 hours. At the end of 24 hours, the solution was vacuum filtered with a 0.45 μm millipore filter and a sample of the treated solution was sent for ICP analysis.

Table 3-14 summarizes the test procedures for this part of the study.

Table 3-14: Summary of test processes for boron removal

<table>
<thead>
<tr>
<th>Test</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 4</td>
<td>Natural sorption capability</td>
</tr>
<tr>
<td>5 - 6</td>
<td>Acid activation</td>
</tr>
<tr>
<td>7 - 8</td>
<td>Amine activation</td>
</tr>
<tr>
<td>9 - 10</td>
<td>Amine precipitation</td>
</tr>
<tr>
<td>11</td>
<td>Ion flotation</td>
</tr>
<tr>
<td>12</td>
<td>Solvent extraction</td>
</tr>
</tbody>
</table>
For tests 1 to 4, natural sorption capability of \textit{Sh}, \textit{Ba}, \textit{Sc}, and zeolite samples was tested according to section 3.4.4.1.

For test 5 and 6, 100 g sample of \textit{Sh} and Zeolite was leached at pH 3 for 24 hours. The acid treated sample was washed and dried at 40°C temperature to a constant weight. A sub-sample of the treated sorbents was used in the sorption test described in section 3.4.4.1.

For tests 7 and 8, activation of \textit{Sh} was conducted by DAH (Dodecylamine hydrochloride). A 100g \textit{Sh} sample and a 100g zeolite sample was conditioned with 25 g/L DAH solution in a shaking flask for 24 hours. A sub-sample of activated sorbents was used in the sorption test described in section 3.4.4.1.

For tests 9 and 10, precipitations tests with amine were conducted in two different amine concentrations of above and below the amine critical micelle concentration, respectively.

For test 9, a 150 ml sample of effluent was in contact with 3.75 g amine (DAH) in a shaking flask for 24 hours. The solution was filtered at 0.45 μm and a sub-sample of the filtered solution was sent for ICP analysis.

For test 10, 1 ml of 0.1 g/L DAH was added to the 100 ml boron effluent. The solution was mixed for 24 hours in a shaking flask and a sub sample of filtered solution was sent for ICP analysis.
An Ion flotation test (test 11) was conducted on a 150 ml sample of effluent. DAH in 0.1 g/L concentration was added as the collector to the flotation process. After two hours processing, a sample of treated effluent was sent for ICP analysis.

For test 12, the effluent was treated in a solvent extraction (SX) test where chloroform was used as the organic solvent (the heavy phase) and the effluent as the light phase. A 100 ml of effluent was mixed with 100 ml chloroform and was shaken for 2 minutes. A sample of the aqueous solution was sent for ICP analysis.
3.4.5 Results and Discussions

3.4.5.1 Natural Sorption Capability

Results of the natural sorption capability of sorbents, tests 1 to 4, are shown in Table 3-15. \( Sh \) had the highest sorption capability for boron removal followed by natural zeolite, removing 25 and 20 % boron from the effluent, respectively. Based on these results, these two sorbents were selected to conduct further activation tests.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Initial B concentration (ppb)</th>
<th>Final B concentration (ppb)</th>
<th>B removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>260000</td>
<td>216562</td>
<td>17</td>
</tr>
<tr>
<td>Ba</td>
<td>260000</td>
<td>242450</td>
<td>7</td>
</tr>
<tr>
<td>Sh</td>
<td>260000</td>
<td>195418</td>
<td>25</td>
</tr>
<tr>
<td>Ze</td>
<td>260000</td>
<td>206770</td>
<td>20</td>
</tr>
</tbody>
</table>

3.4.5.2 Acid Activation

Results of chemical activation of \( Sh \) and zeolite, tests 5 and 6, are shown in Table 3-16. The acid activation process increased the adsorption capability of both minerals. The adsorption capability increase is more significant for zeolite as the boron removal increased from 21 to 27%. The increase in adsorption of activated zeolite can be related to dissolving the impurities or changing the mineral structure leading to higher surface area and more sorption active sites.
Table 3-16 Sorption of boron on acid activated minerals

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Initial B concentration (ppb)</th>
<th>Final B concentration (ppb)</th>
<th>B removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sh</td>
<td>260000</td>
<td>195418</td>
<td>25</td>
</tr>
<tr>
<td>Acid activated Sh</td>
<td>260000</td>
<td>193000</td>
<td>26</td>
</tr>
<tr>
<td>Ze</td>
<td>260000</td>
<td>206770</td>
<td>20</td>
</tr>
<tr>
<td>Acid activated Ze</td>
<td>260000</td>
<td>190261</td>
<td>27</td>
</tr>
</tbody>
</table>

3.4.5.3 Amine Activation

Zeolite and Sh were surface activated using DAH. Amine concentration used was higher than critical micelle concentration to form admicelles on the surface of the sorbents. Results of the sorption tests (tests 7 and 8) are shown in Table 3-17. The amine treatment had different impact on adsorption. Sorption of boron onto the activated Sh marginally increases as cationic amine present on the surface of the mineral enhances removal of boron compound. The amine activation of zeolite, however, had a slightly negative impact on overall boron removal.

