June 2012

Synergistic and Environmental Benefits of Using Cement Kiln Dust With Slag and Fly Ash in Cemented Paste Tailings

Amajd Tariq
The University of Western Ontario

Supervisor
DR. ERNEST K. YANFUL
The University of Western Ontario

Graduate Program in Civil and Environmental Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

© Amajd Tariq 2012

Follow this and additional works at: https://ir.lib.uwo.ca/etd

Part of the Civil and Environmental Engineering Commons

Recommended Citation
https://ir.lib.uwo.ca/etd/560

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact tadam@uwo.ca, wlswadmin@uwo.ca.
SYNERGISTIC AND ENVIRONMENTAL BENEFITS OF USING CEMENT KILN DUST WITH SLAG AND FLY ASH IN CEMENTED PASTE TAILINGS

(Thesis format: Integrated-Article)

by

Amjad Tariq

Graduate Program in Engineering
Department of Civil and Environmental Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

The School of Graduate and Post Doctoral Studies
The University of Western Ontario
London, Ontario, Canada

© Amjad Tariq 2012
The thesis by

Amjad Tariq

entitled:

Synergistic and Environmental Benefits of Using Cement Kiln Dust with Slag and Fly Ash in Cemented Paste Tailings

is accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Date: ____________________

Chair of the Thesis Examination Board
ABSTRACT

Many researchers have validated the phenomenon of internal sulphate attack in ordinary Portland cement (CSA Type GU) based cemented paste tailings containing sulphide minerals and have observed secondary gypsum as an ubiquitous phase in such matrices. The secondary gypsum, due to its soft nature and swelling and expansive properties, is principally considered to be the sole culprit responsible for subsequent internal cracking and strength degradation of sulphidic paste at later stages. High Portland cement cost and its apparent poor performance in the long-term in sulphate rich environments advocate for the formulation of resilient cemented paste tailings using economical but efficient binders.

This study demonstrates the effectual utilization of selective cement kiln dusts (CKDs) in composite binder systems containing ground granulated blast furnace slag (SL), Type C fly ash (FC) and a small amount of Portland cement. The addition of calcium and alkali rich cement kiln dust in Portland cement-slag and Portland cement-fly ash binder systems functioned as an excellent alkaline activator and accelerator in promoting the hydration mechanisms within cemented paste tailings formulations. High alkaline pore solution created by free calcium rich cement kiln dust (CKD) is capable of disintegrating the solid glassy network of supplementary cementing materials to produce reactive silicate and aluminate compounds. Comparative assessment of a range of binder combinations has been carried out for cemented paste tailings formulations using performance assessment indicators such as unconfined compressive strength, saturated hydraulic conductivity, micro-structure, and contaminant containment capability (leachability).

The short- and long-term performance evaluation of the unconfined compressive strength of blended cements in cemented pastes of sulphidic tailings was carried out over a curing period of 480 days. Cement kiln dusts (DA and DH) containing high CaO content (52.4% and 57.8%, respectively) and low Loss on Ignition (LOI), i.e., 5.1% and 4.8%, respectively, performed best in making cemented paste tailings, whereas the paste mixtures containing DB and DL (with very low free lime and very high LOI) as single
binders in combination with mine tailings (MT) never hardened. The addition of selective CKD, and SL, and/or FC as partial replacement for Portland cement can improve the performance of the cemented paste tailings containing sulphide minerals and alleviate the strength loss associated with Type GU cement based paste. The behavior is attributed to the latent strength acquisition of SL and FC in the blended cements containing DA and DH as a result of proliferating hydration and augmented pozzolanic reactivity. Previous studies carried out by other researchers on hardened cemented paste tailings specimens containing Portland cement-pozzolans binders confirmed the possibility of the presence of un-reacted or un-hydrated particles of slag and fly ash in such matrices. In the present study, SEM was carried out on cemented paste tailings samples to investigate the effect of using calcium and alkali rich CKD on pozzolanic reactivity of binders containing SL and FC. The effect of incorporation of DA or DH in GU/HS-SL and GU/HS-FC binders was analyzed in high magnification modes. No un-reacted grains of SL and/or FC were found within the crushed surfaces of the matrices. The glassy SL was completely disintegrated by the highly alkaline pore solution when attacked by OH⁻ ions. As well, all the amount of FC used in composite binder system was completely exhausted by the accelerated pozzolanic activity. Concomitantly, the observed microstructure delineation of selected cemented paste tailings samples was found to be well acquiescent with their respective mechanical performance (based on the unconfined compressive strength).

The precipitation of calcium hydroxide in Type GU based cemented paste tailings can be inadequate for total blocking of pores within cemented paste tailings matrix. The enhanced pozzolanic reactivity of SL and FC with additional calcium hydroxide produced by the incorporation of high calcium and alkali rich CKD in cemented tailings matrices generated additional hydration products, favoring enhanced pore refinement and densification, which, in turn, reduced the transportability of fluid through the hardened matrices.

Meticulous geochemical characterization of cemented paste tailings formulations is imperative, particularly when binders replace the traditional Portland cement. The leaching behavior of metals in cemented paste tailings formulations was studied using
field mimicking leaching protocols to obtain information on the fixation involving both chemical stabilization and physical encapsulation mechanisms. Leaching test results based on the Synthetic Precipitation Leaching Procedure (US EPA Method 1312) showed that cemented paste tailings formulated with Type GU cement alone are susceptible to contaminant leaching and, therefore, do not eliminate interaction between the monolith and contact waters. On the other hand, optimized cementing blends containing a small amount of Type GU cement and SL activated by DH offer more efficient contaminant fixation capabilities for tailings pastes. Low calcium cement kiln dust (DL) promoted chemical stabilization only within the resultant composites due to lack of cementitious properties and is, therefore, incapable of providing physical encapsulation of the contaminants.

The results advocate the technically beneficial synergy of composite binders containing selective CKDs for paste preparation in contrast with Portland cement alone, Portland cement-slag, and Portland cement-fly ash binder systems in sulphidic mine tailings management. An optimized mix proportion is however required to achieve optimal performance.

**Keywords:** cemented paste tailings; sulphidic mine tailings; cement kiln dust; ground granulated blast furnace slag; fly ash; Portland cement; unconfined compressive strength; saturated hydraulic conductivity; scanning electron microscopy; sulphate attack; acid rock drainage; metals; arsenic; leaching
CO-AUTHORSHIP

The research work described in the thesis was carried out by Amjad Tariq under the direct supervision of Professor Ernest. K. Yanful. The laboratory experimental works were conducted by Amjad Tariq. Professor Yanful was involved in the experimental design, theoretical and data analysis. Professor Yanful provided guidance to the research work and he is a co-author of all the publications derived from the research. The co-authorship of the articles is as follows:

CHAPTER 2

CHAPTER 3
Tariq, A., and Yanful, E.K. (2012a) Enhancing the properties of sulphidic cemented paste tailings by augmented pozzolanic reactivity of slag and Type C fly ash using high calcium CKD. Submitted to Journal of Materials in Civil Engineering

CHAPTER 4
CHAPTER 5

ACKNOWLEDGEMENTS

The present research could not have been viable without the financial support by the Natural Sciences and Research Council of Canada (NSERC) in the form of an Individual Discovery Grant awarded to Ernest K. Yanful and a postgraduate scholarship (PGSD3) awarded to Amjad Tariq.

I would like to express my sincere appreciation and gratitude to my research advisor Dr. Ernest K. Yanful for his continuous encouragement and invaluable guidance throughout the progress of this project. His enthusiasm and positive outlook provided a major impetus in the accomplishment of this thesis.

The generous support of material providers for the research is gratefully appreciated. I would like to express my thanks to Ron Kennedy (Toronto-Zinc), Rick Schwenger (Brunswick-Zn), Cement Association of Canada, and Lafarge, Canada for providing the materials for the project. I wish to extend my appreciation to the administrative and technical staff at the Civil and Environmental Engineering Department, The University of Western Ontario including Tim Stephen, Wilbert Logan, and Melodie Richards for their cooperation. Special thanks to Dr. C.T. Wu, Dr. R.L. Flemming, Mrs. T. Karamaneva (Dept. of Earth Science, UWO) and Mr. Ross Davidson (Surface Science Western, UWO for Scanning Electron Microscopy) for all their assistance in my experimental work. I would like to thank all my friends and graduate fellows for their moral support.

I would like to express my warmest gratitude to my wife, Nazia Amjad and my kids for being so supportive during a hectic schedule throughout my research. I would like to thank my parents Mirza Muhammad Inayat Baig (late) and Gulzar Begum, my mother in law Mukhtar Begum for their unconditional love, prayers, and encouragement.

Above all, to God almighty be all the glory and honor for helping me through yet another phase of my life.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERTIFICATE OF EXAMINATION</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>CO-AUTHORSHIP</td>
<td>vi</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>viii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>xix</td>
</tr>
<tr>
<td>CHAPTER 1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 General</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Cemented paste tailings</td>
<td>1</td>
</tr>
<tr>
<td>1.3 Objectives of the present research</td>
<td>4</td>
</tr>
<tr>
<td>1.4 Originality of thesis and major contributions</td>
<td>5</td>
</tr>
<tr>
<td>1.5 Organization of the thesis</td>
<td>6</td>
</tr>
<tr>
<td>1.6 References</td>
<td>9</td>
</tr>
<tr>
<td>CHAPTER 2 A REVIEW OF BINDERS USED IN TAILINGS</td>
<td>11</td>
</tr>
<tr>
<td>PASTES FOR UNDERGROUND AND SURFACE DISPOSAL PRACTICES</td>
<td></td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>11</td>
</tr>
<tr>
<td>2.2 Underground disposal of cemented paste tailings and associated benefits</td>
<td>15</td>
</tr>
<tr>
<td>2.3 Surface disposal of cemented paste tailings and allied benefits</td>
<td>16</td>
</tr>
<tr>
<td>2.4 Prospective environmental benefits linked with cemented paste tailings technology</td>
<td>16</td>
</tr>
<tr>
<td>2.5 Binding agents for cemented paste tailings formulations</td>
<td>17</td>
</tr>
<tr>
<td>2.5.1 Portland cements</td>
<td>17</td>
</tr>
<tr>
<td>2.5.1.1 Incentives to curtail Portland cement use in cemented paste tailings formulations</td>
<td>22</td>
</tr>
<tr>
<td>2.5.1.1.1 Portland cement price and haulage cost and concordant higher cement consumption</td>
<td>23</td>
</tr>
<tr>
<td>2.5.1.1.3 Significance of sulphates in Portland cement based cemented paste tailings</td>
<td>25</td>
</tr>
<tr>
<td>2.5.2 Pozzolanic materials</td>
<td>29</td>
</tr>
<tr>
<td>2.5.2.1 Natural pozzolans</td>
<td>31</td>
</tr>
<tr>
<td>2.5.2.2 Artificial Pozzolans</td>
<td>32</td>
</tr>
</tbody>
</table>
CHAPTER 3 ENHANCING PROPERTIES OF CEMENTED PASTE TAILINGS BY AUGMENTED POZZOLANIC REACTIVITY OF SLAG AND TYPE C FLY ASH USING HIGH CALCIUM CEMENT KILN DUST

3.1 Introduction 81
3.2 Unconfined compressive strength of cemented paste tailings 86
3.3 Microstructural analysis 87
3.4 Materials and test methods 87
   3.4.1 Mine tailings and binder reagents 87
   3.4.2 Methodologies and test equipments 91
      3.4.2.1 Cemented paste tailings specimen preparation for UCS tests 91
      3.4.2.2 Unconfined compressive strength (UCS) tests 92
      3.4.2.3 Scanning electron microscopy and energy dispersive spectrometry 93
3.5 Results and discussion 93
   3.5.1 Unconfined compressive strength tests on cured cemented paste tailings specimens
3.5.1.1 Cemented paste tailings containing GU and HS 94
3.5.1.2 Cemented paste tailings containing DA, DH, DB and DL as single binders 97
3.5.1.3 Cemented paste tailings with binary binders comprising DA, DH, FC, GU, HS and SL 102
3.5.1.4 Cemented paste tailings with ternary binders containing DA, DH, FC, GU, HS and SL 108
3.5.1.5 Cemented paste tailings with quaternary binders containing DA, DH, FC, GU, HS and SL 110
3.5.2 Microstructural investigation using scanning electron microscopy 115
3.5.2.1 Microstructural investigation of cemented paste tailings containing DA, DH, GU, and HS 115
3.5.2.2 Microstructural investigation of cemented paste tailings with binary and ternary binders containing Type CI fly ash (FC) 117
3.5.2.3 Microstructural investigation of cemented paste tailings with binary and ternary binders containing SL 119
3.5.3 Relationship between microstructure of hardened cemented paste tailings and respective UCS 122
3.6 Conclusions 123
3.7 References 128

CHAPTER 4  EFFECT OF HIGH CALCIUM CEMENT KILN DUST ACTIVATED SLAG AND FLY ASH ON SATURATED HYDRAULIC CONDUCTIVITY OF CEMENTED PASTE TAILINGS 153

4.1 Introduction 153
4.2 Benefits of slag and fly ash activation by high calcium cement dust in cemented paste tailings formulations 154
4.3 Materials and test methods 155
4.3.1 Physical and chemical properties of materials 155
4.3.2 Saturated hydraulic conductivity test specimens and apparatus 158
4.4 Results and discussion 160
4.4.1 Saturated hydraulic conductivity evolution of cemented paste tailings with single and binary binders comprising DA, DH, GU and HS 160
4.4.2 Saturated hydraulic conductivity evolution of cemented paste tailings prepared with MT in combination with binary and ternary binders comprising DA, DH, FC, GU and HS 163
4.4.3 Saturated hydraulic conductivity evolution of cemented paste tailings prepared with MT in combination with binary and ternary binders comprising DA, DH, SL, 165
CHAPTER 5 METAL IMMOBILIZATION IN CEMENTED PASTES TAILINGS USING SLAG AND TYPE C FLY ASH ACTIVATED BY HIGH AND LOW CALCIUM CEMENT KILN DUSTS

5.1 Introduction 190
5.2 Portland cement, ground granulated blast furnace slag, and cement kiln dust based remediation systems for wastes containing metals
  5.2.1 Ground granulated blast furnace slag 194
  5.2.2 Cement kiln dust 196
5.3 Leaching tests
  5.3.1 Limitation of Toxicity Characteristic Leaching Procedure for mineral processing wastes 200
  5.3.2 Synthetic Precipitation Leaching Procedure 201
5.4 Materials and test methods
  5.4.1 Mine tailings and binder reagents/additives 202
  5.4.2 Determination of paste pH 205
  5.4.3 Leaching test procedure 205
5.5 Results and discussion
  5.5.1 Immobilization of Pb in cemented paste tailings containing slag and/or fly ash activated by high and low calcium cement kiln dusts 206
  5.5.2 Immobilization of Zn in cemented paste tailings containing slag and/or fly ash activated by high and low calcium cement kiln dusts 212
  5.5.3 Immobilization of Cd in cemented paste tailings containing slag and/or fly ash activated by high and low calcium cement kiln dusts 215
  5.5.4 Immobilization of Cu in cemented paste tailings containing slag and/or fly ash activated by high and low calcium cement kiln dusts 218
  5.5.5 Immobilization of Hg in cemented paste tailings containing slag and/or fly ash activated by high and low calcium cement kiln dusts 221
  5.5.6 Immobilization of As in cemented paste tailings containing slag and/or fly ash activated by high and low calcium cement kiln dusts 223
CHAPTER 6  CONCLUSIONS AND SCOPE FOR FUTURE RESEARCH

6.1 Conclusions
6.2 Scope for future research

APPENDIX A

APPENDIX B

APPENDIX C

CURRICULUM VITAE
LIST OF TABLES

Table 3.1  Chemical and physical properties of mine tailings (MT) and cementitious materials  138
Table 3.2  Chemical and physical properties of cement kiln dusts  139
Table 3.3  Mixture proportions of mine tailings (MT) and binders reagents  140
Table 3.4  Chemical characteristics of mixing water  141
Table 4.1  Chemical and physical properties of mine tailings (MT) and cementitious materials  179
Table 4.2  Chemical and physical properties of cement kiln dusts  180
Table 4.3  Mixture proportions of mine tailings (MT) and binder reagents  181
Table 5.1  Chemical and physical properties of MT, SL, GU, and FC  239
Table 5.2  Chemical properties of cement kiln dusts  240
Table 5.3  Mixture proportions of mine tailings and binder reagents/additives  241
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure 2.1</th>
<th>Hydration of Portland cement</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.2</td>
<td>Schematic diagram elucidating Portland cement based cemented paste tailings hydration stages and potential interaction with sulphates, along with functional role of pozzolanic materials addition</td>
<td>79</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Ternary phase diagram showing common solidification and chemical fixation reagents</td>
<td>80</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Particle size distributions of MT, GU, HS, SL and FC</td>
<td>142</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Particle size distributions cement kiln dusts (DA, DH, DB and DL)</td>
<td>142</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>X-ray diffractogram of Mattabi mine tailings (MT)</td>
<td>143</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>Unconfined compressive strength (UCS) of cemented paste tailings prepared with MT and binders comprising DA, SL, FC and GU</td>
<td>144</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>Average % change in UCS of cemented paste tailings samples relative to peak (MT and binders comprising DA, SL, FC, and GU)</td>
<td>144</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>Unconfined compressive strength (UCS) of cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and HS</td>
<td>145</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>Average % change in UCS of cemented paste tailings samples relative to peak (MT and binders comprising DA, SL, FC, and HS)</td>
<td>145</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>Unconfined compressive strength (UCS) of cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and GU</td>
<td>146</td>
</tr>
<tr>
<td>Figure 3.9</td>
<td>Average % change in UCS of cemented paste tailings samples relative to peak (MT and binders comprising DH, SL, FC, and GU)</td>
<td>146</td>
</tr>
</tbody>
</table>
Figure 3.10  Unconfined compressive strength (UCS) of cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and HS

Figure 3.11  Average % change in UCS of cemented paste tailings samples relative to peak (MT and binders comprising DH, SL, FC, and HS)

Figure 3.12  SEM backscattered electron image depicting cemented paste tailings fractured surface containing 7%GU cement as binder

Figure 3.13(a)  SEM micrograph showing pyrite grain embedded in cemented paste tailings matrix containing 7% GU cement as binder

Figure 3.13(b)  EDX confirming chemical composition of pyrite grain shown in Fig. 13(a)

Figure 3.14  SEM backscattered electron image depicting cemented paste tailings fractured surface containing (3%HS+8%DA) as binder

Figure 3.15(a)  SEM micrograph showing un-reacted or un-hydrated FC particles in cemented paste tailings prepared with (3%GU+8%FC) as binder

Figure 3.15(b)  SEM micrograph showing hollow shell of FC particle in cemented paste tailings prepared with (3%GU+8%FC)

Figure 3.16  SEM micrograph showing un-reacted or un-hydrated SL particles in cemented paste tailings fractured surface containing (3%GU+8%SL) as binder

Figure 3.17  SEM backscattered electron image depicting Cemented paste tailings fractured surface containing (3%GU+8%DH+8%SL) as binder

Figure 3.18  SEM backscattered electron image depicting cemented paste tailings fractured surface containing (3%HS+8%DH+5%FC+8%SL)

Figure 4.1  Particle size distributions of MT, GU, HS, SL, and FC

Figure 4.2  Particle size distribution of cement kiln dusts (DA and DH)

Figure 4.3  Schematic diagram of fixed wall constant flow rate
Figure 4.4  Hydraulic conductivity apparatus

Schematic of one-permeameter cell of fixed wall hydraulic conductivity apparatus

Figure 4.5  Saturated hydraulic conductivity ($k_s$) evolution of cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and GU

Figure 4.6  Saturated hydraulic conductivity ($k_s$) evolution of cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and HS

Figure 4.7  Saturated hydraulic conductivity ($k_s$) of control MT sample and 28-day cured cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and GU

Figure 4.8  Saturated hydraulic conductivity ($k_s$) of control MT sample and 28-day cured cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and HS

Figure 4.9  Saturated hydraulic conductivity ($k_s$) evolution of cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and GU

Figure 4.10  Saturated hydraulic conductivity ($k_s$) evolution of cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and HS

Figure 4.11  Saturated hydraulic conductivity ($k_s$) of control MT sample and 28-day cured cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and GU

Figure 4.12  Saturated hydraulic conductivity ($k_s$) of control MT sample and 28-day cured cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and HS

Figure 4.13  Saturated hydraulic conductivity ($k_s$) of 28-day and 120-day cured cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and GU

Figure 4.14  Saturated hydraulic conductivity ($k_s$) of 28-day and 120-day cured cemented paste tailings prepared with  

xvii
Figure 4.15  MT and binders comprising DH, SL, FC, and GU
Saturated hydraulic conductivity ($k_s$) of 28-day and 120-day
cured cemented paste tailings prepared with
MT and binders comprising DA, SL, FC, and HS

Figure 4.16  Saturated hydraulic conductivity ($k_s$) of 28-day and 120-day
cured cemented paste tailings prepared with
MT and binders comprising DH, SL, FC, and HS

Figure 5.1  Concentrations of Pb in leachates from control MT sample
and 120-day cured cemented paste tailings samples

Figure 5.2  Solubility of metal hydroxides as a function of pH

Figure 5.3  Concentrations of Zn in leachates from control MT sample
and 120-day cured cemented paste tailings samples

Figure 5.4  Concentrations of Cd in leachates from control MT sample
and 120-day cured cemented paste tailings samples

Figure 5.5  Concentrations of Cu in leachates from control MT sample
and 120-day cured cemented paste tailings samples

Figure 5.6  Concentrations of Hg in leachates from control MT sample
and 120-day cured cemented paste tailings samples

Figure 5.7  Concentrations of As in leachates from control MT sample
and 120-day cured cemented paste tailings samples
NOMENCLATURE

(AFt) Tricalcium aluminate trisulphate hydrate
(AFm) Tricalcium aluminate monosulphate hydrate
(AMD) Acid mine drainage
(ARD) Acid rock drainage
(BET) Braunauer, Emmett, and Teller
(C-A-H) Calcium aluminate hydrate
(C3A) Tricalcium aluminate
(CLSM) Controlled low strength material
(D50) Sieve diameter that 50% of particles by weight passes through
(CKD) Cement kiln dust
(C-S-H) Calcium silicate hydrate
(Cc) Coefficient of curvature
(Cu) Coefficient of uniformity
(C4AH13) Tetra calcium aluminate hydrate
(DH) High calcium cement kiln dust
(DL) Low calcium cement kiln dust
(EDX) Energy dispersive X-ray
(FC) Type C fly ash
(FAF) Type F fly ash
(Gs) Specific gravity
(ICP-AES) Inductively coupled plasma-atomic emission spectrometry
(ks) Saturated hydraulic conductivity
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LOI</strong></td>
<td>Loss on ignition</td>
</tr>
<tr>
<td><strong>MT</strong></td>
<td>Mattabi mine tailings</td>
</tr>
<tr>
<td><strong>PI</strong></td>
<td>Plasticity index</td>
</tr>
<tr>
<td><strong>PKC</strong></td>
<td>Portland composite cement</td>
</tr>
<tr>
<td><strong>PSD</strong></td>
<td>Particle size distribution</td>
</tr>
<tr>
<td><strong>GU</strong></td>
<td>General use hydraulic cement (CSA) equivalent to ASTM Type I</td>
</tr>
<tr>
<td><strong>HS</strong></td>
<td>High sulphate resistant hydraulic cement equivalent to ASTM Type V</td>
</tr>
<tr>
<td><strong>RH</strong></td>
<td>Relative humidity</td>
</tr>
<tr>
<td><strong>S/S</strong></td>
<td>Solidification/stabilization</td>
</tr>
<tr>
<td><strong>SCMs</strong></td>
<td>Supplementary cementing materials</td>
</tr>
<tr>
<td><strong>SEM</strong></td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td><strong>SL</strong></td>
<td>Ground granulated blast furnace slag</td>
</tr>
<tr>
<td><strong>SO₄²⁻</strong></td>
<td>Sulphate content</td>
</tr>
<tr>
<td><strong>SPLP</strong></td>
<td>Synthetic precipitation leaching procedure (USEPA Method 1312)</td>
</tr>
<tr>
<td><strong>TCLP</strong></td>
<td>Toxicity characteristic leaching procedure (USEPA Method 1311)</td>
</tr>
<tr>
<td><strong>U.S. EPA</strong></td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td><strong>UCS</strong></td>
<td>Unconfined compressive strength</td>
</tr>
<tr>
<td><strong>w/c</strong></td>
<td>Water/cement ratio</td>
</tr>
<tr>
<td><strong>ϕ</strong></td>
<td>Angle of internal friction</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION

1.1 General

Mining project proponents are required to ascertain that the resulting waste will be managed in an environmentally sustainable manner in the light of stringent environmental regulations and increased public awareness of environmental issues. The alleviation of environmental threat posed by potentially acid generating mine tailings containing sulphide minerals, in particular necessitates the adoption of efficient technologies to cope with the litany of prospective devastating ecological deterioration associated with acid rock drainage/acid mine drainage (ARD/AMD).