Table 3-17 Sorption of boron on amine activated sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Initial B concentration (ppb)</th>
<th>Final B concentration (ppb)</th>
<th>B removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ze</td>
<td>260000</td>
<td>206770</td>
<td>21</td>
</tr>
<tr>
<td>Amine activated Ze</td>
<td>260000</td>
<td>222443</td>
<td>15</td>
</tr>
<tr>
<td>Sh</td>
<td>260000</td>
<td>195418</td>
<td>26</td>
</tr>
<tr>
<td>Amine activated Sh</td>
<td>260000</td>
<td>183982</td>
<td>30</td>
</tr>
</tbody>
</table>
3.4.5.4 Amine Precipitation and Ion Flotation

Since sorption mechanism of oxianions onto amine activated sorbents is most likely precipitation (Haggerty et al, 1994), tests were conducted aimed at the precipitation of boron compound from the solution. DAH in two concentrations, one below critical micelle concentration and the other above that, were used to precipitate boron compound from the effluent. Results of the precipitation of boron with amine followed by filtration are shown in Table 3-17. The results indicate that only minor boron removal could be obtained by amine precipitation in both concentrations. Therefore, the most likely boron species in the solution are not in simple anionic form that can chemically react with the cationic amine to precipitate. This would explain the poor result of amine surface activation of zeolite and Sh as described in 3.4.5.3.

Reaction of cationic amine with anionic boron compounds should result in complete precipitation. The colloidal precipitates ranging from 0.001 to 0.1 micron in size can not be completely removed during filtration through a 0.45 micron filter. Knowing, the cation used for precipitation is a hydrophobic agent, ion flotation could enhance the process of precipitation removal from the treated solution. Result of ion flotation process, shown in Table 3-19, confirm that the boron precipitate removal can be enhanced using flotation process.
Table 3-18 Boron precipitation with amine followed by filtration (tests 9 and 10)

<table>
<thead>
<tr>
<th>Amine concentration</th>
<th>Initial B concentration (ppb)</th>
<th>Final B concentration (ppb)</th>
<th>B removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Above critical micelle concentration</td>
<td>260000</td>
<td>232393</td>
<td>11</td>
</tr>
<tr>
<td>Below critical micelle concentration</td>
<td>260000</td>
<td>256397</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 3-19 Boron removal using ion flotation (test 11)

<table>
<thead>
<tr>
<th>Treatment technique</th>
<th>Initial B concentration (ppb)</th>
<th>Final B concentration (ppb)</th>
<th>B removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion flotation</td>
<td>260000</td>
<td>196000</td>
<td>25</td>
</tr>
</tbody>
</table>

3.4.5.5 Solvent Extraction

Another common technique in removing a compound, solvent extraction, from a complex solution was employed on boron contaminated effluent. Result of the test is shown in Table 3-20. As results indicate the SX technique was not viable in removing the boron from the solution.

Table 3-20 Result of SX test for boron removal (test 12)

<table>
<thead>
<tr>
<th>Treatment technique</th>
<th>Initial B concentration (ppb)</th>
<th>Final B concentration (ppb)</th>
<th>B removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent Extraction</td>
<td>260000</td>
<td>255200</td>
<td>2</td>
</tr>
</tbody>
</table>
3.4.6 Conclusions and Recommendations

The following conclusions are drawn from the results of the studies for boron ion removal and literature review:

- Acid activation of Sh and zeolite sorbents enhanced the boron removal process.
- Surface activation of Sh marginally enhanced removal of boron in solution but had a slightly negative impact on zeolite overall treatment process.
- Sh had higher natural adsorption capacity than the zeolite in removing boron.
- Altering the chemical composition and the structure of the mineral, more adsorption sites were obtained by acid activation.
- Amine activation enhanced the adsorption capacity of Sh to achieve 30% boron removal, the highest among the treatment tests that were conducted.
- Boron in effluent can be precipitated to maximum 25%, using cationic DAH.
- The highest boron removal was in the range of 25-27% in different treatment processes and the target of 98% boron removal was not achieved. This could be due to the metal anion complex formation and the nature and the charges of the complex species present.
Based on the above conclusions, it is evident that boron is not purely present as borax in the effluent. Therefore, it is essential to further investigate the composition of boron in the solution for further investigation of the treatment methods.
Chapter 4 Supplementary Cementing Materials

4.1 Introduction

In recent years, there has been increased international concern about the long term effects of greenhouse gas emissions on global climate. The most important of these gases is CO$_2$ because of the high quantity of its emissions. Hydraulic cement, the binding agent in concretes, is made by high-temperature combustion of raw materials in a rotary kiln at a rate of 1.6 gigaton per year in the world. It produces 3 to 6 million Btu of energy worldwide every year and 1 ton CO$_2$ per ton of cement. This makes the cement industry one of the top two industrial sources of this greenhouse gas (Oss et al., 2003). It should be taken into consideration that the processing of supplementary cementing materials (SCMs) along with their transportation, contributes only marginally to the production of CO$_2$. For instance, transportation of 1 ton of SCM for 1000 km produces 0.022 tonnes of CO$_2$ (Bouzoubaa et al., 2002).

The use of pozzolanic materials is encouraged in the construction industry where there are available natural pozzolan sources. The importance of using natural pozzolans in the cement industry requires evaluation of their effects on concrete. The use of natural pozzolans as SCMs can increases durability of concrete (Malhotra et al., 1996). Natural pozzolans can enhance other concrete properties such as impermeability, chemical durability, resistance to thermal cracking, and increase in ultimate strength (Ramachandran 1995).
The size and growth of the cement industry makes the reduction of its environmental impacts very important. British Columbia has a significant amount of natural pozzolans that can be characterized as supplementary cementing materials (SCMs) for sustainable development of cement industry. A comprehensive study on British Columbia natural pozzolans in comparison with fly ash brings novel applications to industrial minerals production and sustainable development for cement manufacture (Bouzoubaa et al. 2003).

The objective of this part of the study was to investigate the performance of three natural materials for use as natural pozzolans. Commercially available pozzolanic fly-ash, which is widely used as a SCM, was tested as a basis for comparison. Tests were performed according to ASTM C618 “Standard specifications for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete”.

4.1.1 Benefits of SCMs

SCMs are primarily used for the environmental, economical, and technical benefits to reduce CO₂ emissions, lower the cost of concrete, and enhance workability and durability of the hardened concrete (ecosmart.ca).

When used with Portland cement, SCMs enhance the properties of the hardened concrete through hydraulic or pozzolanic activity, or both. These mineral admixtures are added for a variety of purposes primarily to replace cement, enhance workability of fresh concrete, and increase durability of hardened concrete. Economical factor is also important as
SCMs are generally cheaper than cement (ecosmart.ca). However, the slow strength development of concrete containing SCMs under cold weather conditions is a technical barrier especially in Canada.

The pozzolanic activity occurs at normal temperature with calcium hydroxide formed from hydration of the calcium silicates of cement to produce calcium-silicate hydroxide with cementations properties. Natural pozzolans and fly ash contribute to the strength of the hardened concrete more by pozzolanic reactions, whereas the blast furnace slag contributes more by hydraulic reactions.

The mining industry is a large consumer of Portland cement and SCMs. The main application is mining backfill. In Quebec and Ontario about 200000 tonnes of SCMs are consumed every year in mining applications (Bouzoubaa et al., 2003).

4.1.2 Types of SCMs

There are two ways to use SCMs. Firstly, as a replacement for some of the Portland cement, and secondly, as an addition to concrete. The first method is mainly used to improve durability or reduce heat of hydration, whereas the second method is generally used to improve workability. For this study, tests were conducted to assess materials as a replacement for Portland cement.

SCMs used as cement replacements can be categorized as either natural or artificial. Natural pozzolans are naturally occurring minerals with high surface area and pozzolanic
reactivity. Fly ash, a residue left from burning coal, is an artificial pozzolan which is collected by electro-static separators or bag filters as it flies out with the flue gas stream.

Fly ash and natural pozzolans are two SCMs which are underused in Canada and therefore represent a potential for increased use. For instance, in 2001, only about 11% of the produced fly ash was used in cement and concrete applications (Bouzoubaa et al., 2003).

Unlike natural pozzolans, fly ash is a by-product of coal fired power plants which have already contributed a large amount of CO₂ emission during the burning process of coal. Its quality is very important and varies significantly, depending on the mineralogical contents of the coal used. Poor quality fly ash can have negative effects on concrete, such as increasing the concrete permeability. Also, incomplete combustion of coal leaves carbon in the ash, which absorbs the air entraining agents used in concrete, resulting in low freeze-thaw durability and making the concrete susceptible to frost damage (Bilodeau 2003, Malhotra 2002)

4.1.3 Chemistry of Portland Cement Hydration

An adequate understanding of chemical and physical processes that take place between cement and water is necessary for the full appreciation of cement, SCMs, and concrete properties. Cement is a system composed of different minerals that react with water at different rates, giving hydration products of different compositions and properties.
Calcium silicates in cement hydrate according to the following equations:

\[ 2\text{C}_3\text{S} \text{ (tricalcium silicate)} + 11\text{H} \text{ (water)} \rightarrow \text{C}_3\text{S}_2\text{H}_8 \text{ (C-S-H) (calcium silicate hydrate)} + 3\text{CH} \text{ (calcium hydroxide)} \] [4.1]

\[ 2\text{C}_2\text{S} \text{ (dicalcium silicate)} + 9\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_8 \text{ (C-S-H)} + \text{CH} \] [4.2]

The principle product is calcium silicate hydrate (C-S-H), which is not a well-defined compound. The formula is an approximate description, as the stoichiometry is variable. Calcium hydroxide (CH) is a well crystallized material with a fixed composition.

Both reactions are stoichiometrically similar and the difference is in the amount of calcium hydroxide formed. C\text{\textsubscript{2}}S is less reactive and therefore it hydrates at a slower rate than C\text{\textsubscript{3}}S. Also, the amount of heat liberation is lower for hydration of C\text{\textsubscript{2}}S.

Both reactions are exothermic and increase the temperature of the concrete. During normal constructions, this heat is dissipated to air and soil, therefore, no significant temperature changes are observed. However, in mass concrete projects, such as dams, the generated heat can not be readily released, resulting in high internal temperature. The temperature increase may cause expansion while concrete is hardening, leading to very high stress that might result in cracking.
4.1.3.1 Pozzolanic Reactions

The amorphous silica or reactive alumina of SCMs reacts with calcium hydroxide formed from the hydration of cement to produce calcium silicate hydrate. The principle reaction is as follows (Mindess et al., 2003):

\[
\text{CH} + \text{S (silicate)} + \text{H} \rightarrow \text{C-S-H} \quad [4.3]
\]

The composition of C-S-H is similar to that in the hydrated cement hydration. The reactive alumina in natural pozzolans or calcined clay partially replaces silica in the C-S-H compound, leading to secondary reactions. In these reactions, calcium aluminate hydrates C-A-H form as follows:

\[
\text{CH} + \text{A (aluminate)} + \text{H} \rightarrow \text{C-A-H (calcium aluminate hydrate)} \quad [4.4]
\]

The composition of C-A-H varies and depends on the pozzolan used.

A good pozzolan is required to have a significant quantity of reactive glassy or amorphous material, but for some natural pozzolans (e.g. volcanic tuffs) the crystalline phase can act as a pozzolan. Calcium hydroxide formed from the hydration of cement ionizes and the solution reaches high pH. Under the OH⁻ attack, the crystalline structure is decomposed and depolymerized species are liberated for reaction (Mindess et al., 2003).

Mineralogical studies on tested materials (Figure 4-1) show that Sc has an amorphous phase and therefore is expected that the pozzolanic reaction will occur quite fast.
The amount of SCMs to be used in concrete is limited by the amount of calcium hydroxide made available by the hydration of the cement.

The heat of reaction is about -12kJ/mole of CH for equation [4.3] and -43kJ/mole of C$_2$S for equation [4.2] (Mindess et al., 2003). Therefore addition of SCMs lowers the amount of early heat hydration and reduces early strength. However, it does not affect the long-term strength.