1.2 Cemented paste tailings

In environmentally sensitive areas, where the consumptive utilization of water resources or traditional approaches such as the use of mine waste containment facilities (large dams, etc.) are in conflict with the prevailing environmental policies, innovative technologies such as cemented paste tailings can play a role. Cemented paste tailings is a pumpable, flowable, non-Newtonian fluid generally consisting of mine tailings, water and ordinary Portland cement (Brackebusch 1994). It is normally prepared from dilute slurries of tailings by dewatering it with conventional thickening or filtering. Cemented paste is generally a high density non segregating mixture that contains 70-85% solids by total mass and enough fines (at least 15% particles less than 20 microns) to prevent
settlement (negligible bleed water) and particle segregation when transported through a pipeline for disposal (Landriault 1995, Klein and Simon 2006).

Prompted by the realization that cemented paste tailings perform a variety of load bearing functions (underground backfill) in addition to achieving environmental goals and surface disposal applications, noteworthy advances have been made in exploring appropriate binding materials and their performance in cemented paste response. Cemented paste tailings is an innovative form of amalgamated material currently available to the mining industry in developed countries. Canadian Standards Association (CSA) Type GU or ASTM Type I is the most extensively used binder in cemented pastes formulations. The high cost associated with production and haulage of Portland cement and its alleged average performance as a sole binder in the long term (due to vulnerability to internal sulphate attack) have prompted users to appraise less expensive and technically efficient substitutes for mine tailings paste formulations. The goal of mine tailings paste mixture design is to optimize the available cementitious agents for cost-effectiveness, while enhancing material properties for the final product. The approach to designing environmentally efficient cemented paste tailings is to ensure short- and long-term stability, and effective control over environmental pollutants through the use of composite binder systems with enhanced engineering properties to cater for inherit deficiencies in the individual constituents.
The binder can represent up to 75% of the overall cost of the cemented paste backfill operations when ordinary Portland cement is used as a sole binder (Grice 1998). CSA Type GU cement is customarily used as a sole binder or occasionally blended with other pozzolanic materials known as supplementary cementing materials (SCMs) in cemented paste backfill operations. Such materials include but not limited to fly ash (Weaver and Luka 1970, Amaratunga and Yaschyshyn 1997, Benzaazoua et al. 1999, Hassani et al. 2001, Ramlochan et al. 2004, Godbout et al. 2007), blast furnace slag (Belem et al. 2000, Benzaazoua et al. 2002, Fall and Benzaazoua 2005, Kesimal et al. 2005, Ouellet et al. 2006, Douglas and Malhotra 1989), silica fume (Ercikdi et al. 2009), and waste glass (Archibald et al. 1999, De Souza et al. 1997), etc. These binders are incorporated in order to augment the durability and reduce the binder cost.

The binder is utilized principally to develop sufficient mechanical strength for the paste backfill in terms of certain target dynamic and static load resistances. The rate of strength acquisition with respect to curing time and the ultimate strength at failure are among the key parameters for evaluating the effectiveness of a binder in hardened cemented paste backfills (Hassani et al. 2007). The capital and operating costs associated with cemented paste backfill operations involving cementitious materials and disposal strategies are very much materials and site specific. In general, cost increases in proportion to the percentage of binding materials/additives and transport, distance if such material(s) is not locally available.
1.3 Objectives of the present research

The present research was planned and conducted to address the above cited issues and to achieve the following desired goals:

- To ameliorate the performance of cemented paste tailings containing sulphide minerals for underground and surface disposal practices and to alleviate the strength loss associated with ordinary Portland cement based traditional paste.
- To investigate the potential use of characteristically different cement kiln dusts in enhanced cementitious binder formulations by virtue of their self cementitious properties and alkaline activation capabilities for latent hydraulic and pozzolanic materials such as ground granulated blast furnace slag and Type C fly ash in developing resilient cemented paste tailings.
- To investigate performance and long-term stability of the resultant matrices in comparison with traditional cemented paste tailings containing Portland cement as a sole binder.
- To develop environmentally acceptable cemented paste tailings based on field mimicking leaching tests which can be further used on an industrial scale in order to mitigate or prevent generation of ARD/AMD.
- To elucidate dominating immobilization mechanisms of different contaminants contained in the developed cemented paste tailings containing sulphide minerals.
- To curtail Portland cement use in cemented paste tailings formulations in the light of today's robust engineering design requirements and accompanying higher cement consumption. This will further reduce the cost associated with production of such an energy-intensive material and mitigate the impact of cement industry
on the environment since cement production has been recognized as a major source of \( CO_2 \) emission.

- To utilize cement kiln dust (byproduct of cement industry), since approximately 80% of the total cement kiln dust generated is stockpiled which pose further threat to the environment. The incentives in favor of waste recycling/reduction/minimization advocate the use of such an abundant and discarded industrial by-product in the light of its valuable cementitious and alkaline properties for beneficial considerations such a mine waste management.

1.4 Originality of thesis and major contributions

Selective cement kiln dust has been found to be quite promising in producing controlled low strength materials (CLSM) due to its valuable cementitious properties. A few published papers have mentioned the beneficial use of cement kiln dusts for alkaline amendment of sulphidic waste (Doye and Duchesne 2003, Duchesne and Doye 2005). However, no detailed investigation has been reported on utilizing the cementitious properties of cement kiln dust for sulphidic mine tailings management. Tariq and Nehdi (2007) conducted preliminary investigation on the potential use of cement kiln dust in cemented paste backfill preparation. However, the study did not investigate different cement kiln dusts in combination with ground granulated blast furnace slag and fly ash in making composite cements in sulphidic tailings cemented paste formulations. In addition, the present research is the first attempt to investigate the effectiveness of cement kiln dust as an alkaline activator and accelerator for latent hydraulic materials, such as ground
granulated blast furnace slag and Type C fly ash for production of resilient and environmentally efficient cemented paste tailings. Based on the laboratory investigations, the most promising cement kiln dust (s) have been determined that can be used in the composite binders systems for cemented paste tailings formulations.

1.5 Organization of thesis

This thesis is presented in integrated-article format, with each of the articles in individual chapters containing separate introduction, tables, figures, results and discussion, and references. This thesis contains six chapters and some additional information is presented in appendices at the end of thesis. The details of the organization of the thesis are presented as follows:

Chapter 1 defines the problem, lists the objectives of the research, and presents organization of the thesis.

Chapter 2 provides a detailed review on binders used in tailings pastes for underground and surface disposal practices. It critically examines various S/S techniques in the existing literature, identifying the fundamental mechanisms controlling their performance and the intrinsic parameters of S/S system components, along with the tailings-additive/binder interaction mechanisms. This chapter explains the phenomenon of internal sulphate attack associated with ordinary Portland cement based sulphidic tailings
cemented paste and highlights the incentives to curtail Portland cement use. It also elucidates the prospective use of cement kiln dust as a binder and activator in combination with other pozzolanic materials in cemented paste tailings formulations.

Chapter 3 provides a comparative evaluation of high and low calcium cement kiln dusts in enhancing properties of sulphidic cemented paste tailings by augmented pozzolanic reactivity of slag and Type C fly ash. The unconfined compressive strength and microstructural analysis were selected as major performance evaluation indicators for a range of developed cemented pastes tested in the laboratory. The requisite unconfined compressive strength values for cemented paste tailings for various underground mining operations and surface disposal applications were achieved using different binder combinations, and their respective behaviour under sulphate rich environment was studied. A correlation has been made between the textures of a range of hardened paste specimens with their corresponding UCS values that facilitated the development of a rigorous approach for assessing paste quality.

Chapter 4 investigates the influence of enhanced pozzolanic reactivity of slag and Type C fly ash using calcium and alkali rich cement kiln dust in reducing the saturated hydraulic conductivity of cemented paste tailings formulations using a variety of binder combinations.
Chapter 5 presents a laboratory investigation to evaluate the contaminant containment capabilities of different cemented paste tailings formulated by using blast furnace slag and Type C fly ash activated by high and low calcium cement kiln dusts. This study elucidates dominating immobilization mechanisms for different contaminants contained in sulphidic cemented paste tailings. The efficient combinations of sulphidic tailings-binder have been experimentally optimized satisfying environmental standards.

Chapter 6 presents conclusions and some recommendations for future research trends on the subject in favour of perpetual efforts towards sustainable development.
1.6 References


2.1 Introduction

In Canada and several other industrialized countries, issues pertaining to environmental regulatory compliance have become the impetus for comprehensive engineering design and effective management of mining, other wastes and industrial by-products. This has resulted in a renewed interest within the mining industry to explore and evaluate innovative strategies for managing potentially acid generating mining waste.

The environmental impacts of acid rock drainage (ARD) have been well documented in the literature (Down and Stocks 1977, Ritcey 1989, Gray 1997). The oxidation of iron bearing minerals, in particular the iron sulphides (pyrite and pyrrhotite), produces rock mine drainage (Nordstrom 1982, Yanful and Verma 1999). High reactivity of the iron bearing minerals in the presence of oxidizing fluids coupled with abundant sulphides contained in mining wastes leads to highly acidic drainage (Pratt et al. 1994).

ARD prevention and control practices are generally based on the anticipated future use of land, as well as on technical, economic, and environmental considerations. These techniques aim at restricting the principal components of the acid generation process, (i.e. sulphides, oxygen, and water) and include (a) under-water storage of tailings such as in
constructed surface impoundments and flooded pits (Catalan and Yanful 2002, Samad and Yanful 2005) underground working and natural water bodies, (b) application of covers constructed from low permeability soils, synthetic materials, organic substances and composites (Yanful et al. 1993, Yanful and St-Arnaud 1992, Yanful et al. 2006) or a cover made of oxygen-consuming materials, such as wood waste, straw mulch, etc. (Tremblay 1994, Tassé et al. 1997, Cabral et al. 2000) or capillary barrier materials relying on the high moisture-retention capacity to prevent oxygen ingress (Nicholson et al. 1989), (c) segregation of sulphides or desulphurization (Bois et al. 2005, Benzaazoua et al. 2008), (d) alkaline amendment, i.e., addition of alkaline materials to control the pH of pore waters (Doye and Duchesne 2003, Duchesne and Doye 2005), and (e) biological treatment, i.e. application of bactericides to inhibit bacterial action (Kim et al. 1999).

In some recent high profile mining projects in the United States and Canada, the alleged adverse environmental impacts associated with conventional approaches to reactive tailings management have led to the abandonment of otherwise feasible ventures (Landriault et al. 1997a). Contrary to the conventional thickened tailings for surface disposal applications, binder agents impart chemical stabilization and physical solidification of the cemented paste tailings. This approach is particularly beneficial for environmentally protected disposal of sulphide mine waste because it can minimize the subsequent mobilization of potentially toxic heavy metals and arsenic (As) (Benzaazoua et al. 2004b).
The evolution of current approaches in mine tailings management especially in North America is influenced most significantly by legislation resulting from mishaps associated with tailings storage facility failures and today’s increased public awareness of environmental effects of acid rock drainage (Cincilla et al. 1997). The cemented paste backfill technology was implemented for the first time in 1957 by Bad Grund Mine in Germany in late 1970s (Lerche and Renetzeder 1984). The backfill contained 50:50 mix of medium to fine mill reject aggregate and medium to fine silt size filtered tailings mixed with ordinary Portland cement to a workable consistency which was pumped underground using a combination of vertical and horizontal pipelines. Later on, the Helca Mining Company in their Lucky Friday Mine in Utah, in the United States introduced a congruent system using filtered full plant tailings (Brackebusch 1994). These systems were formerly called ‘high density backfill’ systems until, in the late 1980s, the term ‘Paste Backfill’ was introduced in the mining industry. The acceptance of paste backfill as a viable alternative to hydraulic slurry and rock fill did not actually occur until the early to mid 1990s with the construction and successful operation of several paste backfill systems in Canada (Landriault 2000). Presently, the Canadian and Australian mining industries are probably leaders in the use of paste technology (Brackebusch and Shillabeer 1998, Rankine and Sivakugan 2007).

An eminent feature of paste backfills is high water content, which is usually far in excess of hydration requirements of cementitious materials. The paramount reason for such a high w/c ratio (5-15%) is the requisite consistency and flowability in order to transport the paste through pipelines by pumping or by gravity. In contrast, ordinary cement
concrete and mortars are commonly designed with a w/c ratio under 0.5. Consequently, the resultant paste backfill matrix can have significant disparity in material properties in comparison with ordinary concretes and mortars. These properties include but not limited to compressive strength, density, porosity, hydraulic conductivity, and microstructure of hardened pastes.

Cemented paste tailings is a composite material whose physical, microstructural and mechanical properties evolve from concoct to its hardening. Typically, after a long-term curing time, the paste backfill transforms to a material with physical characteristics between a hard soil and a soft rock (Belem et al. 2000). The material properties (mechanical strength, permeability, etc.) and the contaminants containment capability of the cemented paste can be readily achieved as well as modified by the addition of binder reagents. The selection of binder material(s) largely depends on the disposal scenario (underground or surface), desired engineering properties of resultant monolith, and the level of requisite environmental control over the pollutants leachability.

Portland cement is an energy intensive material whose manufacturing cost along with its recognition as a major source of CO$_2$ emission has made its production a target of criticism among environmentalists. Today’s robust engineering design requirements for cemented paste tailings and recent reports of deterioration of cemented paste backfill containing Portland cement as a sole binder has oriented the mining companies to consider alternate material utilization. Much effort has been made in the past two decades
toward the acquisition of binder replacements for ordinary Portland cement in the formulation of cemented paste tailings.

2.2 Underground disposal of cemented paste tailings and associated benefits

The environmental and economic performance of underground mining operations requires the return of potentially acid generating tailings underground in the form of cemented paste backfill. Several investigators have highlighted the potential advantages associated with cemented paste backfill in underground mining operations and have considered it to be indispensable for most underground mines (Benzaazoua et al. 1999 and 2002, Hassani et al. 2001, Kesimal et al. 2004 and 2005, Fall and Benzaazoua 2005, Ouellet al. 2006 and 2007, Ercikdi et al. 2009a and 2010b). Cemented paste backfill (underground disposal) technology has a number of advantages over other mine tailings management strategies including: (a) deposition into voids created by mine stopes, thus providing an enhanced level of local and regional stability to the ore body in addition to providing a suitable and economical disposal of mining associated waste (Rankine and Sivakugan 2007); (b) about upto 60% decrease in the amount of sulphidic waste that has to be disposed on the surface (Benzaazoua et al. 2004b), thus reducing pollution and negative environmental impacts; (c) increase in the available ore reserves by acting as secondary ground support pillars favouring mine stability; (d) absence of free water in the paste fill system thereby avoiding drainage requirements and resulting in faster stope cycle time; and (e) higher achievable mechanical strength for a comparable amount of binding agents (Thomas et al. 1979, Mitchell and Wong 1982, Benzaazoua et al. 2004a,
Amaratunga and Yaschyshyn 1997). In underground mining applications, paste backfill can serve as a construction material to create a floor to mine on top of, a wall to mine next to, and a roof or head cover to mine under (Landriault et al. 1997b).

### 2.3 Surface disposal of cemented paste tailings and allied benefits

Cemented paste tailings has also been proposed as an innovative approach for surface tailings disposal (Deschamp et al. 2008, Cincilla et al. 1997, Verburg 2002, Theriault et al. 2003, Landriault et al. 2005, Shuttleworth et al. 2005, Bussière 2007). The key benefits of this approach include: (a) improved tailings hydro-geotechnical properties, (b) small amount of free water at the paste surface thereby reducing the dimensions of tailings-retaining structures in the case of underwater storage, (c) homogeneity of paste induces less particles segregation, (d) enhanced strength and durability of the resultant monolith, (e) development of acid neutralization potential and contaminants stabilization capability of the matrix due to addition of alkaline binders (Benzaazoua et al. 2002 and 2004b, Ouellet et al. 2003, Cadden et al. 2003).

### 2.4 Prospective environmental benefits linked with cemented paste tailings technology

The environmental benefits of cemented tailings paste technology include: (a) solidified monolith of hardened paste encapsulates potentially mobile contaminants (metallic and metalloid elements) thereby reducing prospective negative impacts on receiving water
bodies and biota; (b) alkaline cementing agents provide chemical stabilization and transformation of the pollutants within the paste matrix; and (c) low leachate generation due to the colloidal water retention capabilities and extremely low permeability of cemented paste. Another benefit of cemented paste tailings technology is the possibility of co-disposal of mine tailings with a range of industrial byproducts or wastes that can be otherwise chemically challenging for the eco-system if stockpiled (Verburg 1997, Landriault et al. 1997a, Benzaazoua et al 2004b, Coussy et al. 2011).

2.5 Binding agents for cemented paste tailings formulations

2.5.1 Portland cements

Portland cement (CSA Type GU or ASTM Type I) addition has been in the past, and presently remains, the most accepted binder for mine tailings waste solidification (Scoble and Piciacchia 1986). It has been the most extensively used binding agent due to its availability and versatility and has a long history of being considered an adequate solution to mining waste management problems including the disposal of sulphidic tailings (Rawling et al. 1966, Weaver and Luka 1970, Aylmer 1973, Thomas 1973, Manca et al. 1983, Atkinson et al. 1989, Lamos and Clark 1989, Rankine and Sivakugan 2007, Grabinsky et al. 2007 and 2008).

The binder is used principally to develop sufficient mechanical strength for the paste backfill to meet certain dynamic and static load resistance requirements. In cement based
solidification, water in the waste chemically reacts with Portland cement (hereafter Type GU cement) to form hydrated calcium silicate and aluminate compounds, while the solids act as aggregates to form ‘concrete’ (Conner 1993). The addition of Type GU cement has been found to enhance the cohesive component of the shear strength, impart tensile strength and intensify the stiffness of mine tailings paste, while the other granular tailings materials provide shear strength (Hassani et al. 2007a, Ouellet et al. 1998).

The structural development of Type GU based solidified waste results in hydration reactions that stiffen and densify as a monolith and impart reasonable structural integrity to the solidified waste. Type GU cement hydration mechanisms have been studied in depth and reported elsewhere (Taylor 1990, Glasser 1993, Mollah et al. 1995, Hills and Pollard 1997). The four key anhydrous phases constituting a heterogeneous mixture of Type GU cement possess the following compositions: (a) 50-70% of tricalcium silicate ($Ca_3SiO_5$) or $C_3S$ or alite, (b) 20-30% of dicalcium silicate ($Ca_2SiO_4$) or $\beta-C_2S$ or belite, (c) 5-12% of tricalcium aluminate ($Ca_3Al_2O_6$) or $C_3A$, and (d) 5-12% of calcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$) or abbreviated as $C_4AF$). The dominant hydration phases under normal conditions are (a) 60-70% of calcium silicate hydrate ($3CaO\cdot 2SiO_2\cdot 3H_2O$), a gel of variable stoichiometry abbreviated as $C-S-H$ (b) 20-25% of calcium hydroxide [$Ca(OH)_2$] or portlandite. These two phases form some 90% w/w of the solid hydration products of Type GU cement paste as an intimate mixture (Hills and Pollard 1997). The rest of the solid products are calcium sulpho-aluminates: tricalcium aluminate trisulphate hydrate ($C_3A\cdot 3CaSO_4\cdot 32H_2O$) or ettringite an $Aft$ phase) and tricalcium aluminate monosulphate hydrate ($C_3A\cdot CaSO_4\cdot 12H_2O$) or monosulphate (an $AFm$ phase).
(Skalny et al. 2002). The hydration and subsequent setting and hardening of cement paste that imparts structural integrity to resultant monolith progresses through a series of competing chemical reactions as shown in Figure 2.1.

Sulphate resistant Portland cements (CSA Type HS or ASTM Type V) were developed by Thorvaldson in the 1930s (Swenson and Mackenzie 1968) principally by increasing the iron content ($Fe_2O_3$) in raw materials in the Portland cement production processes. This finding led to the development of Portland cement with reduced tricalcium aluminate ($C_3A$) and increased tetra calcium alumino-ferite ($C_4AF$) contents. With regards to the internal sulphate attack in cementitious matrix such as cemented tailings paste, the composition of the cement is potentially an important factor. Sulphate-related deterioration is related to the $C_3A$ content of the cement and the amount of CH formed. The low $C_3A$ concentrations reduce ettringite formation in sulphate resistant cement concrete materials and hence lessen the damage of mortars and concrete materials deterioration caused by the sulphates (Puppala et al. 2004). Portland cement with a $C_3A$ content of less than 5%, such as Type HS, is typically considered partially sulphate resistant. Calcium hydroxide produced by the hydration of cement plays an important role in the performance of low $C_3A$ Portland cements exposed to a sulphate environment. It leads to a change in the predominant sulphate deterioration mechanism, potentially resulting in the performance of sulphate resistant Portland cements that can vary from excellent to poor (Irassar et al. 2000). However, it should be noted that utilizing specialty cements such as Type HS cement is relatively an expensive option.
Benzaazoua et al. (2004a) investigated the hardening process of the cement and sulphidic mine tailings pastes. These authors observed that, contrary to ordinary concrete or mortar, the hardening process of cement-tailings mixtures is not only due to the cement hydration, but also to the precipitation of hydrated phases from the pore water of the paste. The hardening process occurs in two main stages. The first stage is dominated by dissolution reactions. The dissolution of tricalcium silicate ($C_3S$) or $(3CaO\cdot SiO_2)$ which is the major anhydrous phase of cement, leads to the release of $Ca^{2+}$, $H_2SiO_4^{2-}$, and $OH^-$ ions. The concentration of calcium ions increases very rapidly during the first curing stages until super-saturation of calcium is reached. The second stage (after super-saturation is reached) is characterized by precipitation reactions and direct hydration of the binder. Dissolution reactions decrease significantly at this stage. The precipitation of hydrated phases such as $C-S-H$ contributes to the hardening of the tailings-cement paste. Portlandite [$Ca(OH)_2$] can also precipitate under some conditions. In addition, if sulphates are present (sulphate contained in cement or sulphates produced from sulphide oxidation), gypsum or sulphony-aluminate phases can also precipitate. Moreover, hydration reactions occur slowly at this stage.