The pozzolanic reaction causes an overall increase in solid volume, thus reducing the porosity of the pastes, which leads to higher strength and durability. This makes SCMs ideal for mass concrete applications, where early high strength is not required and a low heat of hydration is favorable. The slow rate of pozzolanic reaction requires adequate moist curing to maintain the reaction, otherwise the pozzolan acts as non-cementations filler.

As the pozzolan addition increases the normal silica-alumina ratio to a significantly higher value, the sulfate-resistance characteristics of the hydrated paste have been shown to improve significantly, when tested by ASTM C 1012. The calcined clays also contribute to microstructure changes that result in a very low permeability of the cementitious matrix.
Figure 4-1 Rietveld refinement plot for black scoria (Sc)

The hump at 28° is the indication of the amorphous phase

The production cost of SCMs, except for silica fume, is below the price of Portland cement. The only economical barrier is the transportation cost. Therefore the application of these materials is limited by the distance of production to consumption. In special applications like high performance and high strength concretes, additional cost of using SCMs including silica fume is justified (Bouzoubaa et al., 2003).
Concretes containing SCMs develop very good strength over time, exceeding those of similar concretes without mineral admixtures. The pozzolanic activity of a SCM depends on its chemical and mineralogical properties and determines the extent of low early strength. A water reducing admixture can also be used to offset the reductions in early strengths.

Natural pozzolans as SCMs are used extensively for improving the resistance to sulfate attack. The evaluation requires long term exposure of concrete to sulfate solution. The sulfate resistance test is performed according to ASTM C1012 and takes 52 weeks to complete (Rodrigues-Camacho et al., 2002). Due to the lengthy procedure, this evaluation was not performed on SCM materials in this study.

Pozzolans must be in finely divided form to be effective; therefore, ASTM C618 limits the size distribution of pozzolans. However, a more useful assessment is the surface area, since the pozzolanic reaction kinetics is controlled by the amount of surface available for reaction. Particle morphology is an indicator of the pozzolan behavior, as spherical particles have a positive impact on workability, whereas cellular shape particles have high surface area, however, would demand high water.
4.2 Procedures

There are no clear specifications and national guidelines for the use of SCMs in cement and concrete in Canada (Bouzoubaa et al., 2003). In general, the guidelines and specifications specified by the Canadian Standard Association (CSA), similar to the relevant ASTM standard, are considered. In this study, tests were performed according to ASTM C311 “Standard tests methods for sampling and testing fly ash or natural pozzolans for use as a mineral admixture in Portland cement concrete”. The tests include chemical and physical evaluations.

4.2.1 Materials

The following materials were used in conducting the tests:

- Natural materials Sc, Ba, Sh
- Artificial pozzolanic fly ash Fa
- Portland cement

The tests were conducted using graded standard sand (in compliance with ASTM C778).

4.2.2 Chemical Characterizations

The following chemical tests were conducted on Sc, Ba, and Sh for evaluation as a natural pozzolan:

- Major oxides
- Loss on ignition
- Moisture content
Samples were ground to finer than 45 μm and sent for whole rock analysis including the major oxide and loss on ignition tests. Moisture content of the samples was determined by drying about 2 kg samples (w₁) in an oven, giving enough time to reach the constant weight (w₂). The moisture content was calculated as follow:

\[
\text{Moisture content} = \frac{(w₁ - w₂)}{w₁} \times 100
\]

### 4.2.3 Physical Characterizations

Test specimens were made according to ASTM C618 and were tested for uniaxial compressive strength. Sc, Ba, and Sh materials were ground to two sizes of 70% passing 45 μm and 85% passing 45 μm. Portland cement and pozzolanic fly-ash (Fa) were used as received. A total of 96 test specimens were prepared and tested according to the procedure illustrated in Diagram 4-2.

Mortars with flow of 105 mm and higher were moulded, stored and tested for compressive strength to obtain the strength activity index value.
4.2.4 Preparing Mortar for Flowability Test

Flow test determines the ability of the mortar to flow under continuous vibration. According to ASTM, a thin layer of releasing agent was applied on the contacting surface of the 2 inch cube metallic moulds. The mortar mixes containing cement, SCMs, sand, and water were prepared according to Table 4-1. Water was added first to the mixing bowl followed by cement and SCMs and stirred for 30 seconds. The graded sand was
then added in 30 seconds while mixing. The mixer speed was increased to medium and the blend was mixed for 30 seconds. The mixer was stopped for 1\text{\textfrac{1}{2}} minute. In the first 15 seconds the mortar was scrapped down from the side of the bowl and the bowl top was covered for the remaining time of 75 seconds. Mortar preparation for flow table test was completed by mixing at medium speed for 1 minute.

Table 4-1 Quantities of materials for making nine test specimens

<table>
<thead>
<tr>
<th>SCM ratio</th>
<th>0</th>
<th>20%</th>
<th>30%</th>
<th>40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement q</td>
<td>740</td>
<td>592</td>
<td>518</td>
<td>444</td>
</tr>
<tr>
<td>Sand q</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
</tr>
<tr>
<td>Water mL</td>
<td>340</td>
<td>340</td>
<td>340</td>
<td>340</td>
</tr>
<tr>
<td>SCM g</td>
<td>0</td>
<td>148</td>
<td>222</td>
<td>296</td>
</tr>
</tbody>
</table>

4.2.5 Determination of Flow

The flow cone was placed at the center of the flow-table. A layer of mortar about one inch was placed in the mould and was tamped 20 times with the tamper to uniform filling of the mould. The mould was filled with the mortar and tamped for 20 times as described for the first layer. The mould surface was cut off using a trowel with a sawing motion across the top of the mould. The table top was cleaned and dried prior to lifting the mould away. The flow table was immediately dropped through a height of $\frac{1}{2}$ inch 25 times in about 15 seconds. The flow was determined by averaging the measured diameter of the mortar mass at four equispaced intervals.
4.2.6 Moulding Test Specimens

The mortar from the flow table test was brought back to the mixing bowl immediately. The materials that were collected from the side of the bowl were scraped down and the entire batch was remixed for 15 s. The mortar that remained on the paddle was shaken into the mixing bowl. The total time passed from completion of the original mixing was less than $2\frac{1}{2}$ min. Moulding the specimen started by placing a layer of 1 inch of mortar in all of the cubical partitions. As shown in Figure 4-3, the mortar was tamped 32 times in 4 rounds in about 10s to ensure uniform filling of the moulds. In each round the mortar was tamped 8 times with the order shown in Figure 4-3. The mould was filled with the mortar and tamped as described for the first layer. The spilled mortar was brought back into the moulds and the surface was leveled using a trowel with a sawing motion.

![Order of Tamping in Moulding Test Specimens](image)

Round 1 and 3
Round 2 and 4

Figure 4-3 Order of Tamping in Moulding Test Specimens

4.2.7 Specimens Storage

Immediately after completion of moulding, the face surface of the specimens was covered with plastic and the moulds were stored on top of each other to ensure that the
mortar moisture is maintained. After 24 h, the specimens were removed from the moulds and immediately immersed in storage tubs containing saturated lime water.

### 4.2.8 Determination of Strength Activity Index

The specimens were removed from the storage tubs for testing after 1, 4, and 8 weeks. Their surfaces were dried with a cloth, and tested immediately using a hydraulic uniaxial testing machine. Loading was applied to the specimen without interruption. The total maximum load indicated by machine was recorded and the compressive strength was calculated based on the average of three specimens in Pascal. Specimens with over 10% variance from average were considered faulty and discarded. The strength activity index was calculated as an average of compressive strength percentage of the SCM test specimens to the control mix.
4.3 Results and Discussions

4.3.1 Chemical Properties

Chemical characteristics required by ASTM were calculated from the whole rock analysis, shown in Table 2-1, and are presented in Table 4-2. Materials were tested as received for moisture content and the SO$_3$ content of the samples was calculated from the total sulfur of the samples. Assuming all sulfurs are present in form of sulfur trioxide, the amount of sulfur trioxide was calculated as:

\[ \% SO_3 = \% S \times (M_{SO_3}/M_S) \]

This shows the maximum sulfur trioxide is less than 1% in all samples. As Table 4-2 shows all materials meet the chemical requirements indicated by ASTM, however, Sc and Sh need to be dried prior to use. Chemical content (SiO$_2$ + Fe$_2$O$_3$ + Al$_2$O$_3$) is important by the fact that the active glassy phases of pozzolans are generally richer in silica and alumina content.

Table 4-2: Chemical requirements for natural pozzolan by ASTM and values for studied SCMs

<table>
<thead>
<tr>
<th></th>
<th>Required</th>
<th>Sh</th>
<th>Sc</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ %</td>
<td>70.0</td>
<td>75.5</td>
<td>72.4</td>
<td>70.8</td>
</tr>
<tr>
<td>Max Loss on ignition %</td>
<td>10.0</td>
<td>8.6</td>
<td>&lt;1</td>
<td>1.3</td>
</tr>
<tr>
<td>Max SO$_3$ %</td>
<td>4.0</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Max moisture content %</td>
<td>3.0</td>
<td>23.2</td>
<td>5.0</td>
<td>2.8</td>
</tr>
</tbody>
</table>
4.3.2 Physical Properties

4.3.2.1 Fineness and Specific Surface Area

SCMs were ground below 45 μm to meet the physical requirements according to the ASTM standard. Natural pozzolans were tested in two sizes of 70% passing 45 μm (coarse size) and 85% passing 45 μm (fine size), with 5% error margin. The size analysis was used to show the effect of size distribution on strength activity index. The commercially available fly ash was similar to the coarse size distribution (i.e. around 70% passing 45μm).

The specific surface area of the materials were determined using the BET method. The results are shown in Table 4-3. Surface area of the materials increased with decreasing particle size, as expected. Sh has a much higher surface area than the Ba, Sc, and Fa. Pozzolanic reactivity depends on the surface area, therefore, it is expected that the Sh would have faster pozzolanic reactions, resulting in enhanced early strength development. On the other hand, the cementation process requires more water for casting of finer materials, resulting in lower workability.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size %pass 45μm</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>Fine 85</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>Coarse 70</td>
<td>1.00</td>
</tr>
<tr>
<td>Ba</td>
<td>Fine 85</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>Coarse 70</td>
<td>1.16</td>
</tr>
<tr>
<td>Sh</td>
<td>Fine 85</td>
<td>43.02</td>
</tr>
<tr>
<td></td>
<td>Coarse 70</td>
<td>40.19</td>
</tr>
<tr>
<td>Fa</td>
<td>Coarse 70</td>
<td>0.83</td>
</tr>
</tbody>
</table>
4.3.2.2 Flowability

Flowability of the SCM mortars is shown in Figure 4-4. All mortars meet the minimum flow of 105 mm required by ASTM; therefore, the water content of the mixes remained constant for all the tests.

Where used as partial replacements for Portland cement, the SCMs showed different water demand for moulding. As expected, $S_h$, having the highest specific surface area, had the lowest slump and the most viscous paste. The particles could also be flocculated by the electrostatic force and held water to increase the viscosity. Mortars with higher flow, being less viscous, facilitate filling the moulds; therefore, less tamping pressure was needed to achieve an efficient moulding. The highest flow was achieved by $B_a$ mix. This SCM could be used as a water reducing admixture to enhance concrete properties.
Figure 4-4 Flow of control and 20% SCM mortars. The flow for all mortars exceeded the required 110mm.