Kesimal et al. (2004) determined the strength gain of the tailings with the addition of PKC (Portland composite cement)/B-type binder currently used in the paste plant in Turkey. Additionally, PKC/A-type binder was chosen to compare the tailings in terms of strength gain. It was found that for high sulphide bearing tailings, neither binder was effective or suitable to provide adequate long-term strength for paste backfilling operations, although paste backfill samples developed high early strength at 28 days of
curing. The main conclusion made from this experimental study was that the presence of sulphide-rich compounds could cause deterioration in the hardened paste matrix due to sulphate attack.

Benzaazoua et al. (2004b) investigated the geochemical behaviour of European gold cemented paste backfill. It was observed that the dissolution of portlandite (which forms in excess in lime rich mixtures) was coupled to the precipitation of arsenic containing compounds, which immobilizes this toxic element. The transfer of contaminants inside paste samples was minimized due to the low permeability of the paste and the in situ precipitation of calcium sulphates and arsenates. These leaching tests showed that lime rich cement has a high retention potential for arsenic, even though its porosity is increased by the dissolution of portlandite at the periphery of leached specimens. The calcium content of the binding agent was found to be the main factor in arsenic fixation. A cemented paste rich in portlandite establishes pH conditions and calcium activity that are favourable for the inhibition of arsenopyrite oxidation. Additionally, the carbonation of portlandite at the leaching front was reported be the factor for some arsenic release as revealed by optical and SEM microscopy. However, the observed weathering fronts remained small even in long duration experiments.

Deschamps et al. (2008) stabilized sulphide- rich acid generating mine tailings (Acidity Potential = 953 kg of CaCO$_3$/t) using surface paste technology by adding 2 wt. % of Type GU cement. The pH of the leachate from column tests remained above 8 during the entire
experiment, while the pH of the unceemented tailings became acidic and reached approximately 4 at the end of the leaching tests. These results demonstrated that surface paste disposal could be an effective method to manage acid generating tailings through the addition of small amounts of binder. However, detailed field scale and long-term tests were identified by the authors to be necessary before field application.

Ercikdi et al. (2009a) noted that the mechanical performance of a binder in cemented paste backfill of sulphide-rich tailings is strongly associated with its susceptibility to sulphate attack. These authors concluded that ordinary and sulphate resistant cement binders alone are not particularly suitable for cemented paste backfill of sulphide-rich tailings at low binder dosages (e.g. 5 wt. %) for the maintenance of long-term mechanical strength.

2.5.1.1 Incentives to curtail Portland cement use in sulphidic tailings cemented paste formulations

2.5.1.1.1 Portland cement price and haulage cost

Binder cost represents a significant fraction of the operational cost of mining operations. Literature substantiates that approximately 69% of the total underground mining operations in Ontario (~65% in Canada) employed some form of backfill support (Mining Sourcebook 1994). According to Hassani et al. (2007b), backfill accounts for approximately 20% of underground mining operational cost and, from this total amount,
75% is binder cost when Type GU cement is used as a sole binding reagent. The 1993 Canadian Minerals Year Book notes that the Ontario mining industry alone consumed 5-6% of the total Canadian Portland cement production with an estimated cost of CAD $75 million annually in the consolidation of backfill in underground mining operations. The high energy cost associated with cement production along with the remoteness of operating mining sites result in the high cost of Type GU cement. The unit cost of cemented paste tailings technology becomes significantly higher, particularly where rich mixes consuming more Portland cement are employed. With regard to the aforementioned statistics, Portland cement appears to be the most expensive component of cemented paste operations and hence becomes the primary setback in its use as a sole binder. Concomitantly, the cement industry is one of the leading industrial emitters of greenhouse gases, particularly CO$_2$ (Mehta, 2002). Cement production is an energy-intensive process and each tonne of Portland cement produced emits approximately 1 tonne of CO$_2$ into the atmosphere contributing to global warming (Worrell et al. 2001). Its increased manufacturing cost along with its recognition as a major source of CO$_2$ emission has made cement production a target of criticism among environmentalists.

2.5.1.1.2 Robust engineering design requirements and concordant higher cement consumption

The variability and complexity of mine waste materials and behaviour of cement in the individual composite matrices preclude a universally accepted generalized methodology for solidification of mine tailings. The rate of strength acquisition and the ultimate
strength at failure are among the key parameters for evaluating the effectiveness of a binder in hardened cemented matrices such as cemented backfills (Thomas et al. 1979). Research has shown that even a specific amount of Portland cement cannot produce and maintain the same mechanical strength performance parameters for solidified waste obtained from different mining operations. Moreover, researchers have reported diverse strength requirements for cemented paste fills depending on their specific applications in mining operations. For instance, Hassani and Bois (1992) suggested 0.24 to 4.3 MPa, whereas, Ramlochen et al. (2004) reported 0.5 to 5 MPa. In the light of wide variations that exist in the recommended target strengths, 3-8% Portland cement to total solids ratio is commonly used for the mixture design of paste backfills. According to Grice (1998), most backfilling operations/applications utilize up to 7% Portland cement to acquire a reasonable compressive strength. Such a high proportion of Portland cement can be a financial burden on mining industry.

Benzzazoua et al. (2004a) explained that the binder effect in cemented paste backfill formulations lies in its chemistry and its proportions in the tailings-binder mixture. The different binders produce altogether different mechanical strength for a given type of tailings. Since the cost of binder is the major material cost in paste backfill operations, it is important and necessary to identify economical but effective binders for optimization of binder composition.
2.5.1.1.3 Significance of sulphates in Portland cement based cemented paste tailings

Sulphidic cemented paste backfill containing Type GU cement as a sole binder has been established to be vulnerable to internal sulphate attack and subsequent progressive loss of structural integrity under certain conditions. In internal sulphate attack, the deterioration of hardened mortars and concrete is brought about by the action of sulphates present in the original mix in excessive amount, or in those formed from sulphur compounds other than sulphates, also present in the starting material (Skalny et al. 2002).

Several studies (Benzaazoua et al. 1999 and 2002, Hassani et al. 2001, Fall and Benzaazoua 2005, Kesimal et al. 2005, Ouellet et al. 2006, Ercikdi et al. 2009b and 2010a, Ouellet et al. 1998, De Souza et al. 1997) conducted on cemented paste tailings have confirmed that sulphates present in tailings water and those produced by the oxidation of pyrite FeS$_2$ (in a basic pH medium created by cement hydration) can react with free calcium ions produced by the dissolution of unstable portlandite [Ca(OH)$_2$], giving rise to the precipitation of swelling secondary gypsum (CaSO$_4\cdot$2H$_2$O) and highly expansive ettringite (3CaSO$_4$$\cdot$3CaO$\cdot$Al$_2$O$_3$$\cdot$32H$_2$O). Researchers have confirmed the phenomenon of internal sulphate attack in ordinary Portland cement based sulphidic tailings cemented paste and have observed secondary gypsum as an ubiquitous phase in such matrices. This secondary gypsum can create softening and swelling effects in the cement solidified matrices such as mortars and concretes and can be a possible source of backfill internal cracking and subsequent strength deterioration over time (Cohen and Mather 1991, Tian and Cohen 2000, Mehta 1983).
Fall and Benzaazoua (2005) argued that sulphate present in cemented paste tailings significantly influences strength parameters. This effect is intimately related to the sulphate concentration, curing time and the amount and chemical composition of the cement. Bellmann et al. (2006) analyzed the influence of sulphate solution concentration on the formation of gypsum in concretes. The results revealed that portlandite reacted to form gypsum at a minimal sulphate concentration of approximately 1400 ppm (pH~12.5). As well, at moderate sulphate concentrations (up to 1500-3000 ppm), gypsum formation is either not possible or cannot lead to the damage of the cementitious matrix because of the very low super-saturation and swelling pressure. Portland cement alone produces a relatively porous treated waste in stabilization processes (Means et al. 1995). The undesired oxidation of sulphide minerals within tailings before solidification using Portland cement and/or the high porosity within the solidified matrices, such as cemented paste can produce acidity (low pH conditions), metal remobilization, sulphate ions release and dissolution of formed hydrates (Fall and Benzaazoua 2005). At a pH <12, partial or total dissolution of portlandite and decalcification of C-S-H phases giving rise to calcium release from hydrates can be expected. This situation in turn increases the micro and meso-porosity of the cementitious matrix (Belem and Benzaazoua 2008).

Sulphates present in mine tailings pastes perform various functions depending on their concentrations. Such sulphates can contribute to early strength gain by virtue of filling pores with hydrated cement products and through the precipitation of hydrated sulphates along with modification of pore-structure below a concentration of 2000 ppm, However, depending on sulphate concentration, cement proportion, and curing time, the positive
effect of strength acquisition due to the presence of sulphates can have a negative effect (Fall and Benzaazoua 2005). According to Benzaazoua et al. (2004a), the inhibition stage of cemented paste likely occurs at a sulphate concentration range of 200-8000 ppm. For sulphate concentration of 8000 to 10,000 ppm, the precipitation of gypsum is possible and can contribute to the strength development within paste matrix. However, if the sulphate contents exceed 10,000 ppm, massive and detrimental precipitation of swelling secondary gypsum may be expected, which can be a source for an internal sulphate attack in cementitious matrix (Belem and Benzaazoua 2008). The generated volume of hydration products can be far in excess of the available pore volume, thereby creating internal stresses that can lead to expansion and, subsequently micro-cracking. According to Divet (1996), the expansive products resulting from the undesired chemical reactions between sulphates and Portland cement hydration can generate internal stresses of 70 to 200 MPa due to crystallization pressure, which can be a source of drastic deterioration in the cemented matrix. These phenomena can culminate in the loss of initially developed strength within cemented paste tailings.

Fall and Pokheral (2010) investigated the coupled effect of sulphate and temperature on the strength development of cemented paste backfill and argued that initial sulphate contents (>15,000 ppm) led to the absorption of a larger amount of sulphate ions by the C-S-H. The experimental results provided strong indications that binding of sulphate to C-S-H can lead to the formation of lower quality C-S-H, which, in turn, results in the decrease in the strength of Portland cement based paste backfill.
Additional water is normally required in paste backfill design in order to meet workability and pumpability requirements, therefore, the volumetric water content of paste backfill is always far in excess of the binder hydration requirements (Belem and Benzaazoua 2008). The additional water in paste backfill design can be either tailings process water, lake water, or municipal water. The sulphate salts content and pH of process water within tailings and additional water required to make desired consistency are important for paste backfill strength acquisition, durability and stability in the long-term. Acidic water and sulphate salts can also attack cementitious bonds within the paste backfill composite, leading to loss of strength, durability, and stability (Lawrence 1992, Wang and Villaescusa 2001, Benzaazoua et al. 2002 and 2004a, Fall and Benzaazoua 2005, Fall and Pokharel 2010). This phenomenon can be particularly more pronounced in cemented paste tailings due to its low cement content and high concentration of sulphates. The relatively low cement content in mine tailings paste containing high sulphur concentration causes significant dilution of the binder within cemented paste matrix, which may lead to (a) vulnerable pH buffering initially fixed by portlandite (~12.5), and (b) development of cohesion in the cemented matrix due to entanglement of hydrated phases as a result of grain residue in the tailings-binder mixture. Such conditions can result in progressive decrease in pH accompanied by dissolution of hydrates, i.e. release of \( OH^- \) ions and further formation of metal hydroxides (Benzaazoua et al. 1999).

The mining industry faces the need to appraise the cost benefits of binding agent addition to upgrade the mechanical properties of cemented backfill in underground mining
operations to cope with ground stability issues and to enhance productivity (Scoble and Piciacchia 1986). Consequently, there exists sufficient incentive to curtail Portland cement consumption without impairing the mine tailings paste performance. The high cost of portland cement as well as its alleged poor performance as a sole binder in the long term and today’s robust engineering design requirements for cemented paste tailings has prompted users to appraise less expensive and technically efficient substitutes for mine tailings paste formulations.

2.5.2 Pozzolanic materials

In recent years, there have been remarkable efforts in utilizing a variety of pozzolanic materials and industrial by-products in formulating cemented paste backfills in the mining industry not only to reduce Portland cement consumption but also to upgrade product performance. The use of pozzolanic or supplementary cementitious materials in cemented paste tailings as partial replacement for cement has also gained considerable interest. The matrices incorporating supplementary cementing materials, such as cemented paste tailings, exhibit unique characteristics that often make them more durable than Type GU cement based composites.

Pozzolans represent any siliceous or aluminosiliceous materials of amorphous rather than crystalline nature and of sufficient fineness, which are capable of reacting with lime in the presence of water to form insoluble cementitious products such as, hydrated calcium silicates (ASTM C595). Pozzolans serve as sources of reactive silica and, in the absence
of lime, normally do not possess self-cementing characteristics. The beneficial effect of the incorporation of pozzolanic materials on the overall strength and stability of cementitious matrices, such as cemented paste tailings, can be attributed mainly to the consumption of $Ca(OH)_2$ liberated during the hydration of Portland cement through pozzolanic reactions. The hydration reaction produces secondary $C-S-H$ that also decreases the capillary porosity of mortars and enhances significantly the paste-aggregate interface causing a reduction of sulphate ions diffusion and the transport of sulphate ions from solution to mortar (Irassar et al. 2000).

The contributing hydration products associated with internal sulphate attack mechanisms in Type GU cement based matrices are the monosulphate hydrate ($C_4ASH_{12}$), calcium aluminate hydrate ($C-A-H$), and calcium hydroxide ($CH$). The deterioration associated with sulphate attack can be controlled by either limiting or eliminating monosulphate hydrate and calcium aluminate hydrate in cement. This can be accomplished by limiting $C_3A$ content in Portland cement or by substituting a portion of cement by appropriate blending materials such as artificial or natural pozzolan (Mehta 1986). The latter option can utilize by-products from a variety of sources to not only ameliorate product performance and increase technical benefits but also reduce cement utilization favouring reduced carbon emission and therefore supporting sustainable development.
2.5.2.1 Natural pozzolans

Natural pozzolans, such as volcanic tuff and pumice, used in the manufacturing of blended cements may be considered as alternate and economical pozzolanic materials for cemented paste tailings (Ercikdi et al. 2010b). Natural pozzolan addition enhances the sulphate resistance of low C₃A Portland cements principally due to the calcium hydroxide reduction in mortars, which delays and thwarts gypsum formation. The phenomenon is more pronounced at paste-aggregate interface. Mortars with pozzolans show much reduced expansion and high retention of strength in sulphate rich environments instead of C₃S content of cement (Irassar et al. 2000).

Ercikdi et al. (2009b) and (2010b) examined the use of natural pozzolans, such as the volcanic tuffs (Akkus Trass and Fatsa Trass) and pumice as a partial replacement for Portland cement in cemented paste backfill of sulphide-rich tailings (26.2% sulphides). The pozzolanic activity of the natural materials was found to be intimately related to their respective reactive silica content. The incorporation of the natural pozzolans at 10-30 wt% was shown to slow down the rate of development of strength of CPB specimens. Only pumice appeared to mitigate the long-term stability of cemented paste backfill samples using a higher dose (up to 30 wt %) by virtue of its high pozzolanic activity compared with the other pozzolans tested.
2.5.2.2 Artificial Pozzolans

According to Malhotra and Mehta (1996), artificial pozzolans or supplementary cementing materials provide engineering, economical, and ecological (environmental) benefits for the cement and concrete industry and some knowledge transposition has also been employed in upgraded cemented paste tailings formulations as evident by the exhaustive collection reported in the following sections.

2.5.2.2.1 Pulverized coal ash or fly ash based binders

Fly ash is a by-product of coal burning power plants, and is often composed of predominantly silt-sized, spherical and amorphous ferro-aluminosilicate minerals (Sale et al. 1997). In Canada references for specification is given by CSA A3001 (2003), whilst a similar document in the United States is ASTM C618 (2003). According to the Canadian Standards Association specifications (CSA A3001) the ashes are classified as low lime Type F ash ($CaO \leq 8\%$), medium lime Type CI ($8\% < CaO \leq 20\%$), and high lime Type CH ($CaO > 20\%$). Two major types of fly ash are specified in ASTM C618 based on their chemical composition, which is highly dependent upon the type of coal burned: Class C fly ash and Class F fly ash. The sum of three major oxides, namely $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ has a minimum value of 50% for Class C fly ash and 70% for class F fly ash. Class C fly ash produced from burning subbituminous and some lignite coal is generally composed of 50 to 90% calcium aluminosilicate glass manifested as solids and hollow spheres. The crystalline phases include relatively chemically inactive phases such as quartz, mullite, ferrite, spinal, and hematite. Class C fly ash possesses cementitious
properties in addition to its pozzolanic properties, and is capable of counteracting the acid potential of mine waste due to its high calcium content (Roy and Griffin 1982). Class F fly ash is also known as low lime fly ash generally contains CaO content less than 10% and usually produced from anthracite and bituminous coals, classified into class F fly ash (Ravindra 1986).

Partial replacement of Portland cement with fly ash in mine tailings pastes formulations has been investigated by several researchers (Weaver and Luka 1970, Manca et al. 1983, Yu and Counter, 1988, Udd and Annor, 1993, Amaratunga and Yaschyshyn 1997, Amaratunga and Hein 1997, Benzaazoua et al. 1999, Bernier et al. 1999, Hassani et al. 2001 and 2007a, Yilmaz et al. 2008, Godbout et al. 2007). Hassani et al. (2001) evaluated the stability of high sulphate paste fill containing cement alone and Portland cement-Class C fly ash in a sulphate-rich environment. It was found that Portland cement alone is not a suitable binder to provide the long-term stability for paste backfill due to the formation of calcium aluminate compounds. However, cement in conjunction with Class C fly ash manifested a more resilient matrix in the long-term despite a longer curing period for strength attainment. In another study, Hassani et al. (2007a) investigated the effect of binder on classified tailings and blended tailings/sand backfill systems. It was found that that an increase in binder amount produced a corresponding increase in unconfined compressive strength regardless of the type of backfill. Of the mixtures investigated, those containing classified base metal mine tailings exhibited higher compressive strengths than tailings-sand backfills at similar binder compositions.
Regarding the binder composition, the use of 50% fly ash as a replacement for Portland cement yielded compressive strengths exceeding that of Portland cement alone.

Bernier et al. (1999) conducted laboratory investigation before the implementation of cemented paste backfill at Brunswick Mining Division, Noranda Inc. and reported decreased cured paste strength containing ordinary Portland cement as a sole binder after 90 to 120 days. A moderate pulse of secondary ettringite formation along with white cluster of gypsum was considered a cause of strength deterioration around 120 days of curing. Partial substitution of ordinary Portland cement with Class F fly ash in binder was reported to improve the sulphate resistance of resulting paste.

Benzaazoua et al. (1999) conducted physical, chemical and mineralogical characterization of paste backfill using in-situ cores collected from a stope. The hardened paste backfill samples contained sulphide tailings (16.8% S) and 4.5 wt. % binders (mix of fly ash (40%) and ASTM Type I (60%). Chemical and mineralogical analysis revealed that the presence of sulphides in the tailings caused dissolution of the calcic phases of the cement hydrates and promoted the formation of swelling phases, which in turn induced a deterioration of the cemented backfill. The partial replacement of fly ash was also shown to improve the sulphate resistance of paste backfill.
Ramlochan et al. (2004) conducted microstructural investigation and chemical investigations of hardened mixtures of paste backfills using scanning electron microscopy. The binder used for the mixtures consisted of 50% Portland cement and 50% fly ash. The binder content expressed as the mass of cementitious material relative to the total mass of solid constituents (cementitious materials plus tailings) were 0.05, 0.15, and 0.70, respectively. It was concluded that binders with high proportions of a low to moderate lime fly ash are not suitable for use in paste backfill mixtures, whereas, high-lime fly ashes (Class C fly ash) would likely be more appropriate for paste backfills, and can be used in greater proportions for resilient paste backfill matrices.

Yu and Counter (1988) studied the use of fly ash as a binder for consolidated backfill. They demonstrated that Class C fly ash was capable of replacing 60% of the Portland cement when a three-month curing period was allowed, and 33% of the Portland cement when only a one-month curing period was available providing a considerable cost savings.

Amaratunga and Hein (1997) evaluated the effect of mixing fine gold mill tailings in the form of agglomerated tailings pellets with different binders on the strength and stiffness characteristics of a total tailings cemented paste fill. The addition of agglomerated fine tailings pellets to create an agglomerated tailings paste fill, resulted in a 133% increase in compressive strength and a 466% increase in modulus of elasticity when compared to total tailings paste fills of the same consistency and binder content. Binder dosages of
3%, 5%, and 7% in various Portland cement-fly ash combinations were used. The authors concluded that partial substitution of Portland cement with Class C fly ash to produce high modulus paste fill is economical and does not greatly compromise paste fill strength or stiffness.

2.5.2.2.2 Slag based binders in cemented paste tailings formulations

Pyrometallurgical processes used to produce iron, zinc, copper and lead generate slag as a byproduct. Metallurgists classify slag as either basic or acidic: the more basic the slag, the greater its hydraulic activity in the presence of alkaline activators (Hewlett 2001). Slag generally requires grinding to develop the fineness and reactivity when required for use as a partial replacement of cement or other activator, and can typically replace more cement than fly ash for the same strength levels, depending on the fineness of the grind. Doube and Bakker (1986) have defined two parameters that determine the hydraulic properties of slag: chemical composition and vitreous state or glassiness.

2.5.2.2.2.1 Ferrous slag

Ground granulated blast furnace slag (hereafter SL) is extensively used in the concrete industry because of its excellent cementitious and pozzolanic properties. SL is a nonmetallic byproduct of iron manufacturing and consists essentially of silicates and aluminosilicates of calcium and other bases, which is developed in a molten condition simultaneously with iron in a blast furnace, then water chilled rapidly by immersion in
water to form glassy granular particles, and then ground to cement fineness or finer (ACI Committee 233, Bouzoubaa 2005). The $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, and $\text{MgO}$ contents of SL are higher than those of typically found in Type GU cement, whereas, $\text{Fe}_2\text{O}_3$ and $\text{CaO}$ are lower. Most slags hydrate by themselves, while some need activators (alkalis or lime) for their hydration mechanisms. In order to produce a slag with good pozzolanic properties, it is required to be in an amorphous state, rather than crystalline state. An excellent reactive slag can be readily achieved by grinding solid slag, which increases its surface area.