Conducting tests at the same w/cm (water to cementitious materials ratio), additional cement replacement with BA and FA from 20% to 40% leads to higher slump for test specimens.

Figure 4-5 Flow of additional cement replacement
4.3.2.3 Strength Activity Index

The average compressive strength of the mortar specimens was calculated from the ultimate force applied to the specimens before breaking. The values are shown in Table 4-4.

<table>
<thead>
<tr>
<th>Curing time (weeks)</th>
<th>1</th>
<th>4</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc f</td>
<td>34.6</td>
<td>43.2</td>
<td>48.0</td>
</tr>
<tr>
<td>Sc c</td>
<td>31.3</td>
<td>40.2</td>
<td>42.1</td>
</tr>
<tr>
<td>Ba f</td>
<td>33.8</td>
<td>41.4</td>
<td>46.6</td>
</tr>
<tr>
<td>Ba c</td>
<td>29.8</td>
<td>35.7</td>
<td>39.2</td>
</tr>
<tr>
<td>Sh f</td>
<td>42.0</td>
<td>53.0</td>
<td>55.3</td>
</tr>
<tr>
<td>Sh c</td>
<td>28.9</td>
<td>34.1</td>
<td>36.2</td>
</tr>
<tr>
<td>Fa</td>
<td>32.7</td>
<td>43.9</td>
<td>46.2</td>
</tr>
<tr>
<td>Control</td>
<td>40.9</td>
<td>44.5</td>
<td>47.0</td>
</tr>
</tbody>
</table>

The average strength activity index was calculated for the test specimens described in section 4.2.8 and is shown in Figure 4-6. The control specimen contains no supplementary cementing materials.

Strength activity index with Portland cement was measured in an accelerated test to evaluate the contribution of the SCM in longer strength development of the concrete. Based on ASTM, specification compliance is met when the 7 day or 28 day strength activity index is at least 75%. As Figure 4-6 demonstrates, at 28 days all materials studied are in compliance with the standard requirement for use as a natural pozzolan.
Figure 4-6 Strength activity index of test specimens based on 28 day control specimen

As the figure shows, starting from 7 days, fine Sh enhances the mortar compressive strength at all ages. Comparing to the control specimen, it increases the strength by about 20% to 120% in 28 days and by about 15% in 56 days from 110% to 125%. Increased compressive strength is related to higher specific surface area of the material, which leads to faster pozzolanic reaction and thus higher compressive strength at all times. At 28 day testing, the compressive strength of the Shc was increased by 56% when ground longer to Shf.
Prolonged grinding of the *Ba* and *Sc* materials has the same effect as *Sh*, resulting in higher compressive strength at all ages.

At 7 days of curing time, except for the *Shf* specimen, the compressive strength of the SCM specimens was less than that of the control specimen. This can be explained by a slow pozzolanic reaction resulting in lower compressive strength compared to the control at early stages. However, the compressive strength develops at a faster rate than the control. The rate depends on the pozzolanic activity of the SCMs. Fly ash and fine SCMs achieved at least 93% of the control in 4 weeks. At 8 weeks, given enough time to develop the pozzolanic reaction, all SCMs reached the compressive strength of at least 98% of the control. Fine *Sh* and *Sc* gained higher compressive strength than the control and *Fa*, at this age.

As expected, participation of amorphous phase of *Sc* resulted in faster pozzolanic reaction and therefore higher compressive strength than *Ba* at all ages.

The results show that grinding of the SCMs to finer sizes increased the compressive strength of the mortars at all ages. The compressive strength of *Sh* mortar increased significantly when ground to 85% passing 45 μm. Considering the size distribution of the natural pozzolans and *Fa*, the *Fa* specimen produced higher compressive strength than that of the coarse natural pozzolans.
Compressive strength development of cement-SCM admixtures is shown in Figure 4-7. The pozzolanic reaction influences the cement hydration and SCM specimens start to strengthen at a faster trend than the control specimen due to the pozzolanic reaction. Therefore, it is expected that the specimens containing fly ash and fine SCMs gain higher strength than the control specimen after 56 days. This shows the pozzolans' advantage of higher compressive strength in long term performance, even with low early compressive strength.

Figure 4-7 Trend of the strength activity index based on 28 day control specimen
Mortars with more than 20% SCMs were prepared to assess the performance of high SCM mortars. Figure 4-8 and Figure 4-9 show the results of the compressive strength tests on mortars containing 20 to 40% \( Ba \) and \( Fa \) at 7 and 28 days. The results indicate that when the percentage replacement of the cement by the \( Ba \) and \( Fa \) was increased from 20 to 40 percent, there was noticeable loss in compressive strength of the mortars at all ages. This can be explained as the cementation is controlled mainly by the pozzolanic reaction and not by hydraulic reaction in natural pozzolans and fly ash. Reducing the amount of portland cement, lowers the production of calcium hydroxide required for the pozzolanic reaction. Therefore, the excess pozzolans act as filler instead of cementations material causing lower overall compressive strength.

Figure 4-8 Relative compressive strength of SCM to control specimens at 7 days
Figure 4.9: Relative compressive strength of SCM to control specimens at 28 days.
4.4 Conclusions

Based on the results and literature review, the following conclusions are drawn:

- *Ba, Sc*, and dried *Sh*, comply with the specification of ASTM C618 for use as a natural pozzolan in portland cement concrete.

- Due to the higher Fe content, the SCMs tested give a reddish color to the concrete.

- Fine *Sh* when replaced cement up to 20% had the highest compressive strength at all ages.

- Prolonged grinding of *Sh* resulted in higher surface area, higher pozzolanic reaction leading to significant increase in the compressive strength, exceeding the compressive strength of *Fa* and control specimen.

- Participation of amorphous phase of *Sc* resulted in faster pozzolanic reaction and therefore higher compressive strength than *Ba* at all ages.

- Cement replacement with natural pozzolan and fly ash from 20 to 40% reduces the compressive strength of the mortars at all ages acting as fillers.

- *Ba* can be potentially used as a water reducing admixture to produce a high strength concrete

- Without water reduction, high slump concretes can be produced by *Ba* as water reducing material.
• Higher than 20% replacement of cement by Sh may require a plasticizer agent to maintain the flowability.

• SCM specimens show slow early strength development compared to the control specimen, due to the slow kinetics of the pozzolanic reaction. SCMs, however, enhance the long term strength.

• After 8 weeks, fine Sh, Sc, and Ba specimens exceed the compressive strength of the fly ash specimen, making these pozzolans suitable for mass concrete projects where early high strength is not required and low heat of hydration is favorable.

• Finer grinding of the Sh, Ba, and Sc materials results in higher surface area, higher pozzolanic reaction, and higher compressive strength at all ages.

• Naturally calcined shale is a highly desirable natural pozzolan, in which the calcination process to enhance the physical properties of the pozzolan occurs naturally, requiring no energy consumption to achieve this treatment.

• Use of natural pozzolans as SCMs is favorable due to the environmental, technical, and economical benefits. However, processing, transportation, slow setting time, and low early strength are among the barriers affecting the use of these materials where the applications are far away from production site and/or fast form work removal is required.

• Natural pozzolans exhibit superior long term performance when compared to regular Portland cement and are suitable for special applications like dams and where environmentally friendly concrete is promoted.
The slow setting time and strength development of natural pozzolans and fly ash studied, except fine Sh, limit the use of these materials in applications where fast form work removal is required.

- SCMs are environmentally friendly, as the energy consumption and the overall CO₂ emissions associated with the production of the SCMs concrete are reduced.
Chapter 5 Conclusions and Recommendations

Based on the literature review and conducted tests in this study the main conclusions are:

- *Sh* was an efficient adsorbent removing more than 99% of the copper and zinc from the effluent. The dissolved copper concentration meets the regulatory limits of the Canadian Fisheries Act. The loading capacities for the *Sh* for the removal of these ions are 2.21 and 1.91 mg/g, respectively. It can be speculated that the adsorption of copper and zinc onto *Sh* in low pH occurs chemically on the organic content of this material.

- The HDS treatment process when supplemented by the adsorption process, presents a reliable treatment process in removing metal ions in mine water to the regulatory limits. In particular, post treatment should serve to reduce fluctuations in the effluent discharge level.

- *Ba* is highly capable of removing more than 99.9% of molybdenum and arsenic ions in solutions. Treated water meets the regulations as outlined in the Canadian water quality guideline for discharge.

- *Ba* can be used in a pretreatment adsorption process for removal of As and Mo from a acid rock drainage effluent.

- Considering the fact that the performance of natural *Ba* is higher and its production cost is cheaper than *Ac*, *Ba* can replace *Ac* in adsorption processes to remove As and Mo anions.
• Altering the chemical composition and the structure of the mineral, more adsorption sites were obtained by acid activation.

• The highest boron removal was in the range of 25-27% in different treatment processes and the target of 98% boron removal was not achieved. This could be due to the metal anion-complex formation and the nature and the charges of the complex species present. Therefore, it is essential to further investigate the composition of boron in the solution for further investigation of the treatment methods.

• $Ba$, $Sc$, and dried $Sh$, comply with the specification of ASTM C618 for use as a natural pozzolan in Portland cement concrete, producing colorful concretes.

• Fine $Sh$ when replaced cement up to 20% had the highest compressive strength at all ages. Naturally calcined shale is a highly desirable natural pozzolan in which the calcination process to enhance the physical properties of the pozzolan occurs naturally requiring no energy consumption to achieve this treatment.

• After 8 weeks, fine $Sh$, $Sc$, and $Ba$ specimens exceed the compressive strength of the fly ash specimen, making these pozzolans suitable for mass concrete applications where early high strength is not required and low heat of hydration is favorable.

• Use of natural pozzolans as SCMs is favorable due to the environmental, technical, and economical benefits. However, processing, transportation, slow setting time, and low early strength are among the barriers affecting the use of
these materials where the applications are far away from production site and/or fast form work removal is required.
Based on the results and conclusions of the presented study the following future work is recommended:

- Further testing is required to determine the kinetics of adsorption tests.

- Further testing is required to evaluate the supplemented treatment process for Britannia mine in a continuous process.

- Further testing is recommended to assess the possibility of regenerating the adsorbent bed.

- Further testing is recommended to evaluate the performance of the metal loaded adsorbents as pozzolans for long term storage. Leaching tests need to be conducted according to British Columbia Special Waste Extraction Procedure (BC SWEP) in order to assess the leachability of adsorbed metal ions.
Chapter 6 References

Al-Asheh, S.; Banat, F. “Adsorption of copper and zinc by oil shale” Department of Chemical Engineering, Jordan University of Science and Technology, Irbid, Jordan. Environmental Geology (Berlin, Germany), 40(6), 693-697. 2001.