During the hydration of Portland cement-slag binder systems, the calcium silicate glass in the slag becomes soluble in the alkaline pore solutions provided by the initial reactions of the Portland cement and reacts to form secondary growths of calcium silicate hydrates ($C\text{-}S\text{-}H$). These calcium silicate hydrates are analogous to those formed from Portland cement, but the Ca/Si ratio is lower (Hooton 2000). The enhanced amount of $C\text{-}S\text{-}H$ in such matrices boosts the compressive strength of the resultant mortars such as cemented paste tailings. The initial rate of reaction between slag and water is slower than that of Portland cement and water. This also indicates a concordant slower strength acquisition process in slag based binder systems. However, both materials react at early ages (Regourd 1986). Slags are generally capable of sustaining their hydration reaction for long curing periods in the presence of water, lime, and alkalis and can be successfully used as binding agent in mine backfills (McGuire 1978). When SL combines with Portland cement, the hydroxyl ions released during cement hydration attack the glassy structure of the SL and facilitate hydration. Slag hydration products reduce pore sizes and enhance cemented paste densification (Lawler 2007).
In Portland cement-slag systems, the Portland cement component begins to hydrate first followed by reaction with slag, which releases calcium and aluminum ions into solution. Later on, slag reacts with alkali hydroxide and is followed by reaction with $Ca(OH)_2$ to form more $C-S-H$ gel (Neville 1995). Slag develops its cementitious properties far too slowly to be of practical use unless its hydration is activated by the addition of calcium compound such as Portland cement. In slag-Portland cement systems, two activators play important roles for slag activation, namely, the gypsum as sulphate activator, and the portlandite $Ca(OH)_2$ liberated by the hydration of clinker silicates $C_3S$ and $C_2S$ (lime activation). The release of alkali ($Ca^{2+}$) and hydroxyl ($OH^-$) ions during the hydration of Portland cement raises the pH of the pore solutions that triggers the hydration reactions for cement-slag systems. The silica glasses become soluble in the alkaline solution, giving rise to secondary growths of calcium silicate hydrate, which further fills the capillary pore space left by prior hydration products of Portland cement (Hooton 2000). Ettringite is also a key hydration product in Portland cement-slag systems (Juenger et al. 2006).

The hydration mechanism of a combination of ground granulated blast furnace slag and Portland cement is slightly more complex than that of a Portland cement alone. The hydration reactions involve the activation of the SL by alkalis and sulphates to form its own hydration products. Some of these mingle with the Portland cement hydration products to form further hydrates, which have a pore blocking effect. The resultant hardened cemented matrix has more of the very small gel pores and fewer of the much larger capillary pores for the same total pore volume. However, the rate of strength

Belem et al. (2000) used polymetallic tailings containing 16% and 5% sulphur to produce various paste backfill mixtures using Portland cement, slag, and fly ash-based binders. The mechanical behaviour of the backfill was investigated through uniaxial and triaxial compression testing. It was concluded that the mid-term (91 days) mechanical strength increased as the proportion of binder increased regardless of the curing time, the tailings type or the binder type used in the mixture and hydration of the binders directly related to the particle size distribution and the mineralogy (sulphur content) of the tailings. Moreover, the long-term (112 days) cohesion C and angle of internal friction (\(\phi\)) of the backfill depended on the binder type and its mode of hydration. The triaxial compression test results demonstrated that the cohesion of the backfill increased and the angle of friction decreased with an increase in the percentage of binder material. The slag based binder outranked all the other binders tested in imparting strength parameters of the resultant mine tailings pastes.

Ouellet et al. (2007) used ground silica to simulate tailings in paste backfill preparation with cementitious binders. It was observed that cemented paste backfill specimens made
with a mix of Portland cement-slag binder showed the highest percentage of fine pores and the highest UCS values. The fineness of the slag particles induced more effective water to binder cementitious effect than that of the other binders studied. Luo et al. (2003) and Niu et al. (2002) demonstrated that slag has a greater impact on pore refinement in Portland cement pastes, which in turn is responsible for the decreased permeability coefficient of the resultant matrix.

Benzaazoua et al. (2002) demonstrated that cemented paste backfill specimens produced from sulphide-rich tailings (32% S) using a mixture of Portland cement (20 wt%) and granulated blast furnace slag (80 wt%) as binder at 3-6 wt% binder dosage failed to attain any compressive strength over 91 days of curing period while those specimens from the tailings with low (5.2% S) and moderate (15.9% S) sulphide produced relatively higher compressive strengths. The authors concluded from these results that slag is not particularly appropriate for cemented paste backfill of high sulphide tailings but it can be readily used for low to medium grade sulphide tailings (< 32 % S).

Belem et al. (2001) demonstrated that the addition of blast furnace slag-Portland cement modified tailings pore size distribution in cemented paste backfill. The addition of only 5% wt. by dry mass of tailings decreased approximately the threshold diameter from 2 to 1 micron. This refinement of the pore size effectively reduced the hydraulic conductivity of the cemented paste backfill. However, the hydration process of cement-slag system is slower than that of Portland cement alone (Demirboga 2007).
Ercikdi et al. (2009a) evaluated the compressive strength trends of cemented paste backfill specimens prepared from ASTM Type I containing 20, 40 and 60 wt% granulated blast furnace slag as an admixture at 5 wt% binder dosage over 360 days. The rate and extent of the development of strength of cemented paste backfill specimens was observed to decrease with increasing amount of slag in the binder phase. Only the specimens containing 20 wt% slag were able to produce the desired industrially accepted compressive strength threshold of 0.7 MPa over the curing periods, although the addition of slag greatly mitigated the deterioration in the stability of paste backfill specimens i.e. only 4.7% loss in strength at 20% slag, but none at 40% and 60% slag. The strength acquisition characteristics of cemented paste backfill samples at the replacement levels higher than 20 wt% slag may be improved by increasing the total binder dosage.

Ramlochan et al. (2004) observed that the relative volume of interstitial space occupied by hydration products was greater when a binder consisting of blast-furnace slag and a small amount of Portland cement was used than when one with equal parts of Portland cement and fly ash was used. Consequently, higher compressive strengths were achieved with the former than with the latter at comparable water-to-cementitious-material ratios. The authors argued that blast furnace slag can be used in greater proportions in cemented paste backfill formulations and addition of lime to the binder can be beneficial in the activation of supplementary cementing material such as slag in order to attain finer structure of resultant paste backfill.
Godbout et al. (2007) observed that the proportion of binder has a direct impact on the reduction of hydraulic conductivity of cemented paste backfill. A higher proportion of binder leads to a correspondingly greater reduction in hydraulic conductivity. Based on the materials used in their research the authors concluded that Portland cement-slag binders outperformed cement-fly ash binders in the reduction of hydraulic conductivity of cemented paste backfill.

Douglas and Malhotra (1989) evaluated the potential use of SL as a replacement for Portland cement and lime in cemented mine backfill. The research used a variety of slags with different particle sizes, different tailings-binder ratios, along with lime content. It was found that a variety of slag-lime binders produced strength of 1 MPa after 28 days of curing, and the slag-cement binder performance outranked than both the slag-lime and Portland cement binders in formulating cemented tailings matrices.

Nantel and Lecuyer (1983) observed that 28 days compressive strength attained by mixtures of tailings-slag at a ratio of 90:10 was 0.35 MPa. According to the investigators, such values of strength were capable of filling some existing mine-out areas where further mining was not desirable.

Hassani et al. (2001) observed that the addition of hemihydrates (gypsum) as an activator in Portland cement-ferrous slag binder in making sulphidic paste backfill resulted in high
early compressive strengths, but left the composite vulnerable to sulphate attack due to expansive secondary gypsum formation within the matrix. Moreover, replacing hemihydrate with lime did not affect the strength results significantly but took considerably longer period of curing time to activate the pozzolanic properties of the slag compared to the hemihydrates.

Gollop and Taylor (1996) reported that by increasing the slag content in cement mortars from 69% to 92%, sulphate resistance could be significantly improved when exposed to sulphates. Moreover, the addition of 5% gypsum to cement containing 65% slag could result in an improvement in the sulphate resistance. Lea (1970) suggested that with aluminum oxide \( (Al_2O_3) \) content of less than 11 wt%, SL can aid greatly in inhibiting the detrimental effects of sulphate attack in cementitious matrices. Slags with higher \( Al_2O_3 \) content (\( >11\% \)) can provide additional alumina to the system and increase the potential for ettringite formation (especially in high \( w/c \) matrices such as cemented paste tailings). In the presence of additional sulphate in the mix, alumina from slag can react to form ettringite in the early stages of hydration. The alumina from slag is thus bound in ettringite that forms while mortar is still in the plastic state, and is not available for further reaction at later stages where it can instigate detrimental effect on hardened matrix.
2.5.2.2.2 Non-ferrous slag

SL has excellent cementitious properties, whereas base metal (copper, nickel, etc.) slags have limited properties. Thomas (1973 and 1979) tested non-ferrous slag (air cooled copper converter slag and air cooled dezinced lead smelter slag) for tailings solidification applications and reported those slags as non-pozzolanic. He further experimented and found that such slags can be converted to pozzolanic materials by re-melting and quenching making them capable of replacing some Portland cement. Atkinson et al. (1989) utilized both lime and gypsum to activate a copper slag. A mix containing 5.4% copper slag, 0.93% gypsum, and 0.75% lime attained a compressive strength of 1 MPa at 28 days of curing.

McGuire (1978) demonstrated that granulated nickel slag when quenched and ground to the fineness of cement possesses pozzolanic properties capable of binding hydraulic tailings. Yu and Counter (1983) evaluated the pozzolanic properties of ground copper slag and indicated that the compressive strength of a sand mixture with 2.5% Portland cement and 9% ground slag yielded strength equivalent to that of the same sand mixture with 5% cement, after a curing period of 112 days.

2.5.2.2.3 Ground Waste Glass as a partial replacement of Portland cement

Soda-lime glass is the most frequently manufactured form of container glass, e.g., bottles, pots, blown glass (decorative), and flat glass (doors, window). According to US EPA
(1990), soda-lime glass production is approximately 77% of the total glass production in the United States, and is generally a mixture of $\text{SiO}_2$ (~75%), $\text{Na}_2\text{CO}_3$ (~15%), and $\text{CaCO}_3$ (~10%). Waste glass in finely ground state contains relatively large quantities of silicon and calcium, by virtue of which it can be used as pozzolanic material in the concrete industry.

Archibald et al. (1999) conducted strength comparison for a range of normal Portland cement and ground waste glass-consolidated slurry and paste backfill products with 100% cement-consolidated products as control standard materials. In the case of slurry and paste backfill mixtures, up to 35% of the Portland cement binder replacement with ground waste glass material demonstrated excellent strength characteristics. Ground waste glass was found to be capable of providing equivalent or better backfill strength characteristics than normal Portland cement up to 224 days of curing.

De Souza et al. (1997) studied glass fill for potential use in cemented backfill applications. The investigation indicated that 15% and 25% replacement of cement with glass provided equivalent or improved compressive strength response and improved the Young’s Modulus for most of the backfills studied, albeit, some tailings-binder mixtures experienced considerable strength loss after 28 days of curing as the result of massive sulphate attack. Sargeant et al. (2007) reported that ground waste glass was effective as a
replacement for ordinary Portland cement up to 15 wt% in the cemented paste backfill of low grade sulphide tailings (2.69% $S$).

In another study, Archibald et al. (1995) demonstrated that ground waste glass can be an effective partial replacement for normal Portland cement to consolidate mine backfill mixtures depending on the degree of pozzolanic reactivity of the different ground waste glass materials. However, base metal mine tailings consolidated with both Portland cement and Portland cement-waste glass binders were found to be susceptible to long-term strength deterioration as a result of sulphate attack. It was concluded that a cement-waste glass composite binder containing 15 to 35% waste glass, with construction sand had a higher strength than the same aggregate mixed with 4.76% normal Portland cement.

2.5.2.3 Cement-pozzolan system induced functional modifications in tailings cemented pastes

The utilization of pozzolanic additives in cemented paste tailings performs a variety of functions that can rejuvenate the properties of hardened mine tailings paste. The dominant modifications induced by the use of pozzolanic additives are discussed in the subsequent sections.
2.5.2.3.1 Refinement of cemented paste tailings pore structure

The properties of cemented paste tailings are largely governed by the volume and distribution of pores in the matrix. Porosity in cemented matrices consists of the space originally occupied by water in fresh mortars and concrete (water-to-cement ratio) minus the volume of new solids formed as the cement hydrates, i.e., the degree of hydration (Hooton 2000). The incorporation of pozzolanic materials results in transformation of hydrates within cemented paste matrix. The calcium silicate glass in the pozzolanic additive, such as blast furnace slag or fly ash, becomes soluble in the alkaline pore solutions provided by the initial hydration of ordinary Portland cement and reacts to form secondary growths of calcium silicate hydrates (C-S-H). These calcium silicate hydrates are analogous to those from Portland cement, but the calcium to silica ratio is lower. These additional hydration products serve to improve the microstructure of cemented paste tailings leading to lower porosity and permeability mainly due to mineral precipitation. Apart from the porosity reduction by virtue of Portland cement hydration, these secondary hydrated mineral precipitates play a role to fill the void spaces or micropores within the matrix. These hydration products in turn act as barrier against moisture and oxygen ingress, and hence alleviate the oxidation of pyrite present in the matrix (Belem et al. 2002, Benzaazoua 2002 and 2004b, Fall and Benzaazoua 2005, Ercikdi et al. 2009b).
2.5.2.3.2 Densification of interfacial transition zone surrounding tailings grains

The voids created by water particle movement and space not occupied by solid components of cemented paste tailings are known to make a major contribution to porosity and permeability of matrix. Cemented paste tailings containing ordinary Portland cement alone as a sole binder is characterized by a relatively porous matrix. Its relatively lower compressive strength and higher hydraulic conductivity can be attributed to the high capillary porosity of the interfacial transition zone between the large tailings particles and the cement matrix. Hooton (2000) argued that grains of supplementary cementing materials such as slag near interfacial transition zones react (often later) with the local calcium hydroxide crystals originally produced by cement hydration to generate more $C-S-H$. The secondary $C-S-H$ growth fills the weak and permeable transition zones, improving concrete strength and attenuating both flow and ionic diffusion along the pathways within the matrix, such as cemented paste tailings.

Fall and Samb (2008) investigated the pore structure of cemented paste backfill containing ordinary Portland cement and reported that the porosity of the interfacial transition zone is intimately related to the strength characteristics of hardened matrix. The higher the porosity of the interfacial transition zone, the weaker the bond between tailings grains. The size of capillary voids is much larger at the interfacial zone (i.e., the region at the interface of the coarse tailings grains and the hydrated cement paste) compared to the bulk cement paste. The incorporation of reactive artificial pozzolans such as fly ash, slag, and natural pozzolans cause both grain and pore refinements. This occurs primarily due
to the production of Pozzolanic C-S-H and efficient packing of cementitious materials particles, leading to improved microstructure. An increase in reactive mineral admixture may or may not decrease the total porosity of the matrix; however, it decreases the fraction of total capillary pores with increased discontinuity between the pores resulting in the reduction of hydraulic conductivity (Marsh et al. 1985, Manmohan and Mehta 1981).

Figure 2.2 is a pictorial illustration elucidating the occurrence of Portland cement hydration process within cemented paste tailings enriched with sulphide minerals (pyrite, pyrrhotite), as well as the potential functional influence of Pozzolanic materials when used as partial replacement of ordinary Portland cement. Upon mixing with water OH⁻ ions are released, which buffer the pore solution at a pH between 12 and 13. Contingent upon the formation of primary C-S-H, the rate of hardening of cemented paste tailings increases. Concomitantly, portlandite forms which then further reacts with supplementary cementing materials or Pozzolans to generate additional C-S-H. Mortars containing Pozzolans undergo very low expansion and maintain high strength in sulphate rich environment as compared to the C₃S content of cement (Irassar et al. 2000). This could also improve the microstructure producing a denser particle packing with the likely reduction in porosity and permeability. In the absence of Pozzolanic additives, high contents of sulphate (> 10,000 ppm) present in tailings and/or process water can react with portlandite and tricalcium aluminate (C₃A) to form secondary gypsum with swelling properties (Fall and Benzaazoua 2005). This can result in an internal sulphate attack and
therefore endanger the structural integrity of cemented paste tailings (Belem and Benzaazoua 2008, Ercikdi et al. 2009a).

2.5.3 Potential utilization of cement kiln dust in cemented paste tailings formulations

Cement kiln dust (hereafter CKD) is an alkaline particulate material collected from cement kiln exhaust gases during the process of cement manufacturing. CKD consists of entrained particles of clinker, un-reacted and partially calcined raw materials, and fuel ash enriched with alkali sulphates, and other volatiles. According to the United States Environmental Protection Agency (US EPA 2008), 13-17 million short tons of CKD are generated per year. Fresh CKD can be categorized as belonging to one of four groups, based on the kiln process used and the degree of separation in the dust collection system (Collins and Emery 1983). There are two types of cement kiln processes: wet-process kilns, which receive feed materials in a slurry form; and dry-process kilns, which accept raw materials in pulverized dry state. In both of these processes, cement kiln dust can be collected in two methods: (a) part of the dust separated and returned to the kiln from the dust collection system, or (b) the total quantity of dust generated can be recycled or discarded as necessitated (Siddique 2006).

Apart from returning it to the kiln in cement manufacturing processes, the principal uses of cement kiln dust include (a) blending cements (Bhatty 1984); (b) soil improvement in
pavement applications (Miller and Azad 2000); (c) stabilization/solidification of wastes (Conner 1990, MacKay and Emery 1992); (d) liners and cover material for landfills (Ballivy et al. 1992) (e) neutralizing agent for agricultural lands (Taylor 1987); (f) controlled low-strength material (CLSM) (Williams 2005).

The physical, chemical, and mineralogical compositions of CKDs are determined by the raw materials used to produce clinker, type of kiln operation and fuel, and individual plant practices including dust collection systems (Pavia and Regan 2010, Dyer et al. 1999). CKD generated from dry-process kilns generally has a higher calcium content (CaO), whereas, oil or gas fired kilns liberate dust rich in K2O (Adaska and Taubert 2008, Siddique 2006). CKD contains considerable amounts of silica, alumina, and ferric oxide; and erratic quantities of sulphur, chlorine and alkalis which tend to be higher than those in Portland cement (Pavia and Regan 2010). A significant portion of the dust is soluble in water and the resulting solutions are highly alkaline and caustic (Dyer et al. 1999, Pavia and Regan 2010).

CKD consists mainly of partially calcined material with a chemical composition similar to that of cement kiln raw feed and contains the main oxides CaO, Al2O3, SiO2, and Fe2O3 in proportions that produce intrinsic cementitious properties (Kamon and Nontananandh 1991, Miller and Azad 2000, Wang et al. 2002, Pierce et al. 2003). The free lime (CaO) present in CKD has been found to be the most effective predictor of the
reactivity of a particular CKD and the amount and nature of the hydration products generated, and therefore, is a measure of its effectiveness as a cementitious stabilizer/binder (Boynton 1980, Bhatty 1984, Konsta-Gdoutos and Shah 2003, Lachemi et al. 2008). The quantity of free or available lime as well as alkalis ($Na_2O$, $K_2O$) varies broadly between cement kiln dusts, which results in making some cement kiln dusts more reactive than the others.

The loss on ignition (LOI) is also a controlling parameter in the reactivity of cement kiln dusts. Higher LOI substantiates that a particular CKD is high in slow-reacting calcium carbonate and low in reactive free lime. Moreover, high LOI dusts contain a higher percentage of bound water within its chemical structure and, therefore, less free lime ($CaO$) is available to react and can also interfere with the hydration process. The variability of the LOI of CKD is an indication of the varying amounts of decarburization of the $CaCO_3$ in the clinker-making raw materials (Maslehuddin et al. 2008). A lower LOI of a particular CKD indicates lower $CaCO_3$ and higher free lime content is available. These $CaCO_3$ particles are inert and, therefore, do not participate in the hydration reactions (Konsta-Gdoutos and Shah 2003). In addition to the above mentioned factors governing the chemical (richness in sulphates, alkalis, and chlorides, etc.) and physical makeup of cement kiln dusts, its storage or disposal scenarios can have pronounced effect on reactivity. Long-term landfilled cement kiln dusts can be less reactive and, therefore, less cementitious due to loss of free lime as a result of carbonation.
Based on the statistics regarding the composition of cement kiln dust from 63 different sources the lower and upper quartiles for total CaO content are 19.4 to 61.3%, for free CaO are 0.0 to 27.2%, for SiO₂ are 2.2 to 34.3%, for Al₂O₃ are 1.1 to 10.5%, for Fe₂O₃ are 0.2 to 6.0%, for MgO are 0.5 to 3.5%, for SO₃ are 0.02 to 17.4%, for K₂O are 0.1 to 15.3%, for Na₂O are 0.0 to 6.3%, and for LOI are 4.2 to 42.4%, respectively (Sreekrishnavilasam et al. 2006).

A few published papers have highlighted the beneficial use of CKDs for the alkaline amendment of sulphidic waste (Doye and Duchesne 2003, Duchesne and Doye 2005). However, no detailed investigation has been reported on utilizing the cementitious properties of CKDs for solidification/stabilization of mine tailings. Tariq and Nehdi (2007) conducted preliminary work on the use of cement kiln dust in paste backfill formulations and examined the strength development of paste backfill prepared using mine tailings and industrial by-products (cement kiln dust and Class F and Class C fly ash) with or without Portland cement. It was concluded that industrial by-products (used either as single binder or as partial replacement for Portland cement) can be effective in producing more resilient backfill mixtures.
2.5.3.1 CKD as an activator and accelerator for pozzolans used in cemented paste tailings

Research has demonstrated that CKD can act as alkaline accelerator for latent hydraulic substances including ground granulated blast furnace slag and as alkaline activator for different aluminosilicate materials used in mortars and concretes (Sprouse 1984, Xu and Sarker 1995, Konsta-Gdoutos and Shah 2003, Buchwald and Schulz 2005). The solubility of $Si, Ca, Al$ and $Mg$ in cementitious matrices are pH dependent. The equilibrium solubility of silica is low at pH below ~11 (Sreekrishnavilasam and Santagata 2006). Highly alkaline pore solution created by free calcium rich cement kiln dust is capable of disintegrating the solid glassy network of ground granulated blast furnace slag to produce reactive silicate and aluminate species when attacked by ($OH^{-}$) ions. The activation or dissolution rate of supplementary cementing materials with latent pozzolanic properties depends on the alkali concentration of the reacting system (Wang et al. 2007). The total alkalis ($Na_2O_{eq}$) present in cement kiln dusts can effectively trigger the activation mechanism of SL. In cement-slag systems, the slag grains can also accelerate the hydration of Portland cement by acting as nucleation sites for $C-S-H$ to precipitate out of solution and grow onto (Hooton 2000). The activation of the solids contained in pozzolanic materials by the highly alkaline environments created by cement kiln dust containing alkaline hydroxides, alkaline silicates and/or alkaline carbonates can result in high compressive strength in mortars and concretes (Song and Jennings 1999, Konsta-Gdoutos and Shah 2003, Buchwald and Schulz 2005).
CKD with its high alkaline soluble fraction can be added as an activator in blended cements containing fly ash and hydraulic slags enabling them to undergo cementitious reactions (Dyer et al. 1999). However, the inconsistencies in physical and chemical properties of CKD can affect such hydration mechanisms. The resultant hydration products and strength development are also dependent on a particular type and characteristics of CKD under consideration. Adequate initial alkali concentration and presence of sulphates are both considered vital for the activation of slag in CKD-slag systems. The hydration processes, hydration products, and resulting enhanced strength are principally determined by the free CaO content of a particular CKD (Amin et al. 1995, Konsta-Gdoutos et al. 2003).

Pozzolanic processes involve siliceous and aluminosilicate materials that form cementitious substances when combined with a cementitious material (such as CKD) and water. Many factors such as the particle size, silicate content, composition and crystal structure of the silicate, degree of hydration, calcium magnesium ratio, among others determine the rate and extent of long-term hydration reactions of CKD-fly ash systems (Conner 1990). The effectiveness of fly ash as a binder depends on its alkalinity equivalent, which is indicated by the amount of calcium oxide (CaO) present. It also depends on its reactive silica, carbon and iron contents, fineness, and particle size (Cabrera and Gray 1973, Ravina 1980). CKD-slag systems are analogous to GU-slag systems in hydration processes since CKD also serves to activate slag resulting in precipitation and accumulation of hydration products. The early age hydration products are highly contingent upon inherit chemical characteristics of CKD under consideration,
however, later hydration products essentially include $C-S-H$ gel and the stable sulphoaluminate hydrate ettringite and are responsible for enhanced strength development (Konsta-Gdoutos et al. 2003).

Blast furnace slag possesses latent hydraulic reactivity however; its hydration in pure water is particularly slow under normal conditions due to the development of aluminosilicate coatings on slag grains that prevent hydration reactions from proceeding. Moreover, high glass content of blast furnace slag also requires elevated alkaline conditions for chemical hydration (Zeghichi et al. 2005, Juenger et al. 2006, Sreekrishnavilasam and Santagata 2006). This can be readily achieved with basic reactors such as calcium hydroxide obtained from the addition of sufficient amount of Portland cement, calcium sulphates or other calcium and alkali rich compounds such as CKD.

2.5.4 Significance of ternary oxide combinations for cementitious or/and pozzolanic reagents in mine tailings solidification applications

The compositional characteristics of Portland cement and other reagents commonly involved in cement based solidification processes can be best depicted with the aid of a ternary diagram using the three oxides combinations, $(SiO_2)$, $(CaO+MgO)$, $(Al_2O_3+Fe_2O_3)$ as shown in Figure 2.3. All of these reagents have the same active ingredients as far as solidification reactions/processes are concerned (Popovics 1970, Conner 1990). This ternary diagram can be used for preliminary screening of materials
used as binders and for identifying means for strengthening the cementing and durability characteristics of the resultant cementitious matrices. The more the binder tends towards the $SiO_2$ pole, the higher would be the durability of the cement-based composite (Skalny and Daugherty 1972, Conner 1990, Benzaazoua et al. 2002). For instance, cement kiln dust and slag exists adjacent to the zone occupied by the Portland cements enhancing their cementitious properties under normal conditions. Lime ($CaO$) rich cement kiln dust can push slag towards more effective zone when mixed with it. Since pozzolanic materials such as slag and fly ash need excess lime or portlandite or $Ca(OH)_2$ as activator in pozzolanic reactions to exhibit their cementitious properties, the addition of CKD to Portland cement can be advantageous. However, other factors to be considered in formulating the mixture design include characteristics of the material to be solidified/stabilized other than physical and chemical compositions of the supplementary cementing material/additive, such as the degree of glassiness, which must also be taken into account (Bernier et al. 1999).

### 2.5.5 Calcium sulphate substances

Calcium sulphate dihydrate ($CaSO_4\cdot2H_2O$) or gypsum is a naturally occurring material and can be calcined to produce calcium sulphate hemihydrate ($CaSO_4\cdot1/2H_2O$) and calcium sulphate anhydrite (anhydrous calcium sulphate or $CaSO_4$) (McAdie 1964, Ridge and Beretka 1969, Combe and Smith 1971, Khalil 1982, Kuntze et al. 1989, Deutsch et al. 1994).
Petrolito et al. (2001) tested the unconfined compressive strength of a variety of β-hemihydrate-tailings and Portland cement-tailings cured mixtures. It was shown that one day compressive strength attained by gypsum based specimens containing approximately 20 wt.% hemihydrates was 1MPa, whereas, approximately two and half to four times more hemihydrate than cement was used to achieve a comparable unconfined compressive strength.

Amaratunga and Hmidi (1997) investigated the use of gypsum β-hemihydrates (the most economical form of calcined gypsum) and Portland cement in cold bonded agglomeration of fine gold mill tailings. It was concluded that a higher strength of the resultant pellets can be achieved in the cold bonded agglomeration process by adding a moderate amount of gypsum β-hemihydrate to ordinary Portland cement as a binder instead of using Portland cement alone.

Petrolito et al. (1998) determined the unconfined compression strength of a variety of β-hemihydrate/tailings and cement/tailings specimens. The results revealed that typical target strengths can be achieved with calcined gypsum using between 2.5 to 4 times the amounts of Portland cement. It was also noted that gypsum attained maximum strength relatively quickly (1 to 10 days) compared to cement (around 28 days). Udd and Annor (1993) investigated the use of naturally occurring anhydrite (anhydrous calcium sulphate)
in formulating backfill material using mill tailings. The results were promising; however, higher binder dose was determined to achieve desired backfill strength.

### 2.5.6 Sodium silicate

Sodium silicate is produced by smelting sand with sodium carbonate at high temperature (~1200°C) and can be used as a possible replacement for cement. Hassani et al. (2007b) investigated the use of sodium silicate as a partial or total replacement for cement in stabilized sand backfill. It was recorded that finding the optimum dose of sodium silicate for a mine fill could present a considerable challenge in such operations. Firstly, sodium silicate is much more expensive than cement and, secondly, the effects of sodium silicate percentages revealed that sand paste fill samples with 4% sodium silicate binder had lower strength values than sand paste fill samples made of 2% binder. However, sodium silicate based paste backfill could produce the strength required to allow for a faster mining cycle. It was concluded that the material can be used as an additive to cement in stabilized backfills due to considerable advantages including (a) lower hydration heat compared to cement and, hence, lower risk of thermal cracking in thick structures, (b) reduced setting time, and, (c) higher cement replacement capability.

### 2.5.7 Metal sulphide (pyrrhotite) as binder

Swain (1973) demonstrated that the use of the oxidation products of pyrrhotite could be used as a satisfactory cementing agent for backfill. A concentration of 8% by weight pyrrhotite in an inert matrix with tailings:slag ratio of 4:1 produced a repeatable high
value of the unconfined compressive strength (1.8 MPa) in controlled conditions of
drainage and subsequent aeration. Barsotti (1978) also examined the binding capacity of
pyrrhotite tailings and concluded that the oxidation of sulphide minerals is vital for
impacting self cementing properties within the tailings. However, such chemical reactions
are generally intricate to control and can result in an unreliable binding and disrupting
production schedules that can jeopardize public safety.

2.6 Summary and conclusions

The use of cemented paste tailings for surface and underground disposal of acid-
generating tailings as an alternative to conventional or traditional strategies is opening a
new era in mineral waste management practices. The mining industry faces the need to
appraise the cost benefits of binding-agent in addition to upgrading the mechanical
properties of cemented paste tailings operations, namely, (a) underground backfill to cope
with ground stability issues and as an effort for higher productivity, and (b) surface
disposal application as a control technique aiming at restricting contaminants leaching by
solidification/stabilization of sulphidic mine tailings.

- Sulphidic cemented paste tailings containing Type GU cement as a sole binder
  has been established to be vulnerable to internal sulphate attack and subsequent
  progressive loss of structural integrity under certain conditions. A range of
  binders/additives have been successfully utilized to ameliorate the performance of
  sulphidic cemented paste tailings. The beneficial effect of the incorporation of
natural and artificial pozzolans on the overall strength and stability of cemented paste tailings can be attributed mainly to the consumption of $Ca(OH)_2$ liberated during the hydration of Portland cement through pozzolanic reactions to produce secondary $C-S-H$, that also decreases the capillary porosity of mortars and enhances significantly the paste-aggregate interface causing a reduction in sulphate ions diffusion and the transport. Utilization of pozzolanic additives in cemented paste tailings performs a variety of functions that can rejuvenate material properties of the resultant matrices including the refinement of pore structure and densification of interfacial transition zone surrounding tailings grains. The normal range of ordinary Portland cement replacement is 30-50% by fly ash, 20-60% by SL, and 15-35% by waste glass based on dry mass of cement.

- Binders with high proportions of a low lime fly ash are not desirable for use in paste backfill mixtures. Slags and high lime fly ashes (CSA Type C fly ash) would likely be more suitable for paste backfills, and can be used in greater proportions. Other materials including ground waste glass, calcium sulphate material, and sodium silicate have shown promising results in mine tailings paste formulations.

- Research into the incorporation of other materials that could chemically activate and accelerate slag and fly ash is also warranted in order to achieve the desirable technical and economic advantages. Both slag and fly ash rely on excess calcium hydroxide produced by the addition of ample Portland cement in order to complete pozzolanic reactions. Blast furnace slag possesses latent hydraulic reactivity however; its hydration in pure water is particularly slow under normal
conditions due to the development of aluminosilicate coatings on slag grains that prevent hydration reactions from occurring. High glass content of blast furnace slag also requires elevated alkaline conditions for chemical hydration, which is generally achieved by basic reactors such as calcium hydroxide obtained by the addition of sufficient amount of Portland cement.

- The rigorous approach suggested by the researchers in the form of a ternary diagram (Figure 2.3) for preparing more resilient cementitious matrices for wastes can be applied to evaluate CKD in cemented paste tailings formulations. Lime (CaO) rich cement kiln dust can push slag towards more effective zone when mixed with it. Since pozzolanic materials such as slag and fly ash need excess lime or portlandite [Ca(OH)₂] as an activator in pozzolanic reactions to exhibit their cementitious properties, addition of cement kiln dust in combination with a small addition of Portland cement can be more advantageous in generating enhanced durable and useful calcium-silica-hydrate (C-S-H). These reactions can increase long-term strength of solidified matrices, reduce permeability, thereby increasing the strength and durability.

- The normal range of Portland cement replacement is exclusively applied to binary binder systems containing Portland cement and pozzolanic additives. Ternary and quaternary binder blends may involve different replacement levels for which laboratory optimization is required. Utilization of CKD as a partial replacement of Portland cement in combination with slag and fly ash may offer potential benefits including the reduction of binder cost (reduced Portland cement use) and amelioration of stability for cemented paste tailings produced from sulphide rich
tailings. However, variability of CKD and its interaction with mine waste constituents can thwart the formulation of a generalized recipe for solidification of mine tailings, and further necessitate research to explore the optimal waste-binder proportion of the stabilized system components.

- The mining industry may be able to realize substantial public benefit from adopting the use of Portland cement replacement using a range of industrial by-products and other appropriate materials. In particular, reduction of landfill inventories of environmental challenging CKD can serve to establish a major role of the mining industry in terms of very positive environmental stewardship.

- The wide-reaching use of cemented paste tailings worldwide will continue to increase for ground and surface disposal applications, with innovative, more efficient and cost-effective binder explorations being incorporated to the cemented paste design and implementation.
2.7 References


Mining Sourcebook (1994) Canadian Mining Sourcebook (103rd Edition), Southam Magazine Group, Southam Inc.


Taylor, O. (1987) Flue Dust: A Concrete Idea? Soybean Digest, St. Louis, Missouri, USA.


US EPA (2008) Study on increasing the usage of recovered mineral components in federally funded projects involving procurement of cement or concrete to address the safe, accountable, flexible, efficient transportation equity act: A legacy for users.


Figure 2.1 Hydration of Portland cement (After Cocke 1990)
Fresh mixture of sulphide-rich and sulphate-rich cemented paste tailings

(\text{OH}^-) \text{ release on cement hydration: } 12 \leq \text{pH} \leq 13

Dissolution/hydration reactions
Hydration/precipitation reactions

- Portlandite \( \text{Ca(OH)}_2 \)
- Pozzolanic reactions
- Pozzolanic admixtures (slag, fly ash, silica fume, etc)
- Sulphide oxidation in presence of H\(\text{2}O \) and O\(\text{2} \)
- Formation of \( \text{SO}_4^{2-} \) and H\(+\)
- Acid and sulphate attack decalcification of C-S-H

Primary C-S-H
- C-S-H gel (cumulative)
- Gypsum \( \text{CaSO}_4.2\text{H}_2\text{O} \)

Secondary
- Ettringite \( 3\text{CaSO}_4.3\text{CaO.Al}_2\text{O}_3.32\text{H}_2\text{O} \)

Figure 2.2 Schematic diagram elucidating Portland cement based cemented paste tailings hydration stages and potential interaction with sulphates along with functional role of pozzolanic materials addition (Modified after Belem and Benzaazoua 2008, and Ercikdi et al. 2009b)
Figure 2.3 Ternary phase diagram showing common solidification and chemical fixation reagents (After Popovics 1970 and Conner 1990)
CHAPTER 3
ENHANCING PROPERTIES OF SULPHIDIC TAILINGS CEMENTED PASTE BY AUGMENTED POZZOLANIC REACTIVITY OF SLAG AND TYPE C FLY ASH USING HIGH CALCIUM CEMENT KILN DUST

3.1 Introduction

The alleviation of environmental threat posed by potentially acid generating mine tailings containing sulphide minerals, in particular, necessitates the adoption of efficient technologies to cope with the litany of prospective devastating ecological deterioration associated with acid rock drainage. Cemented paste tailings (surface disposal) or cemented paste backfill (underground disposal) technology is currently practiced in the mining industry in many industrialized countries including Canada, for managing sulphidic mine tailings. The technology is considered a viable alternative to other tailings management strategies for surface and underground disposal due to indispensable benefits including: (a) solidification and stabilization of sulphidic tailings for surface disposal with adequate structural integrity and efficient control over heavy metal leachability (Cincilla et al. 1997, Verburg 2002, Theriault al. 2003, Landriault et al. 2005, Shuttleworth et al. 2005, Bussière 2007, Godbout et al. 2007, Deschamp et al. 2008); (b) underground disposal of sulphidic tailings in the form of cemented paste backfill, thus reducing the associated environmental pollution; (c) increase in the available ore reserves by acting as secondary ground support pillars for mine stability; (d) the absence of free water in the paste fill system thereby eliminating the need for drainage requirements, which results in faster stope cycle time ;(e) higher achievable mechanical strength for a comparable amount of binding agents  (Thomas et al. 1979, Mitchell and Wong 1982,
Udd and Annor 1993, Brackebusch 1994, Amaratunga and Hein 1997, Benzaazoua et al. 2004, Ouellet et al. 1998, Le Roux et al. 2005, Belem and Benzaazoua 2008). Furthermore, stringent environmental policy favouring safer disposal of sulphidic tailings, increased public awareness, and costly alternate remedial options (mine effluent treatments, etc.) are additional grounds for adopting cemented paste technology at many mine sites around the world.

According to Ouellet et al. (2007), cemented paste tailings may be designated a controlled low strength material (CLSM) by virtue of its inherit material properties (ACI 1999). For instance, the hydraulic binder or cement content is customarily low (3 to 7 wt% of dry tailings), ratio of water to cementitious material (w/c) is generally high (5-15%), and unconfined compressive strength is routinely between 0.5 to 5 MPa (Ouellet et al. 2007, Hassani et al. 2007a, Ramlochan et al. 2004). Canadian Standards Association (CSA) Type General Use hydraulic cement (GU) or ASTM Type I ordinary Portland cement is customarily used as a the sole binder in developing paste for a range of mine tailings materials including polymetallic mine tailings, and up to 7 wt% (of dry tailings) of GU is considered adequate to ensure cemented paste fill or backfill stability in most mining applications/operations. The polymetallic mine tailings material itself is considered to be the primary source of reactive sulphides within paste in a proportion that may reach up to 60% (Fall and Benzaazoua 2005, Kesimal et al. 2004, Cayouette 2003). Among other sulphide minerals, pyrite ($FeS_2$) and pyrrhotite ($Fe_1.5S$) are the most commonly occurring sulphides in tailings material. These minerals are known to react with oxygen in the presence of water to produce low pH drainage (acidity), metal
hydroxides and sulphates (Evangelou 1995). Thus, sulphate ions can be inherently available in tailings either through sulphide mineral oxidation or from tailings process water, and can react with ordinary Portland cement in the presence of water while developing cemented paste. Researchers have validated the deleterious effects of sulphates present in sulphidic tailings on the overall strength and stability of cemented paste backfill (Bernier et al. 1999, Hassani et al. 2001, Benzaazoua et al. 1999 and 2002, Fall and Benzaazoua 2005, Ouellet et al. 2006, Ercikdi et al. 2009a). This phenomenon can be pronounced in paste due to its very low cement content and high concentration of sulphates. Moreover, the presence of sulphide minerals can lead to acid generation through the oxidation of tailings, in addition to the deleterious effects of internal sulphate attack caused by soluble sulphates in the cement based solidified/stabilized composite (Benzaazoua et al. 1999, Hassani et al. 2001).

The binder can represent up to 75% of the overall cost of the cemented paste backfill operations when ordinary Portland cement is used as sole binder (Grice 1998). CSA Type GU cement is customarily used as sole binder or occasionally blended with other pozzolanic materials known as supplementary cementing materials (SCMs) in cemented paste backfill operations. Such materials include but not limited to fly ash (Weaver and Luka 1970, Amaratunga and Yaschyshyn 1997, Benzaazoua et al. 1999, Hassani et al. 2001, Ramlochan et al. 2004, Yilmaz et al. 2008, Godbout et al. 2007), blast furnace slag (Belem et al. 2000, Benzaazoua et al. 2002, Fall and Benzaazoua 2005, Kesimal et al. 2005, Ouellet et al. 2006, Douglas and Malhotra 1989), silica fume (Ercikdi et al. 2009b), and waste glass (Archibald et al. 1999, De Souza et al. 1997). These binders are
incorporated to augment the durability as well as the strength of the mixture, and appreciably reduce the binder costs. The binder is utilized principally to develop sufficient mechanical strength for the paste backfill in terms of certain target dynamic and static load resistances. The rate of strength acquisition with respect to curing time and the ultimate strength at failure are among the key parameters for evaluating the effectiveness of a binder in hardened cemented paste backfills (Hassani et al. 2007a). The capital and operating costs associated with cemented paste tailings operations involving cementitious materials and disposal strategies are very much materials and site specific.

Cement kiln dust (CKD) is a particulate material collected from cement kiln exhaust gases in the process of cement manufacturing and consists of entrained particles of clinker, un-reacted and partially calcined raw materials, and fuel ash enriched with alkali sulphates, and other volatiles (Abeln et al. 1993). The physical, chemical, and mineralogical compositions of cement kiln dust are determined by the raw materials used to produce clinker, type of kiln operation and fuel, and individual plant practices including dust collection system (Pavia and Regan 2010, Dyer et al. 1999). CKD consists mainly of partially calcined material with a chemical composition similar to that of cement kiln raw feed and contains mostly oxides such as \(CaO\), \(Al_2O_3\), \(SiO_2\), and \(Fe_2O_3\) in proportions that produce intrinsic cementitious properties (Kamon and Nontananandh 1991, Miller and Azad 2000, Wang et al. 2002, Pierce et al. 2003). Cement kiln dust also contains varying quantities of sulphur, chlorine and alkalis that tend to be in greater quantity than those present in Portland cement (Pavia and Regan 2010). It is expected that cement kiln dust in composite binder systems can function as an alkali activator and
promote hydration of pozzolanic materials (ground granulated blast furnace slag and fly ash) by virtue of high alkali content, particularly $Na_2O$ and $K_2O$, favouring enhanced material properties of cemented paste tailings.

Selective cement kiln dust has been found to be quite promising in producing CLSM due to its valuable cementitious properties. A few published papers have mentioned the beneficial use of cement kiln dust for alkaline amendment of sulphidic waste (Doye and Duchesne 2003). However, to the present authors’ knowledge, no detailed investigation has been reported on utilizing the cementitious properties of cement kiln dusts for sulphidic mine tailings management. Tariq and Nehdi (2007) conducted a preliminary investigation of the potential use of cement kiln dust in cemented paste backfill preparation. However, the study did not investigate the use of composite cements comprising characteristically different cement kiln dusts in combination with pozzolanic materials (ground granulated blast furnace slag and fly ash) in high sulphide tailings cemented paste formulations.

In the present study, the short-and long-term performance evaluation of blended cements (containing cement kiln dusts, ground granulated blast furnace slag, Type CI fly ash, and Portland cements) in cemented pastes of sulphidic tailings was carried out over a curing period of 480 days. This period is well beyond the reported initiation period of UCS decline (~90 days) for sulphidic cemented paste tailings containing ordinary Portland cement (Hassani et al. 2002, Kesimal et al. 2005, Ouellet et al. 2006, Ercikdi et al. 2009a,
The unconfined compressive strength and micro-structure were selected as major performance evaluation indicators for the developed cemented pastes.

### 3.2 Unconfined compressive strength (UCS) of cemented paste tailings

Unconfined compressive strength (UCS) has been recognized as one of the major parameters in the design of cemented paste backfill systems and is a major consideration in assessing mineworkers’ safety. The UCS test has been extensively used by several researchers in laboratory optimization processes (Weaver and Luka 1970, Brackebusch 1994, Ouellet et al., 1998, Kesimal et al. 2004, Fall and Benzaazoua 2005), as well as in field investigations involving in-situ evaluation of hardened cemented paste backfill. Another reason for its wide use as an evaluation criterion is that UCS testing is relatively inexpensive and can be incorporated in routine quality control programs at mine sites (Fall and Pokharel 2010). A paste can be engineered to yield the requisite mechanical strength for a particular intended application. In underground mining operations, the mechanical stability is a desirable property of a mining backfill to withstand underground stresses (Fall and Benzaazoua 2005). For underground disposal, a compressive strength between 0.15 and 0.3 MPa is required to eliminate liquefaction (Bloss 2002). In open stoping operations, when free-standing wall faces are exposed during pillar recovery, a compressive strength of up to 1 MPa is desired to maintain cemented backfill solidity (Hassani and Archibald 1998, Belem and Benzaazoua 2003). When the paste backfill is used for roof support, strength values higher than 4 MPa are required (Grice 1998).
Surface disposal scenarios necessitate a minimum compressive strength requirement of 0.345 MPa for cemented waste such as paste fill (US EPA 1989).

3.3 Microstructural analysis

Microstructural analysis using Scanning Electron Microscopy (SEM) is a powerful technique to elucidate the microstructure and texture of a hardened cemented matrix such as mine tailings pastes, whereas, Energy Dispersive Spectrometry (EDS) coupled with the SEM can be employed to aid the identification of minerals and cementitious phases present. Such combined analysis can provide valuable information on the microstructure, hydration products, and other features that can be used in identifying the cause of mechanical strength attainment or decline for paste specimens prepared using varied binder reagents. Furthermore, the correlation between the textures of a range of hardened paste specimens with their corresponding UCS values facilitated the development of a rigorous approach for assessing paste quality.

3.4 Materials and methods

3.4.1 Mine tailings and binder reagents/additives

The tailings used in the present study were obtained from Mattabi mine located in Ignace, Ontario. The tailings were transported in sealed containers to control further oxidation. The physical, chemical, and mineralogical characteristics of the tailings (hereafter MT) were determined by preparing subsamples in accordance with the relevant standards,
established methodologies and test procedures. Laboratory analysis carried out on MT in accordance with ASTM D4318 revealed that the tailings sample had a liquid limit (LL) of 22%, a plastic limit (PL) of 18%, and plasticity index (PI) of 4%.