Natural Resources Canada. nrcan.gc.ca


Figure A-6-1 Map of Quesnel, BC, Canada

Source: Data management section, Ministry of Environment, Lands, and Parks
Table A1-6-1 Results of whole rock analysis

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>MgO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>TiO2</th>
<th>P2O5</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLES</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>CS</td>
<td>48.78</td>
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<td>0.68</td>
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<tr>
<td>BS</td>
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<td>8.26</td>
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<td>3.93</td>
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Table A1-6-2 Results of quantitative phase analysis (wt. %)

<table>
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<tr>
<th>ELEMENT</th>
<th>Ba</th>
<th>Ni</th>
<th>Sr</th>
<th>Zr</th>
<th>Y</th>
<th>Nb</th>
<th>Sc</th>
<th>LOI</th>
<th>TOT/C</th>
<th>TOT/S</th>
<th>SUM</th>
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<tbody>
<tr>
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<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
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<td>ppm</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>CS</td>
<td>1535</td>
<td>45</td>
<td>275</td>
<td>239</td>
<td>34</td>
<td>&lt;10</td>
<td>20</td>
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<td>0.06</td>
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<td>BS</td>
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<td>864</td>
<td>214</td>
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<td>38</td>
<td>19</td>
<td>&lt;1</td>
<td>0.03</td>
<td>0.07</td>
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<td>RB</td>
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<td>26</td>
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<td>18</td>
<td>1.3</td>
<td>0.07</td>
<td>0.09</td>
<td>100.23</td>
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</table>

Table A-6-2 Results of quantitative phase analysis (wt. %)

<table>
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<tr>
<th>Ideal Formula</th>
<th>Sh</th>
<th>Sc</th>
<th>Ba</th>
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</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>25</td>
<td>1.8</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>SiO₂</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>K-feldspar</td>
<td>KAl₃Si₅O₈</td>
<td>18.7</td>
<td></td>
</tr>
<tr>
<td>Plagioclase</td>
<td>NaAl₃Si₂O₈ – CaAl₂Si₂O₈</td>
<td>3.8</td>
<td>2.6</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₂AlSi₅O₁₀(OH)₂</td>
<td>42.2</td>
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<td>Chlorite</td>
<td>(Mg,Fe²⁺)₅Al(Si₃Al)O₁₀(OH)₈</td>
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<td></td>
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<tr>
<td>Tremolite</td>
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Quantitative phase analysis by Rietveld method

The three samples “Calcined Shale”, “Black Scoria” and “Red Basalt” were ground into fine powder to the optimum grain-size range for X-ray analysis (<10μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 5 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-70°2θ with CuKα radiation on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer equipped with a diffracted-beam graphite monochromator crystal, 2 mm (1°) divergence and antiscatter slits, 0.6 mm receiving slit and incident-beam Soller slit. The long fine-focus Cu X-ray tube was operated at 40 kV and 40 mA, using a take-off angle of 6°.

The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF-4 using Search-Match software by Siemens (Bruker). X-ray powder-diffraction data were refined with the Rietveld program Topas 2.1 (Bruker AXS). The results of quantitative phase analysis by Rietveld refinement are given in Table 1. Results of quantitative phase analysis represent the relative amounts of crystalline phases normalized to 100%. Rietveld refinement plots for the samples are shown in Figure A-6-2 to Figure A-6-4.
Figure A-6-2 Rietveld refinement plot for sample “Calcined Shale”

(blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Colored lines are individual diffraction patterns of all phases.
Figure A-6-3 Rietveld refinement plot for sample “Black Scoria”

(blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Colored lines are individual diffraction patterns of all phases. Note the large “amorphous” hump centred at about 28°2θ; this hump is likely from the presence of glass.
Figure A-6-4 Rietveld refinement plot for sample "Red Basalt"

(blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Colored lines are individual diffraction patterns of all phases.
Appendix B: Water Treatment

Langmuir Equation Derivation

In an adsorption test, the sorbate will be sorbed onto the adsorbent until the equilibrium is reached. One factor determining the amount of sorbed materials is the number of adsorption sites available in the adsorbent which can be quantified by the ratio \( \frac{x}{m} \) or \( q_e \). There is a maximum value for this ratio, \( Q_0 \), which is the greatest possible ratio. In the equilibrium process some of the sorbates adsorbed will be desorbed back into the solution. While desorption takes place, some sorbates will be adsorbed again onto the adsorbent.

The rate of adsorption is proportional to the concentration of sorbates in solution, and the amount of adsorption sites left vacant by desorption. The difference of \( q_e \) and \( Q_0 \) is proportional to the number of adsorption sites available for adsorption. Therefore, the rate of adsorption is equal to \( k_s c_e (Q_0 - q_e) \), where \( k_s \) is the proportional constant.

In desorption process, more desorption takes place than sorption. The rate of desorption can be expressed as \( k_d q_e \) where \( k_d \) is the desorption proportionally constant. The process is in equilibrium, therefore the rate of adsorption is equal to the rate of desorption:

\[
k_s c_e (Q_0 - q_e) = k_d q_e \quad [A.1]
\]

Naming constant ratio \( k_s/k_d \), \( b \), the equation solves for \( q_e \):

\[
b c_e (Q_0 - q_e) = q_e \quad [A.2]
\]
or

\[ q_e (1 + bc_e) = Q_0 bc_e \quad [A.3] \]

or

\[ q_e = \frac{(Q_0 bc_e)}{(1 + bc_e)} \quad [A.4] \]

Due to the nature of derivation explained, the equation is valid only for unimolecular layer adsorption.
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Table B-6-4 Results of loading capacity tests

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Figure B-6-5 Copper concentration in treated solution at pH 8
Figure B-6-6 Zinc concentration in treated solution at pH 8

Figure B-6-7 Freundlich equilibrium isotherm of copper adsorbed onto Sh
Figure B-6-8 Freundlich equilibrium isotherm of zinc adsorbed onto Sh
Appendix C: Supplementary Cementing Materials

Table C-6-5: Maximum force applied (in KN) to 20% replaced SCM and control specimens in compressive strength test

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Table C-6-6: Maximum force applied (in KN) to 30% replaced SCM specimens in compressive strength test

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Table C-6-7 Maximum force applied (in KN) to 40% replaced SCM specimens in compressive strength test

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