All cementing materials, supplementary cementing materials and cement kiln dusts samples used in the present study were provided by Cement Association of Canada (CAC). The cementing materials complied with Canadian Standards Association (CSA) A3001-03 including CSA Type General Use hydraulic cement (GU hereafter) and CSA Type High Sulphate resistant hydraulic cement (hereafter HS). The supplementary cementing materials used were ground granulated blast furnace slag (SL hereafter) and CSA Type CI (intermediate calcium) fly ash (FC hereafter).

The particle size distributions of MT, GU, HS, SL, FC, and all four cement kiln dust samples were obtained using a Mastersizer (Malvern Instruments) laser diffraction particle size analyzer and have been presented in Figures 3.1 and 3.2. The MT sample contained approximately 67% fines (< 75 microns) and 33% sand size particles (> 75 microns) (Figure 3.1). Based on the Unified Soil Classification System (USCS), the tailings were classified as ‘sandy silt’ or ML (ASTM D2487). The MT sample contained approximately 25% fines (< 20 microns). MT, SL, HS, FC and GU were found to have medium grain sizes of 40.1, 10.1, 15.0, 20.0 and 14.5 μm, respectively (Figure 3.1). The calculated values of coefficient of uniformity (Cu) and coefficient of curvature (Cc) for MT were 6 and 1, respectively. Additionally, the specific surface area of these materials
was determined using the Braunauer, Emmett, and Teller (BET) method and the results are presented in Tables 3.1 and 3.2. The specific gravity ($G_s$) of the tailings and binders/additives was measured in accordance with ASTM D854. The results are presented in Tables 3.1-3.2.

The chemical compositions of MT, GU, HS, SL, FC, and all the four cement kiln dusts used in this study were determined by a combination of X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Major oxides were determined by fusion XRF and the results are presented in Tables 3.1-3.2. MT sample was determined to contain 37.8 wt% $Fe_2O_3$ and approximately 12 wt% $S$ substantiating pyrite as major mineral present. The high loss on ignition value for MT tailings (19.4%) is indicative of loss of sulphur, as pyrite is burned off in LOI determination. A qualitative assessment of tailings mineralogy using powder X-ray diffraction (XRD) and Bruker D8 coupled with a semi-quantitative X-ray fluorescence analysis indicated the dominance of quartz (~42%) and pyrite (~40%). The other minerals identified were ~5% changoite ($Na_2Zn(SO_4)_2\cdot4H_2O$), ~5% linarite ($PbCuSO_4(OH)_2$), ~4% lanarkite ($Pb_2(SO_4)O$), and ~4% sidorenkite ($Na_3Mn(PO_4)(CO_3)$) as shown in Fig. 3.3.

Sulphate concentration in mine tailings process water was determined using an ion chromatograph (Waters® HCLP PUMP 515, Waters® 432 Conductivity meter). An injection volume of 50 mL was used for each sample with 20 minutes running time. The average of three results per sample was taken to ascertain the accuracy of each test. The
process water used in the cemented paste tailings preparation had a sulphate concentration of 13,730 mg/L. The main chemical characteristics of mixing water (process water) are listed in Table 3.4.

Type GU cement had a Bogue’s composition of 58.4% for tricalcium silicate (C₃S), 18.6% for dicalcium silicate (C₂S), 10.6% for tricalcium aluminate (C₃A) and 8.4 % for tetracalcium aluminoferrite (C₄AF). Type HS cement contained 60.3% C₃S, 22.3% C₂S, 4.0% C₃A, and 12.6% C₄AF.

The slag used in the present study met the specifications of CAN/CSA A3001-03. Lea (1970) suggested that with aluminum oxide (Al₂O₃) content of less than 11 wt%, SL can aid greatly in inhibiting the detrimental effects of sulphate attack in cementitious matrices.

The fly ash used in the present study had a cumulative SiO₂, Al₂O₃, and Fe₂O₃ content of less than 70%. In accordance with Canadian Standard Association (CSA A3001-03), the fly ash would be classified as CSA Type CI (medium calcium oxide contents fly ash) based on the determined chemical composition and CaO contents (16.9%).

CKD samples were obtained from cement manufacturing plants across Canada (see Appendix A.1). Four different cement kiln dusts (hereafter called DA, DH, DB, and DL)
were chosen in order to cover the range of high to low CaO, as well as high to low loss on ignition (LOI). DH had the highest CaO content (57.8%) followed by DA (52.4%), DB (34.7%), and DL (31.8%). DH had lowest LOI value (4.8%) followed by DA (5.1%), DL (31.1%), and DB (30.2%). The un-reacted or free calcium oxide, CaO (lime), was highest in DH (26.3%) followed by DA (22.8%) as determined by ASTM C25. The free CaO content in the remaining two cement kiln dusts was significantly low with 2.1 wt.% in DB and 1.3 wt.% in DL. The chemical compositions and physical properties of MT, GU, HS, SL and FC are presented in Table 3.1, whilst Table 3.2 contains the chemical and physical characteristics determined for all the four cement kiln dusts.

3.4.2 Methodologies and equipments

3.4.2.1 Cemented paste tailings specimens preparation for UCS tests

The constituents of each cemented paste tailings batch (various proportions of different binders recorded in Table 3.3, a predetermined amount of MT, mine tailings process water were weighed and mixed. An electrical Hobart A200 model mixer was used according to ASTM C305 for a mixing time of 5 minutes until a smooth consistency was achieved (Kesimal et al. 2004). The paste was then tested for its consistency using a slump cone apparatus in accordance with ASTM C143. The final slump (the difference in height between the top of the cone and the surface of the paste after removing the cone) was measured. The water contents of the paste mixtures ranged between 22.1% to 22.6% to provide ~180 mm (7 inches) slump, which is recommended to satisfy p umpability requirements for disposal (Hassani et al. 2001, Benzaazoua et al. 2002, Kesimal et al.
Specimens for UCS tests were prepared by pouring the mixtures into cylindrical, plastic, polyvinyl chloride moulds with a height to diameter ratios of 2 (104 mm in diameter and 208 mm in height). Seven holes (each 2 mm in diameter) were drilled into the bottom of each cylinder to allow bleed water drainage (Kesimal et al. 2004) (see Appendix A.2). The paste mixtures were poured into the moulds in one-third increments (by volume) and compacted as mentioned for the slump test (see Appendix A.3). Despite the holes in the bottom of cylinder, no bleed water drainage was observed, confirming undrained conditions of the samples. After placing caps on plastic cylinder moulds, they were placed in a humidity chamber maintained at 100% relative humidity (RH) and 25±2°C (analogous to underground mine conditions) until testing (see Appendix A.4).

3.4.2.2 Unconfined compressive strength (UCS) tests

The unconfined compressive strength (UCS) tests were performed in accordance with ASTM C39 on approximately 330 cemented paste specimens at curing ages of 7, 14, 28, 56, 90, 120, 150, 180, 270, 360, and 480 days. The tests were performed using Super ‘L’ Tinius Olsen Universal Testing Machine (UTM) at a uniform loading rate of 0.025mm/min (see Appendix A.5 and A.6). For each test at the specified curing time, there was very good reproducibility between triplicate specimens for each MT-binder mixture, confirming specimen homogeneity. The average of three results per sample was taken to ascertain the statistical significance of each UCS test. In order to conduct rigorous mechanical performance evaluation, UCS tests were carried out up to 480 days.
3.4.2.3 Scanning electron microscopy and Energy dispersive spectrometry

A LEO 440 SEM instrument operated at an accelerating voltage of 20 kV and equipped with a Gresham light element detector was used at different magnifications. The back-scattered electron mode (BSE) was selected in order to achieve images with the chemical contrast superimposed on the relief contrast. Additionally, energy dispersive spectrometry (EDS) of an X-ray probe coupled with the SEM (Quartz XOne EDX) was also employed to aid in the identification of minerals and cementitious phases present in cured paste specimen. An EDX spectrometer, capable of detecting all elements with atomic number above 5 (that is, carbon to uranium) with a minimum detection limit of ~0.5 wt% for most elements, was used. The samples were given a thin sputter deposited gold coating in order to alleviate charging problems during SEM examination.

3.5 Results and discussion

3.5.1 Unconfined compressive strength (UCS) tests on cured cemented paste tailings specimens

The short-and long-term performance evaluation of blended cements (containing cement kiln dusts, slag, Type CI fly ash, and Portland cement) in sulphidic tailings cemented pastes was carried out over a curing period of 480 days. The evolution of UCS and subsequent gain or loss of strength in the long-term for pastes formulated with MT, different cement kiln dusts, Portland cements (Type GU and Type HS), and binary, ternary and quaternary blended cements containing ground granulated blast furnace slag
(SL) and Class C fly ash (FC) (listed in Table 3.3) is described in the following paragraphs.

The disparity in the strength acquisition trends for paste samples prepared with homogenized MT and a range of laboratory optimized individual binders and their combinations can be observed in Figures 3.4, 3.6, 3.8, and 3.10. Ordinary Portland cement or Type GU cement is the most commonly used binder in cemented paste formulations for a range of mining wastes. Type GU cement based paste was included in the study to evaluate and compare alternate or technically superior binding agent (s) and cementing material (s).

3.5.1.1 Cemented paste tailings containing GU and HS

The paste mixture prepared with mine tailings and 7%GU cement by dry mass of MT attained a UCS value of 2.1 MPa at 56 days of curing (Figure 3.4). Portland cement based solidification of the waste owe their effectiveness to the formation of hydrated calcium silicate and aluminate compounds when water in such waste for example, (mine tailings paste) chemically reacts with cement to form calcium silicate hydrate (C-S-H) gel, while the solids act as aggregates to form a ‘concrete’ (Conner 1993). The mechanism of formation of C-S-H from tricalcium silicate (C₃S) and dicalcium silicate (C₂S) has strong implications in the solidification processes of wastes (such as sulphidic mine tailings), providing physical encapsulation and entrapment that encloses the non-bonded tailings particles in cemented tailings solidified or stabilized matrix (Gougar et al. 1996).
The compressive strength of Type GU based cemented paste tailings declined after 56 days of curing and continued to degrade until the end of testing regime. The observed UCS value at the end of testing was 1.52 MPa. Many researchers have validated the phenomenon of internal sulphate attack in ordinary Portland cement (Type GU) based sulphidic paste backfill (Benzaazoua et al. 1999 and 2002, Hassani et al. 2002, Fall and Benzaazoua 2005, Kesimal et al. 2005, Ouellet et al. 2006, Ercikdi et al. 2009a, 2009b, and 2010a). According to these investigators, sulphates present in the sulphate-rich water of tailings and those produced by the oxidation of pyrite $FeS_2$ (in a basic pH medium) can react with free calcium ions produced by the dissolution of unstable portlandite generated by cement hydration, giving rise to the precipitation of swelling secondary gypsum ($CaSO_4\cdot2H_2O$), and highly expansive ettringite ($3CaSO_4\cdot3CaO\cdotAl_2O_3\cdot32H_2O$) produced from the reaction of sulphates with $C_3A$. These expansive products can generate immense internal stresses of (70-200) MPa due to crystallization pressure (Divet 1998, Subauste and Odler 2002) which can be a source of deterioration in the cemented matrix. Tian and Cohen (2000) also noted that sulphate attack in Portland cement concrete often arises from each of two major sulphate reactions: (a) sulphate ions react with tricalcium aluminate ($C_3A$) constituent of ordinary Portland cement and its hydration products to form ettringite with an increase in volume that results in expansion and subsequent cracking of the concrete; (b) sulphate ions react with calcium hydroxide ($CH$) to form gypsum. They further argued that sulphate attack mechanism is complicated and that the expansion and cracking of Portland cement concrete should not be exclusively attributed to ettringite formation since tensile stresses during gypsum formation may also play a
role in expansion and the subsequent cracking of the concrete matrix. The above cited workers testing cemented paste backfill prepared with high sulphide mine tailings and ordinary Portland cement as binder have witnessed secondary gypsum as a ubiquitous phase in such matrices. The secondary gypsum, due to its softening and expansive characteristics in cement based composites such as cemented paste backfill, has been generally considered to be the sole culprit, and often claimed to be responsible for the reduction of mechanical strength around after 56 and 90 days (Benzaazoua et al. 1999 and 2002, Hassani et al. 2002, Fall and Benzaazoua 2005, Kesimal et al. 2005, Ouellet et al. 2006, Ercikdi et al. 2009a and 2009b).

The ostensible degradation in UCS can be attributed to the collective effect of the mineral phases (mainly secondary gypsum and ettringite) resulting from cement hydration in paste matrix and the chemical reactions of sulphates with Type GU cement hydration products. The presence of sulphides in the tailings can cause dissolution of the calcic phases of the hydration products and promoted the formation of swelling phases, which in turn induced deterioration of the cemented matrix. Moreover, the negative effects of mixing water containing magnesium ions (3.72 mg/L) and sodium ions (3.19 mg/L) (Table 3.4) can be an additional possible cause of strength degradation (Cohen and Bentur 1988, Bonen and Cohen 1992, Fall and Benzaazoua 2005). The average percentage drop in unconfined compressive strength following the use of 7%GU as binder is graphically displayed in Figure 3.5. The quantification of strength loss for this particular case was 27.6% from 56 days to 480 days of curing. Binders rich in calcium aluminate compounds but with such as Type GU Portland cement, is more susceptible to
aggressive aqueous media and is particularly vulnerable to sulphate attack in sulphidic mine tailings cemented paste backfill matrices (Benzaazoua et al. 2002).

The observed UCS values due to the addition of 7% HS to MT were 1.98 and 1.76 MPa, respectively, at 90 days and 480 days of curing. The compressive strength reduction (Figure 3.7) shows a 10.8% loss during 56-480 days of curing; compared to 27.6% loss in the case of GU based paste. Type HS Portland cement is known to reduce the amount of alumina available in cement based composites. The lower tricalcium aluminate ($C_3A$) content of CSA Type HS (~3%) cement relative to CSA Type GU (~10%) cement imparts sulphate resistance properties due to decreased hydration derivatives (ettringite mineral and secondary gypsum) in sulphate rich environments. Thus, Type HS cement mitigated the negative effects of strength degradation in paste to a great extent by reducing the amount of expansive ettringite and secondary gypsum (Puppala et al. 2004, Ercikidi et al. 2009a). It is evident from Figure 3.6 that the rate of strength development of paste samples containing 7% HS was consistently slower than those of 7% GU.

3.5.1.2 Cemented paste tailings containing DA, DH, DB, and DL as single binders

MT-cement kiln dust specimens containing DA and DH separately as single binders at 8% by dry mass of tailings were tested for UCS. The measured values at 56 days of curing were 0.38 and 0.47 MPa, respectively, as shown in Figures 3.4 and 3.8, respectively. DA and DH having high free $CaO$ contents (22.8% and 26.3%, respectively) and corresponding to the total $CaO$ contents (52.4% and 57.8%, respectively).
respectively) were used individually as a single binder to prepare pastes with sulphidic mine tailings. Mohamed (2002) summarized the processes involved in the hydration of individual components of cement kiln dust and the nature of bonds between hydration products in cement kiln dust stabilized soils. The hydration phases of cement kiln dust are analogous to those of Portland cement (GU) and include tricalcium silicate (C$_3$S), dicalcium silicate (C$_2$S), tricalcium aluminate (C$_3$A), and tetra calcium alumino-ferrite (C$_4$AF). According to Mohamed (2002), the first two phases are the main cementitious products that bind adjacent cement kiln dust grains together during hardening and form a hardened skeleton that encloses unaltered tailings particles. The compressive strength acquisition in the early days of curing is due to alkali sulphates contained in the cement kiln dusts, which are known to accelerate hydration reactions, resulting in rapid setting and hardening (Park 2000). As shown in Table 3.2, the DA and DH used had total alkalis (Na$_2$O)$_{eq}$ contents of 3.6% and 4.0%, respectively, both much higher than Type GU cement (~ 0.3%). The hydration of cement kiln dust creates $C-S-H$ gel and $CH$ in a similar manner to that of Type GU cement and creates strong bonds between minerals, and forms a cellular matrix that encloses the non-bonded tailings particles in cemented tailings.

The free lime ($CaO$) content of cement kiln dust (CKD) is of paramount importance in determining the reactivity of CKD and the amount and nature of the hydration products generated. It is, therefore, a measure of CKD effectiveness as a cementitious stabilizer/binder (Boynton 1980, Bhatt 1984, Konsta-Gdoutos and Shah 2003, Lachemi et al. 2008). The free lime present in the CKD converts into calcium hydroxide (CH) in
the early stages of hydration. It is noteworthy that the UCS values for paste specimens containing DA and DH are comparable despite the difference in their free CaO contents (22.8% and 26.3%, respectively). The combination of both physical and chemical characteristics is critical to the strength acquisition of cement kiln dust based paste. The fine and uniform size distribution of DA provided a higher specific surface (1968 m$^2$/kg) in comparison with DH (1782 m$^2$/kg) and promoted more intense chemical reaction within MT-DA matrix (Konsta-Gdoutos and Shah 2003). The increase in fineness of DA contributed to a corresponding increase in reactivity, promoting a higher compressive strength. This can be a reason for comparable performance of DA and DH in UCS tests performed on cemented paste specimens. According to Conner (1990), cement kiln dust can produce hard, reasonably strong solids due to cementitious and pozzolanic reactions and continue to gain strength with time. As well, the cementing ability of cement kiln dust allows it to be a partial or full substitute for Portland cement in various solidification applications of wastes.

The compressive strength values peaked at 56 days for both DA and DH, respectively, thereafter, a trend of strength decline until 480 days of curing was observed for both CKDs. Figures 3.5 and 3.9 represent the loss of strength in terms of percentage decline of compressive strength between peaks and 480 days of curing period which is 23.5% and 24.5% for DA and DH, respectively. The hydration products of cement kiln dust are analogous to the hydration products of Portland cement (Mohamed 2002), and can also react with available sulphates and induce similar deterioration effects in the hardened matrix to those occurring in Type GU Portland cement matrices. It is evident also from
Figures 3.5 and 3.9 that the magnitude of strength losses in 8%DA and 8%DH based paste are somewhat lower than that of 7% Type GU cement based paste.

The cemented paste mixtures containing DB and DL as single binders in combination with MT were never hardened. The chemical composition of cement kiln dust varies widely due to the uniqueness of the raw materials used in cement manufacturing at each individual plant. The principal chemical constituent of cement kiln dust is calcium, which exists largely in the form of calcium carbonate (CaCO$_3$) or unreacted limestone, calcium sulphate (CaSO$_4$), and free calcium oxide (CaO) (Duchesne and Reardon 1998, Peethamparan et al. 2008). According to Boynton (1980), free calcium oxide or free lime is a measure of the CaO content that is readily available for chemical reactions and reacts with water to form calcium hydroxide. The quantity of free or available lime as well as alkalis (Na$_2$O, K$_2$O) varies widely between cement kiln dusts, which render some cement kiln dusts more reactive than others. In addition to the above mentioned factors governing the chemical and physical makeup of cement kiln dusts, their storage or disposal scenarios can have pronounced effect on reactivity. For instance, the exposure of stockpiled cement kiln dust to moisture can lead to the hydration of free lime with a decrease in free CaO content and increase in loss on ignition (LOI) value (Williams 2005).

Of the CKD chemical properties, the high loss on ignition (LOI) substantiates the fact that the cement kiln dust is high in slow-reacting calcium carbonate and low in reactive
free lime available for hydration (Bhatty and Todres 1996). The LOI can be considered a controlling parameter in the reactivity of cement kiln dusts (Lachemi et al. 2008). High LOI dusts contain a higher percentage of bound water within its chemical structure and less CaO is available to react in cement kiln dust based mortars (Adaska and Taubert 2008). Moreover, high LOI can also interfere with the hydration processes of cement kiln dusts (Bhatty and Todres 1996, Adaska and Taubert 2008). In the present case, very low free CaO contents of DB (2.1%) and DL (1.3%) thwart the hardening of paste specimens containing these types of cement kiln dusts even after a curing period of 56 days. The high LOI values of DB (30.2%) and DL (31.1%) further confirmed the absence of lime required for hardening and strength development. Williams (2005) investigated the effects of different cement kiln dusts on the hardened properties of CLSM with emphasis on their CaO and LOI contents. Cement kiln dust with high values of LOI produced very low UCS values for the laboratory made CLSMs. A high LOI has not been defined numerically, however, a cement kiln dust with an LOI of 28% has been described as high (Parsons and Justin 2004). The chemical analysis revealed that DH and DB had LOI values well above the prescribed criteria regarding suitability of cement kiln dust as a sole binder in CLSM, such as cemented paste tailings. Consequently, long-term landfilled cement kiln dusts (DB and DL) were presumed redundant for the present research thrust.
3.5.1.3 Cemented paste tailings with binary blends comprising DA, DH, FC, GU, HS, and SL

The formulated binder containing 8%DA+8%FC and 8%DH+8%FC mixed with MT produced UCS value of 0.45 and 0.75 MPa at 28 days of curing, respectively, and continued to increase until 90 days as depicted in Figures 3.4 and 3.8. In mortars and concrete containing pozzolans, certain activation methods can be helpful to enhance the hydraulic reactivity of pozzolanic materials such as fly ash (Jueshi et al. 2001). The pozzolanic reactivity of fly ash depends on its reactive silica, free lime, carbon and iron content, fineness, flame temperature in furnace, and particle size (Cabrera and Gray 1973, Ravina 1980). The fly ash used in the present study had 16.9% CaO and 42.3% SiO$_2$. Research has demonstrated that if cement kiln dust and fly ash are appropriately blended, the alkalis from cement kiln dust can activate hydration of almost all types of fly ashes including low quality ash (Class F fly ash with lower calcium content) and blends can generate an effective cementitious material for waste stabilization (Taylor 1990).

The chemical activation of FC could readily be achieved to enhance its hydraulic reactivity by the addition of free calcium rich cement kiln dust, accelerating the pozzolanic reactions that result in improved mechanical performance of cemented composites such as mine tailings paste (Wang et al. 2007). Collins (1985) also investigated the compressive strength behaviour of cement kiln dust-fly ash mixtures and observed that even the traditional 28-day curing time (generally assumed for Portland cements) is not sufficient to develop full strength in these systems (Conner 1990). Thus,
the UCS increase beyond 28 days depicted in Figures 3.4 and 3.8 is in agreement with previous research and should be accounted for in evaluating cement kiln dust-fly ash systems.

The major crystalline hydration product of a cement kiln dust-fly ash binder is ettringite (Wang et al. 2004). The strength acquisition in low-strength materials is dependent on the development of a proper mixture design (Digioia and Brendal 1992). DH based binder (8%DH+8%FC) with the same mixture proportion developed superior compressive strength (0.81 MPa) at 90 days of curing as compared to DA (0.51 MPa). Higher values of calcium oxide (57.8%) and lower LOI (4.8%) of DH can be attributed to such high mechanical strength acquisition of the developed paste. The mechanism of interaction between cement kiln dusts (DA and DH) and FC in increasing the compressive strength of the resultant monoliths is attributed to the cumulative calcium oxide of the individual additives and enhanced pozzolanic reactivity of fly ash by virtue of adding alkali rich cement kiln dust. A decline in the compressive strength was observed leading to a strength loss of 19.7% for 8%DA+8%FC and 20.2% for 8%DH+8%FC, respectively, between the 90th and 480th day of curing as evident in Figures 3.5 and 3.9. Although these combinations also showed compressive strength decline at later ages, but the magnitude of strength degradation was lower than that of paste specimens containing DA and DH individually as sole binders.
The paste mixtures made with 3%GU+8%FC and 3%HS+8%FC attained UCS values of 1.3 MPa and 1.6 MPa at 90 days of curing as shown in Figure 3.4 and 3.6. According to Yu and Counter (1988), a minimum portion of Portland cement in the mix is necessary when using fly ash, in addition to the requirement for an early compressive strength development. The observed loss in strength for the paste mixtures prepared with 3%GU+8%FC and 3%HS+8%FC between 90 and 480 days of curing was 21.6% and 8.3%, respectively, as shown in the Figures 3.5 and 3.7.

Strength development in paste specimens prepared from 8%DA+8%SL and 8%DH+8%SL peaked at 90 days with UCS values of 0.71 and 1.1 MPa, respectively, as evident from Figures 3.4 and 3.8. Cement kiln dust can act as alkaline accelerator for latent hydraulic substances and as alkali activators for different aluminosilicate materials, including ground-granulated blast furnace slag (Sprouse 1984, Xu and Sarker 1995, Konsta-Gdoutos and Shah 2003, Buchwald and Schulz 2005). Highly alkaline pore solution created by free calcium rich cement kiln dust is capable of disintegrating the solid glassy network of ground granulated blast furnace slag to produce reactive silicate and aluminate species when attacked by \( \text{OH}^- \) ions. The activation or dissolution rate of supplementary cementing materials with latent pozzolanic properties mainly depends on the alkali concentration of the reacting system (Wang et al. 2007). The total calculated alkalis (\( \text{Na}_2\text{O}_{eq} \)) present in DA (3.6%) and DH (4.0%) effectively triggered the activation mechanism of SL. The activation of the solids contained in pozzolanic materials by the highly alkaline environments created by DA and DH containing alkali hydroxides, alkali silicates and/or alkali carbonates can result in high compressive strength in cemented
paste tailings specimens (Song and Jennings 1999, Konsta-Gdoutos and Shah 2003, Buchwald and Schulz 2005).

Figures 3.4 and 3.8 confirm that the compressive strength of paste comprising CKD-slag additives increase with curing time substantiating the activation of slag by CKD as a result of proliferating hydration and pozzolanic reactions (Detwiler et al. 1996). According to Konsta-Gdoutos and Shah (2003), the formation and precipitation of cement kiln dust-slag hydration products are analogous to the one found in a typical GU-slag systems, however, the variation of chemical and physical characteristics of cement kiln dust can generate different hydration products at early hydration ages. Later on, C-S-H gel and the stable sulfoaluminate hydrate ettringite are the major hydration products in cement kiln dust-slag systems and are responsible for increased strength development.

The increased dose of DA was also tested in combination with 8%SL but it resulted in reduced compressive strength, compared to that of paste containing 8%DA+8%SL observed for paste specimens. Konsta-Gdoutos and Shah (2003) conducted a study involving a higher dose of SL in CKD-slag systems in making concrete and argued that when the free lime content of the CKD exceeds the requirement for pozzolanic reactions, the excess non-crystalline portlandite can be a source of subsequent durability issues and reduced UCS for the cemented matrix. A drop in the compressive strength was observed for both 8%DA+8%SL and 8%DH+8%SL based binders leading to a compressive
strength loss of 14\% and 15.7\%, respectively, between the 90th and 480th day of curing as seen in Figure 3.5 and 3.9.

The paste mixtures prepared with 3\%GU+8\%SL and 3\%HS+8\%SL attained values of 1.3 MPa and 1.2 MPa, respectively, at 56 days of curing (Figures 3.4 and 3.6). The combination of slag and Portland cement as binder in sulphidic paste formulation has been found to be promising by other researchers (Belem et al. 2000, Benzaazoua et al. 2002, Fall and Benzaazoua 2005, Kesimal et al. 2005, Ouellet et al. 2006, Ercikdi et al. 2009). The resulting paste has been shown to have superior material properties such as pore size refinement, matrix densification, improved mechanical performance and reduced hydraulic conductivity. Shoaib et al. (2000) argued that slag is characterized by slow rate of hydration when mixed with water; a protective film deficient in $Ca^{2+}$ is rapidly formed covering slag particles inhibiting further hydration. A small amount of Portland cement is needed to supply $Ca(OH)_2$ during the setting and hardening period in order to accelerate the reaction of glassy slag. The observed loss in strength between 56th day and 480th days of curing was 16.3\% and 2.3\%, respectively, as evident from Figures 3.5 and 3.7. The use of HS instead of GU can be advantageous in sulphidic tailings paste systems to mitigate sulphate attack phenomenon, principally due to its reduced $C_A$ content (~3\%) in comparison with GU cement (~10\%).

The effects of adding 3\%GU+8\%DA, 3\%GU+8\%DH, 3\%HS+8\%DA, and 3\%HS+8\%DH on UCS of treated tailings are shown in Figures 3.4, 3.6, 3.8, and 3.10,
respectively. The data show that the UCS of paste mixtures increased substantially as a result of additive-binder synergy. The peak mechanical strength attained by the pastes comprising DA or DH alone (0.32 and 0.55 MPa, respectively) are much lower than those observed in combination with GU and HS Portland cements. The aforementioned binder combinations peaked at 56 days of curing with UCS values of 1.6, 2.0, 1.7, and 1.6 MPa, respectively.

A laboratory investigation was conducted by Al-Refeai and Al-Karni (1999) in which dune sand was treated with cement kiln dust and Portland cement. It was found that the UCS of sand increased substantially through cementation; however, the obtained UCS value for cement kiln dust was lower than that of GU cement and increasing GU content caused a corresponding increase in the strength of the treated sand. This behaviour was attributed to the higher LOI value of cement kiln dust used (4.4%) as compared to the Portland cement (less than 1%). The results indicated that a combination of GU and cement kiln dust can intensify the development in strength of the treated sand. From the data (Figure 3.8) for 3%GU+8%DH binder, the UCS of paste is about 4 times that of 8%DH alone at 90 days of curing. Cement kiln dusts contain high proportions of alkali sulphates \((K_2SO_4 \text{ and } Na_2SO_4)\), which are also known to accelerate hydration reactions when used with Portland cement, resulting in enhanced strength development.
3.5.1.4 Ternary blends comprising DA, DH, FC, GU, HS, and SL

The observed UCS peak values for ternary binder blends, i.e., 3%GU+8%DA+5%FC, 3%GU+8%DH+5%FC, 3%GU+8%DA+8%SL, and 3%GU+8%DH+8%SL were 2.2, 2.8, 2.4, and 2.9 MPa, respectively, as shown in the Figures 3.4 and 3.8. Bhatty (1984 and 1985) studied the effect of blended cements comprising ordinary Portland cement, cement kiln dust and Type CI fly ash. The findings revealed that cements containing cement kiln dust alone had a comparatively reduced strength, setting time, and workability, however, the addition of cement kiln dust-fly ash systems lowered the alkali contents in the composite binder, thereby resulting in enhanced UCS. Dyer et al. (1999) investigated ternary binder blends cement kiln dust, fly ash, and Portland cement and concluded that cement kiln dust accelerated the hydration mechanisms of the composite binders. Williams (2005) concluded that CKD as a cement and fly ash replacement is beneficial in CLSM. The chemical activation of FC could readily be achieved to enhance its hydraulic reactivity by the addition of cement kiln dust in Portland cement-fly ash systems, accelerating the pozzolanic reactions that result in improved mechanical performance of cement-based composites (Wang et al. 2007).

In hydration processes of Portland cement-slag binder systems, the calcium silicate glass in the slag becomes soluble in the alkaline pore solutions provided by the initial reactions of the Portland cement giving rise to the secondary growths of calcium silicate hydrates (C-S-Hs). The enhanced amount of C-S-H in the matrix further reinforces the compressive strength of the concretes and mortars (Hooton 2000). The combined effect
of $C\cdot S\cdot H$ as a result of hydration of Type GU cement, cement kiln dust, and SL produced cemented paste tailings with UCS values of 2.4 and 2.9 MPa for ternary binders containing DA and DH, i.e., 3%GU+8%DA+8%SL and 3%GU+8%DH+8%SL respectively, at 90 days of curing.

The percentage decline in the compressive strengths for the paste specimens containing binders 3%GU+8%DA+5%FC, 3%GU+8%DH+5%FC, 3%GU+8%DA+8%SL, and 3%GU+8%DH+8%SL at 480th day of curing were 9.2%, 10.1%, 7.3%, and 7.4%, respectively as evident by the Figures 3.5 and 3.9.

The observed compressive strength value for paste specimens made with 3%HS+8%DA+5%FC, 3%HS+8%DA+8%SL, 3%HS+8%DH+5%FC, and 3%HS+8%DH+8%SL were 2.3, 2.4, 2.3, and 2.8 MPa, respectively, at 90 days and continued to increase until 480 days of curing period as shown by the Figures 3.6 and 3.10, respectively. Contrary to the DA and DH based ternary binders containing 3%GU, cement kiln dust based binders containing 3%HS continued to acquire compressive strength until the final testing regime. Figures 3.7 and 3.11 display the percentage increase in UCS values from 90th day to 480th day for the above mentioned ternary binder combinations containing 3%HS. Among all the four ternary binders containing HS, the binder 3%HS+8%DH+8%SL attained the maximum value of 2.9 MPa at 480th day of curing (Figure 3.10) with a percentage increase of 4.8% (Figure 3.11) between 90 days and 480 days of curing. The addition of pozzolanic materials (FC and SL) further
enriched the sulphate resistance of low C₃A Portland cement due to reduced availability of calcium hydroxide [Ca(OH)₂] in cemented paste tailings, which retards and thwarts the gypsum formation (Irassar et al. 2000).

3.5.1.5 Quaternary blended cements comprising DA, DH, FC, GU, HS, and SL

Sulphidic cemented paste tailings made with quaternary binders 3%GU+8%DA+5%FC+8%SL, 3%GU+8%DH+5%FC+8%SL, 3%HS+8%DA+5%FC+8%SL, 3%HS+8%DH+5%FC+8%SL peaked at the 480th day of curing with compressive strength values of 3, 4.5, 3.2, and 4 MPa, respectively as portrayed in Figures 3.4, 3.8, 3.6, and 3.10, respectively.

Cement kiln dust by virtue of its highly alkaline soluble fraction has been successfully used as an activating agent for slag and fly ash in blended cementitious matrices, since its principal constituents contain enough Ca²⁺ ions to trigger the reactivity of aluminosilicate glass contained in such pozzolanic materials (Dyer et al. 1999, Detwiler et al. 1996). An optimized mix proportion is however requisite to achieve the optimal performance and tailor-made properties of the resultant matrices. The development of significant compressive strength in cemented paste specimens using ternary and quaternary binder blends indicates that there are synergistic effects in such binder combinations. Berry (1980) examined the compressive strength development of mortars made from blends of supplementary cementing materials and Portland cement and concluded that no interaction exists between slag and fly ash when used simultaneously.
with Portland cement, and each supplementary cementing material was observed to manifest exclusively its own cementitious and pozzolanic characteristics in the hydration processes. According to Wang and Chen (1997), the concurrent use to ground granulated blast furnace slag and fly ash used in Portland cement concrete bring upon principal characteristics of strength, dimensional stability, impermeability, and enhanced workability. Batis et al. (2002) conducted study to investigate the simultaneous use of fly ash and blast furnace slag in Portland cement based composite binder systems. The results revealed that a mix of Portland cement, fly ash, blast furnace slag in a proper ratio enhanced the UCS of the composite. The synergistic effects in blended cements can compensate for the mutual shortcomings and inherit deficiencies of individual binder components (Nehdi 2001, Gambhir 2004). This approach allows acquiring tailor-made compressive strength values for the desired paste applications along with an added benefit of saving on the use of energy exhaustive Portland cements such as Type GU and Type HS.

The unequivocal mechanical strength improvement in paste developed with quaternary binders seems predominantly the result of enhanced pozzolanic reactions in the composite. Cement kiln dust has been found to increase the binder-pozzolan reactions when combined with Portland cement and fly ash (Dyer et al. 1999). These composites were found to have resilient behaviour in the long term. Such composite binder blends containing supplementary cementitious materials have been found to alter the nature of hydration products in cemented matrices by generating more C-S-H. Concomitantly, the production of expansive ettringite ceases due to reduced availability of portlandite,
resulting in decreased production of Friedel salts (Dyer et al. 1999). This results in enhanced micro-structural integrity of the developed pastes.

The observed percentage decline in compressive strength in the paste specimens containing composite binders 3%GU+8%DA+5%FC+8%SL and 3%GU+8%DH+5%FC+8%SL was 2.1% and 2.4%, respectively, shown in Figures 3.5 and 3.9, which are much lower than that of the strength loss produced by the other binders containing 3%GU. Concomitantly, the paste specimens made with quaternary binders containing 3%HS, i.e., 3%HS+8%DA+5%FC+8%SL and 3%HS+8%DH+5%FC+8%SL continued to acquire compressive strength until the final regime of testing. Figures 3.7 and 3.11 demonstrate 7.8% and 6% increase in UCS between 90th day and 480th day of curing for quaternary blend i.e., 3%HS+8%DA+5%FC+8%SL and 3%HS+8%DH+5%FC+8%SL, respectively. The long-term stability was most discernible in case of quaternary binder blends containing Type HS cement.

The strength acquisition trends of the paste specimens prepared with MT and single, binary, ternary and quaternary binders incorporating Type HS cement instead of Type GU cement have been depicted in Figures 3.6 and 3.10. A closer examination reveals that paste samples containing HS instead of GU are characterized by slightly lower strength a up to 90 days of curing, less vulnerability to strength decline in the mid-term (beyond 90 days of curing), and better structural integrity in the long term (480 days of
curing) in comparison with paste specimens made with Type GU cement. The rate of compressive strength diminution, for the paste specimens containing cement kiln dust with high $CaO$ and low LOI value, FC, and SL (with limited aluminum oxide) as mineral additives, is much lower than that of the specimens prepared with GU cement as a sole binder. The difference can be attributed to the latent strength acquisition of supplementary cementing materials in the blended cement systems.

The loss of strength in the specimen with Type GU as a sole binder can be attributed to sulphate attack resulting mainly from reaction of sulphates with $C_3A$ phase of cement. On the other hand, addition of CKD and mineral additives with Type GU in making pastes not only reduced the availability of calcium aluminate compounds vulnerable to sulphate attack but also triggered the pozzolanic activity of the mineral additives, resulting in more resilient paste matrices having long-term structural integrity. Concomitantly, utilization of HS instead of GU has been found advantageous in sulphidic tailings paste systems to mitigate sulphate attack phenomenon, principally due to its reduced $C_3A$ content (~3%) in comparison with GU cement (~10%). The low $C_3A$ concentration in HS cement favours reduced ettringite formation in concrete materials and hence lessens the deterioration caused by the internal sulphates attack. The latent strength acquisition by virtue of enhanced pozzolanic activity of FC and SL in cement kiln dust based cements coupled with additional cementitious properties of selective CKD (DA and DH) can rejuvenate the resultant matrices.
The above analysis demonstrate that the strength acquisition process of all sulphidic mine tailings paste specimens was similar in respect that all specimens attained mechanical strength over an initial curing period of 56 or 90 days of curing period; thereafter, the compressive strength of the specimens tended to dwindle depending on the type and dose of binder/additive except ternary and quaternary binder combinations containing CSA Type HS cement. The mixtures of MT and binders/additives listed in Table 3.3 substantiate a sub-linear and proportional relationship between the observed UCS and the curing time up to 56 or 90 days of curing. Furthermore, the mechanical resistance of paste specimens increases with the corresponding increase in binder amount if only binder quantity is taken into account.

The above discussion also implies that the degree of UCS degradation in paste specimens made with single binder/additive or blended cements from 56th day or 90th day to 480th day of curing was directly proportional to the dosage of GU cement in paste mixtures. A higher percentage of GU cement as binding agent infers a correspondingly increased $C_3A$ content as well as hydration products such as CH susceptible to sulphate attack when sulphidic tailings and process water are mixed for paste formulation creating high sulphate rich environments. However, incorporating mineral additives or supplementary cementing materials (SL and FC) in MT-Portland cement or MT-cement kiln dust (DA and DH) combinations enhanced the durability of composites as substantiated by the lower compressive strength decline at later stages. Additionally, cement kiln dust accelerated hydration of FC and activated less active SL in cemented paste matrices.
resulting in enhanced pozzolanic activity, which, in turn, improved the compressive strengths of hardened paste mixtures.

3.5.2 Microstructural investigation using scanning electron microscopy

3.5.2.1 Microstructural investigation of cemented paste tailings containing DA, DH, GU and HS

The microstructure of selected representative samples of 120-day cured cemented paste tailings was evaluated using fractured surfaces of the crushed specimens. Prior to SEM analysis, the samples were oven dried at 50°C since this temperature did not appear to cause cracking in cured paste specimens. The samples were treated with acetone to prevent further hydration within paste.

Microanalysis using scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) spectroscopy was carried out on cured cemented paste tailings specimens containing 7% GU and sulphidic MT. The results revealed that the paste matrix was iron enriched due to in-situ precipitation as iron hydroxide species as evidenced by rust color. The calcium concentration was considerably exhausted and only a small part of solubilised calcium precipitated as gypsum. Silicon and aluminum were found precipitated as stable hydroxides. These findings were consistent with those of previous research carried out on cemented paste backfill prepared from high sulphide tailings and a comparable amount of ordinary Portland cement (Benzaazoua et al. 1999). The SEM
investigation also depicted (as shown in Figure 3.12) a comparatively loose or porous microstructure (with voids) consistent with the observations made by Ercikdi et al. (2009a). The high water content used in paste formulation produced a hardened microstructure with interstices that were largely void spaces partially filled by the hydration products. The loose microstructure also substantiates the vulnerability of the matrix to ingress and transport of fluid (moisture and air), which can result in oxidation of sulphide minerals contained in the cemented matrix.

The surface analysis of paste specimens containing 7% HS as sole binder had loose microstructure, but EDX did not reveal secondary gypsum. Undoubtedly, the reduced $C_3A$ content of HS cement prevented the development of excessive secondary gypsum in cemented paste matrix. The compressive strength degradation was also controlled since the percentage decline in UCS was 10.8% as compared to the decline observed for 7% GU (27.6%). EDX coupled with X-ray dot mapping conducted on fractured surfaces further allowed the detection of the elements including iron ($Fe$), calcium ($Ca$), aluminum ($Al$), sulphur ($S$), magnesium ($Mg$), and potassium ($K$) (see Appendix A.7 and A.8). Additionally, increased concentrations of $Ca$, $Mg$, and $S$ were dominant at some spots indicating their abundance in the matrix. Figure 3.13(a) depicts pyrite grain embedded in cemented paste matrix, whereas Figure 3.13(b) provides EDX of the spot tested confirming its chemistry.
Microanalysis conducted on fractured rough surface of paste samples containing DA and DH individually as single binder depicted an exceedingly loose microstructure. The surface characteristics of the paste samples with binders containing 8%DA and 8%DH, and cement kiln dust in conjunction with GU, i.e., 3%GU+8%DA and 3%GU+8%DH were similar to those prepared only with 7%GU. Figure 3.14 displays the photomicrograph of cemented paste tailings containing 3%HS+8%DA. The microstructure is still globally loose structure with interstices and void spaces. Peethamparan et al. (2008) investigated the hydration of cement kiln dusts with varying composition. The results revealed that the hydration of cement kiln dust possessing high CaO content generated large amounts of calcium hydroxide, ettringite, and gypsum. On the other hand, the hydration of cement kiln dusts with low CaO contents produced relatively small amounts of hydration products. Moreover, the examination of hydrated sample by XRD revealed that the dominating calcite and quartz peaks remained unchanged, demonstrating the inert nature of the low lime content cement kiln dust. Despite significant amount of hydration products due to synergy of Type HS Portland cement and cement kiln dust in 3%HS+8%DA based cemented paste sample, matrix densification was not unequivocally evident as shown in the Figure 3.14.

3.5.2.2 Microstructural investigation of cemented paste tailings with binary and ternary binders containing Type CI fly ash (FC)

SEM-EDX data obtained on fractured paste samples containing FC in combination with Portland cement as binder are presented in Figures 3.15(a) and 3.15(b). The image in
Figure 3.15(a) is SEM backscattered electron image of paste containing 3%GU+8%FC as binder. The structure included mainly coarse and fine silica particles with voids partially filled by cementitious phases/hydration products. Larger plate shaped particles of tailings were easily distinguishable. Some characteristically discernible fly ash particles were observed since the binder in the composite contained fly ash. EDX confirmed that the grains were un-reacted fly ash particles, which were analogous to the other paste samples containing fly ash. These un-hydrated or un-reacted fly ash particles were evident and easily distinguished due to their spherical shape as shown in Figure 3.15(a). Moreover, most of the small fly ash particles in the matrix had chemically reacted leaving behind a hollow spherical shell as shown in Figure 3.15(b). Ramlochan et al. (2004) and Ouellet (2006) investigated paste backfill prepared with binders containing Portland cement-fly ash and confirmed the possibility of un-reacted fly ash particles within hardened paste backfill matrices.

The SEM back scattered electron image was captured at high magnification for paste samples containing 3%GU+8%DH+5%FC. No un-hydrated or un-reacted fly ash particle was found in the microanalysis performed on crushed surface of cemented paste tailings sample. It can be inferred from this observation that all the FC used in the composite binder system was completely exhausted by the accelerated pozzolanic activity due to the highly alkaline environment created by DH. The surface of the paste sample containing 3%GU+8%DH+5%FC binder was much denser than the crushed surface of the sample made with GU alone as sole binder. The mine tailings grains were evenly dispersed within their matrix. The voids between the coarse particles of the tailings material were
filled with ultrafine particles of binder material and their hydrates depending on their proportion in the composite. Generally, the constituents building the structure of the cemented paste tailings were of much smaller dimensions to give particle packing effects and resulting denser matrix.

The diminutive gaps between larger tailings particles were filled interstitially with smaller tailings grains as well as with hydration products arising from composite cement containing GU, DH and FC as determined by EDX. As opposed to concretes in which cement hydrates develop a pattern of bridging from particles to particles, binder hydration products were not dominant in paste samples. EDX performed on interstices and other spots revealed that hydration products (C-S-H and ettringite) were rich in alkalis and low in Ca/Si, however, calcium hydroxide was not identified as a major residual product. It is common knowledge that calcium hydroxide is the primary crystalline phase generated from the hydration of Portland cement and cement kiln dust, whereas, pozzolanic reactions consume a fair amount of calcium hydroxide when GU and/or cement kiln dust are mixed with mineral admixtures such as fly ash.

3.5.2.3 Microstructural investigation of cemented paste tailings with ternary and quaternary binders containing SL

The MT paste samples prepared with ternary and quaternary blended cements containing slag were particularly different from the other samples. The observed C-S-H gel was in the form of isolated masses in void spaces. A very low value of Ca/Si molar ratio in C-S-
\( H \) gel was observed along with fewer alkalis. Ettringite was also much less in samples containing SL and gypsum was not detected. The use of slag in cemented matrices exposed to sulphate rich environment not only reduce the sulphate ions penetration in the matrices but also dilute/reduce the susceptible \( C_3A \) content of cement (Hooton 2000). Consequently, the reduced portlandite content of the cement paste prevent gypsum formation on ettringite crystals and thus reduces expansion associated with the sulphates (Hooton and Emery 1990).

The SEM back scattered electron images captured at high magnification for paste samples containing SL in combination with GU (3%GU+8%SL) showed unhydrated and partially hydrated SL spherical particles as shown in Figure 3.16. Ramlochan et al. (2004) and Ouellet (2006) investigated paste backfill prepared with binders containing Portland cement-blast furnace slag and confirmed the possibility of un-reacted slag particles within hardened paste backfill matrices. Their results support the present observations; however, their observations included evidence of considerable amount of \( C-S-H \) in the matrix despite lower additions of SL. The present findings regarding substantial amounts of \( C-S-H \) in 3%GU+8%DH+8%SL based paste can be attributed to (i) the synergistic action of Portland cement and cement kiln dust hydration generated additional \( C-S-H \) in the paste composite, and (ii) the fact that CKD promoted the reactivity of SL resulting in enhanced pozzolanic reactions, which, in turn, produced more \( C-S-H \) in paste matrix. Overall, crushed paste sample containing 3%GU+8%DH+8%SL was observed to be more compact than fly ash based binders discussed above and as shown in Figure 3.17.
The cemented paste tailings sample prepared with quaternary binder i.e., 3%HS+8%DH+5%FC+8%SL was also examined in order to assess critically the effect of incorporation of DH in ternary binder containing FC and SL. No un-reacted grain was found within the crushed surface of cemented paste matrix. It can be inferred from this observation that the glassy SL was completely disintegrated by the highly alkaline pore solution when attacked by OH⁻ ions. Concomitantly, the disappearance of FC particles further confirmed the activation action of cement kiln dust when used in combination with pozzolanic materials. The hydration mechanisms of these mineral admixtures in making composites with mine tailings and other materials (GU, HS and DH) can be a ground for such observation. No hydrated cement phase was detected to confirm the use of GU in the preparation of paste samples. This is the reason why paste samples made with HS and GU could not be differentiated by SEM. At the same time, no differentiable hydrated phase of DH was detected. The similarity of hydration mechanisms of GU and DH can be a reason for such evidence in the SEM.

Cemented paste tailings samples containing ternary and quaternary blended cements had much higher degree of structural densification than those made with single and binary binders. The paste sample surface containing 3%HS+8%DH+5%FC+8%SL was analogous to that of crushed rock with dense and compact mass as evident in Figure 3.18. Concurrently, the aforementioned observed UCS values for these mixtures were also superior to those of paste samples prepared with single and binary binders. Therefore, results do show correlation between the observed UCS values and the structural densification of the matrices.
3.5.3 Relationship between microstructure of hardened cemented paste tailings and respective unconfined compressive strength

A few researchers have correlated micro-scale texture or microstructure of cement mortars and other cement based matrices, such as cemented paste backfill, with their respective compressive strength and observed that the structural integrity of such materials is generally acquiescent with the degree of densification and compactness of their microstructure (Benzaazoua et al. 2002, Ouellet et al. 2006, Sobolev et al. 2007, Ercikdi et al. 2009b). The observed microstructure delineation was found to be consistent with their respective mechanical performance at 120 days of curing. For instance, densification of the microstructure is evident in the SEM photomicrographs of the paste specimens containing ternary and quaternary blended cements, compared to the relatively loose and porous microstructure of the paste specimens made with single and binary binders. As an illustration, the peak UCS values for ternary blended cement 3%GU+8%DH+8%SL and quaternary blended cement 3%HS+8%DH+5%FC+8%SL are 2.9 and 4.0 MPa, respectively. These UCS values are in agreement with the respective SEM photomicrographs shown in Figures 3.17 and 3.18. On the other hand, binders 7%GU and 3%HS+8%DA with lower UCS values (2.1 and 1.8 MPa, respectively) show a relatively loose and porous configuration as indicated by their respective SEM images shown in Figure 3.12 and 3.14.
3.6 Conclusions

The short-and long-term performance evaluation of the unconfined compressive strength of blended cements (containing cement kiln dusts, ground granulated blast furnace slag, Type CI fly ash, and Portland cements) in cemented pastes of sulphidic tailings was carried out over a curing period of 480 days. The unconfined compressive strength and microstructure were selected as major performance evaluation indicators for the developed cemented pastes. Based on the laboratory measurements the main findings from the study are summarized as below:

- Strength development in all sulphidic cemented paste tailings specimens was similar in the sense that all specimens attained maximum mechanical strength at the end of an initial curing period of 56 or 90 days; thereafter, the compressive strength of the specimens tended to decrease depending on the type and dose of binder/additive, except ternary and quaternary binder combinations containing Type HS cement. The loss of strength in the specimen with GU as a sole binder may be attributed to the sulphate attack. The presence of sulphates in ordinary Portland cement based cemented paste tailings can cause dissolution of the calcic phases of the cement hydration products and promote the formation of swelling phases, which, in turn, can induce deterioration of the cemented matrices.

- The rate of compressive strength reduction, for paste specimens containing cement kiln dust with high CaO and low LOI value, SL (with limited aluminum oxide), and Type CI fly ash (FC), as mineral additives, was much lower than that of specimens prepared with Type GU cement as a sole binder. Cement kiln dust, by virtue of its highly alkaline soluble fraction, can successfully be used as an
activating agent for slag and fly ash in cemented paste tailings, since its principal constituents contain enough calcium to trigger the reactivity of aluminosilicate glass contained in such pozzolanic materials. Free lime content was found to be the most effective predictor of the reactivity of a particular cement kiln dust. The total calculated alkalis ($Na_2O_{eq}$) present in DA (3.6%) and DH (4.0%) effectively triggered the activation mechanism of SL and FC.

- DA and DH containing high CaO content (52.4% and 57.8%, respectively) and low LOI (5.1% and 4.8%, respectively) performed best in making sulphidic cemented paste tailings, whereas the paste mixtures containing DB and DL (with very low free lime and very high LOI) as single binders in combination with MT never hardened. The LOI is a controlling parameter in the reactivity of cement kiln dusts. High LOI substantiates that the CKD is high in slow-reacting calcium carbonate and low in reactive free lime. Moreover, high LOI dusts contain a high percentage of bound water within its chemical structure and, therefore, less free CaO is available to react. Contrarily, low LOI indicates the presence of low CaCO$_3$ and high free CaO content.

- The utilization of HS instead of GU has been found advantageous in sulphidic paste systems to mitigate sulphate attack, principally due to its reduced $C_3A$ content. FC and SL in HS-cement kiln dust system developed compressive strength at relatively lower rate in comparison with GU-cement kiln dust systems, but attained and maintained higher UCS over long curing periods. The long-term stability was most discernible in the case of quaternary binder blends containing Type HS cement.
• The physical properties of cement kiln dust can impact the resultant paste matrix apart from chemical characteristics. The fine size distribution of DA provided a higher specific surface (1968 m²/kg) in comparison with DH (1782 m²/kg) and promoted more intense chemical reaction within the DA-MT matrix. The increase in fineness of DA contributed to a corresponding increase in reactivity, promoting a higher compressive strength. This can be a reason for comparable performance of DA and DH in UCS tests performed on cemented paste specimens despite lower free lime contents of DA as compared to DH.

• Cement kiln dust compositions vary considerably with kiln process and the raw materials used; therefore, the impact of a particular cement kiln dust as a partial replacement of Portland cements or in combination with pozzolanic additives may not be consistent. The quantity of free or available lime as well as alkalis (Na₂O and K₂O) varies broadly between cement kiln dusts, which results in making some cement kiln dusts more reactive than others. The chemical and physical makeup of cement kiln dusts and their storage or disposal scenarios can have a pronounced effect on reactivity. Long-term, landfilled cement kiln dusts, such as DB and DL, have been found to be less reactive due to lower free lime and higher LOI.

• The addition of selective cement kiln dust, and ground granulated blast furnace slag, and/or fly ash as partial replacement for Portland cement can improve the performance of the sulphidic cemented paste tailings and alleviate the strength loss associated with ordinary Portland cement based paste. The behavior can be attributed to the latent strength acquisition of SL and FC in the blended cements.
containing DA and DH as a result of proliferating hydration and pozzolanic reactions.

- The high water content used in cemented paste tailings containing Type GU and Type HS cement produced hardened porous microstructures with interstices that were largely void spaces partially filled by hydration products. In cemented paste tailings, the fraction of the total void space filled by the hydration products generated by the total cementitious materials determines the strength of cemented matrix. The small particles of supplementary cementing materials help to eliminate pores and micro pores by acting as filler and micro fillers resulting in increased density of the hardened composite.

- Previous studies carried out by other researchers on hardened tailings pastes containing Portland cement-pozzolans binders confirmed the possibility of the presence of un-reacted or un-hydrated particles of slag and fly ash within hardened tailings pastes. In the present study, SEM was carried out on cemented paste tailings to investigate the effect of using calcium and alkali rich cement kiln dust on pozzolanic reactivity of binders containing SL and FC. The effect of incorporation of DA or DH in GU/HS-SL and GU/HS-FC binders was analyzed in high magnification modes. No un-reacted grain of SL or FC was found within the crushed surfaces of the matrices. It can be inferred from these observations that the glassy SL was completely disintegrated by the highly alkaline pore solution when attacked by $OH^-$ ions. As well, all the amount of FC used in composite binder system was completely exhausted by the accelerated pozzolanic activity due to the highly alkaline environment created by DH. The disappearance
of SL and FC particles confirmed the enhanced pozzolanic reactivity of SL and FC when used in combination with selective cement kiln dusts.

- The cumulative physical and chemical effects due to composite binder systems generated denser and stronger hardened cement pastes. The structural integrity of resultant pastes agrees with the degree of densification and compactness of their microstructure. The observed microstructure delineation of selected cemented paste tailings samples was found to be consistent with their respective mechanical performance (based on the unconfined compressive strength).
3.7 References


ACI Committee 229 (1999) Controlled Low-strength Materials (CLSM), ACI 229R-99, American Concrete Institute.


### Table 3.1 Chemical and physical properties of MT and cementitious materials

<table>
<thead>
<tr>
<th>Chemical characteristics</th>
<th>Mattabi mine tailings</th>
<th>Ground granulated blast furnace slag</th>
<th>High sulphate resistant cement</th>
<th>Type CI fly ash</th>
<th>General Use hydraulic cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major oxides (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>31.60</td>
<td>34.98</td>
<td>22.03</td>
<td>42.37</td>
<td>19.87</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.29</td>
<td>0.25</td>
<td>0.18</td>
<td>0.81</td>
<td>0.24</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.03</td>
<td>9.11</td>
<td>3.57</td>
<td>18.66</td>
<td>4.93</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>37.83</td>
<td>1.86</td>
<td>3.67</td>
<td>5.75</td>
<td>2.38</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.85</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.22</td>
<td>9.37</td>
<td>2.87</td>
<td>3.54</td>
<td>2.77</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14</td>
<td>38.56</td>
<td>63.36</td>
<td>16.90</td>
<td>65.37</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.22</td>
<td>0.51</td>
<td>0.42</td>
<td>1.18</td>
<td>0.44</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.27</td>
<td>1.22</td>
<td>0.00</td>
<td>2.53</td>
<td>0.00</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.02</td>
<td>-</td>
<td>0.03</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>L.O.I</td>
<td>19.41</td>
<td>0.43</td>
<td>1.03</td>
<td>5.06</td>
<td>1.93</td>
</tr>
<tr>
<td>Total</td>
<td>97.09</td>
<td>97.14</td>
<td>97.20</td>
<td>97.13</td>
<td>98.00</td>
</tr>
</tbody>
</table>

**Physical characteristics**

<table>
<thead>
<tr>
<th></th>
<th>MT</th>
<th>SL</th>
<th>HS</th>
<th>FC</th>
<th>GU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>3.88</td>
<td>2.86</td>
<td>3.12</td>
<td>2.43</td>
<td>3.13</td>
</tr>
<tr>
<td>(Gs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific surface</td>
<td>322</td>
<td>1983</td>
<td>1070</td>
<td>852</td>
<td>1190</td>
</tr>
<tr>
<td>area BET (m²/kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₅₀ (microns)</td>
<td>40.1</td>
<td>10.1</td>
<td>15.0</td>
<td>20.0</td>
<td>14.5</td>
</tr>
</tbody>
</table>

1CAN/CSA A3001-03 Type CI (Intermediate calcium content fly ash); (SiO₂+Al₂O₃+Fe₂O₃) min % > 50% [SiO₂+Al₂O₃+Fe₂O₃ = 66.78%]; CaO < 20%

2CAN/CSA A3001-03 Type GU: General use hydraulic cement (equivalent to ASTM Type I)

3CAN/CSA A3001-03 Type HS: High sulphate resistant cement (equivalent to ASTM Type V)

4CAN/CSA A3001-03 Type S: Ground granulated blast furnace slag
Table 3.2 Chemical and physical properties of cement kiln dusts

| Chemical characteristics | DA       | DH       | DB       | DL       | Range for major oxides 63 different CKDs
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Major oxides (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>18.6</td>
<td>18.40</td>
<td>17.77</td>
<td>16.43</td>
<td>2.2-34.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.73</td>
<td>3.91</td>
<td>4.33</td>
<td>4.23</td>
<td>1.1-10.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.30</td>
<td>3.41</td>
<td>1.88</td>
<td>3.86</td>
<td>0.2-6.0</td>
</tr>
<tr>
<td>CaO</td>
<td>52.4</td>
<td>57.8</td>
<td>34.68</td>
<td>31.80</td>
<td>19.4-61.3</td>
</tr>
<tr>
<td>MgO</td>
<td>2.56</td>
<td>1.31</td>
<td>1.71</td>
<td>2.98</td>
<td>0.5-3.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.14</td>
<td>0.21</td>
<td>0.18</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td>SO₃</td>
<td>8.62</td>
<td>4.32</td>
<td>6.10</td>
<td>7.61</td>
<td>0.02-17.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.40</td>
<td>4.91</td>
<td>2.25</td>
<td>1.23</td>
<td>0.1-15.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.71</td>
<td>0.81</td>
<td>0.25</td>
<td>0.26</td>
<td>0.0-6.3</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>Total oxides (99.68)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Free CaO (22.8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0-27.2</td>
</tr>
<tr>
<td>Total alkalis= (Na₂O)ₑq (%) 3.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.14-11.42</td>
</tr>
<tr>
<td>Total reactive oxides (TRO) (%) 44.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.86-56.08</td>
</tr>
<tr>
<td>Specific gravity (Gs)</td>
<td>2.86</td>
<td>2.81</td>
<td>2.92</td>
<td>2.93</td>
<td>2.48-2.96</td>
</tr>
<tr>
<td>Specific surface area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET (m²/Kg)</td>
<td>1968</td>
<td>1782</td>
<td>1435</td>
<td>1514</td>
<td>-</td>
</tr>
<tr>
<td>D₅₀ (microns)</td>
<td>10.4</td>
<td>15.2</td>
<td>23.5</td>
<td>27.6</td>
<td>-</td>
</tr>
</tbody>
</table>

*Loss on ignition determined at (950±50°C)*
††XRF sum of total oxides
*Analysis carried out in accordance with ASTM C25-06*
**Total alkalis= (Na₂O)ₑq = (Na₂O+0.658K₂O) (Wang et al. 2007)
***Total reactive oxide content=TRO= [(CaO+MgO)−LOI]−[K₂O+Na₂O] (Collins and Emery 1983)
‡Statistics on composition of 63 different cement kiln dusts from various sources (Sreekrishnavilasam et al. 2006)
‡‡*(Peethamparan et al. 2008, Collins and Emery 1983)*
<table>
<thead>
<tr>
<th>DA based binders containing SL, FC, GU and HS</th>
<th>DH based binders containing SL, FC, GU and HS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT+8%DA+8%FC</td>
<td>MT+8%DH+8%FC</td>
</tr>
<tr>
<td>MT+8%DA+8%SL</td>
<td>MT+8%DH+8%SL</td>
</tr>
<tr>
<td>MT+3%GU+8%DA</td>
<td>MT+3%GU+8%DH</td>
</tr>
<tr>
<td>MT+3%HS+8%DA</td>
<td>MT+3%HS+8%DH</td>
</tr>
<tr>
<td>MT+3%GU+8%DA+5%FC</td>
<td>MT+3%GU+8%DH+5%FC</td>
</tr>
<tr>
<td>MT+3%HS+8%DA+5%FC</td>
<td>MT+3%HS+8%DH+5%FC</td>
</tr>
<tr>
<td>MT+3%GU+8%DA+8%SL</td>
<td>MT+3%GU+8%DH+8%SL</td>
</tr>
<tr>
<td>MT+3%HS+8%DA+8%SL</td>
<td>MT+3%HS+8%DH+8%SL</td>
</tr>
<tr>
<td>MT+3%GU+8%DA+5%FC+8%SL</td>
<td>MT+3%GU+8%DH+5%FC+8%SL</td>
</tr>
<tr>
<td>MT+3%HS+8%DA+5%FC+8%SL</td>
<td>MT+3%HS+8%DH+5%FC+8%SL</td>
</tr>
</tbody>
</table>

**Binders for comparative assessment**

<table>
<thead>
<tr>
<th>Binders for comparative assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT+7%GU</td>
</tr>
<tr>
<td>MT+8%DA</td>
</tr>
<tr>
<td>MT+3%GU+8%FC</td>
</tr>
<tr>
<td>MT+3%GU+8%SL</td>
</tr>
</tbody>
</table>
Table 3.4 Chemical characteristics of mixing water (process water)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (mg/L)</td>
<td>0.37</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>83.27</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>0.76</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>31.23</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>3.72</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>3.19</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>0.81</td>
</tr>
<tr>
<td>SO$_4$ (mg/L)</td>
<td>13,730.16</td>
</tr>
<tr>
<td>pH</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Figure 3.1 Particle size distributions of MT, GU, HS, SL and FC

Figure 3.2 Particle size distributions of cement kiln dusts (DA, DH, DB, and DL)
Figure 3.3 X-ray diffractogram of Mattabi mine tailings (MT)
Figure 3.4 Unconfined compressive strength (UCS) of cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and GU

Figure 3.5 Average % change in UCS of cemented paste tailings samples relative to peak (MT and binders comprising DA, SL, FC, and GU)
Figure 3.6 Unconfined compressive strength (UCS) of cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and HS

Figure 3.7 Average % change in UCS of cemented paste tailings samples relative to peak (MT and binders comprising DA, SL, FC, and HS)
Figure 3.8 Unconfined compressive strength (UCS) of cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and GU

Figure 3.9 Average % change in UCS of cemented paste tailings samples relative to peak (MT and binders comprising DH, SL, FC, and GU)
Figure 3.10 Unconfined compressive strength (UCS) of cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and HS

Figure 3.11 Average % change in UCS of cemented paste tailings samples relative to peak (MT and binders comprising DH, SL, FC, and HS)
Figure 3.12 SEM backscattered electron image depicting cemented paste tailings fractured surface containing 7% GU cement as binder

Figure 3.13(a) SEM micrograph showing pyrite grain embedded in cemented paste tailings containing 7% GU cement as binder
Figure 3.13(b) EDX confirming chemical composition of pyrite grain shown in Figure 13(a)

Figure 3.14 SEM backscattered electron image depicting cemented paste tailings fractured surface containing (3%HS+8%DA) as binder
Figure 3.15 (a) SEM micrograph showing un-reacted or un-hydrated Type CI fly ash (FC) particles in cemented paste tailings prepared with (3%GU+8%FC) as binder

Figure 3.15(b) SEM micrograph showing hallow shell of FC particle in cemented paste tailings prepared with (3%GU+8%FC) as binder
Figure 3.16 SEM micrograph showing un-reacted or un-hydrated SL particles in cemented paste tailings prepared with (3%GU+8%SL) as binder

Figure 3.17 SEM backscattered electron image depicting cemented paste tailings fractured surface containing (3%GU+8%DH+8%SL) as binder
Figure 3.18 SEM backscattered electron image depicting cemented paste tailings fractured surface containing (3% HS+8% DH+5% FC+8% SL) as binder
CHAPTER 4
EFFECT OF HIGH CALCIUM CEMENT KILN DUST ACTIVATED SLAG AND FLY ASH ON SATURATED HYDRAULIC CONDUCTIVITY OF CEMENTED PASTE TAILINGS

4.1 Introduction

The saturated hydraulic conductivity (\(k_s\)) or Darcy’s coefficient of a porous medium is a measure of its ability to transmit water when subjected to a hydraulic gradient. A reasonable estimate of \(k_s\) is particularly desirable in the case of sulphidic mine tailings because iron sulphide compounds (pyrite or pyrrhotite) present in such tailings can oxidize and generate acidic drainage in the presence of moisture and oxygen (Singer and Stumm 1970, Yanful and Orlandea 2000). The acidic drainage is characterized by elevated concentrations of toxic elements that can jeopardize the health of contiguous ecosystem (Ritcey 1989). Hydraulic conductivity is a dominant parameter that controls water flow rate through hardened cemented pastes or backfill structures following flooding. This property also enables to estimate pore water pressure behind the barricades in mining industry. The transport mechanisms as well as leaching potential of the contaminants are mainly governed by hydraulic conductivity (Leven et al. 1996).

The hydraulic conductivity of porous medium such as tailings is influenced by physical and chemical factors related to the medium and permeant in question (Yong et al. 1992). The said property can indirectly delineate the pore structure and pore connectivity for a better understanding of the rate of fluid transfer within the hardened matrix such as
sulphidic cemented paste tailings. A high connectivity of pores and the presence of cracks can accelerate fluid transfer (oxygen and water) within the matrix and the surrounding environment (Fall et al. 2009), while a dense and compact mass, on the other hand, acts as an effective barrier against fluid transfer resulting in a better control of associated environmental pollutants. A maximum hydraulic conductivity of $1 \times 10^{-5} \text{cm/s}$ is permissible for solidified/stabilized wastes planned for land disposal/burial (US EPA 1986).

4.2 Benefits of slag and fly ash activation by high calcium cemented dust in cemented paste tailings formulations

The precipitation of calcium hydroxide in Portland cement based sulphidic cemented paste tailings may be inadequate for total blockage of pores within the paste since Type GU cement alone produces a relatively porous treated waste in solidification/stabilization (S/S) processes (Means et al. 1995). In Portland cement-high calcium and alkali rich cement kiln dust-slag mixes and Portland cement- high calcium alkali rich cement kiln dust-fly ash mixes, the products delivered by the enhanced pozzolanic reactivity of slag and/or Type C fly ash can potentially fill the additional pores in such matrices. The present study was carried out to estimate the influence of enhanced pozzolanic reactivity of slag and Type C fly ash using calcium and alkali rich cement kiln dusts in reducing the saturated hydraulic conductivity of cemented paste tailings formulations.
4.3 Materials and methods

4.3.1 Physical and chemical properties of the materials

The polymetallic sulphidic mine tailings used in the present study were obtained from Mattabi mine, located in Ignace, Ontario. The tailings were transported in sealed containers to prevent further oxidation. The physical, chemical, and mineralogical characteristics of the tailings (hereafter MT) were determined by preparing subsamples in accordance with the relevant standards/methodologies/test procedure. The laboratory analysis carried out on MT sample in accordance with ASTM D4318 revealed that the tailings sample had a liquid limit (LL) of 22%, a plastic limit (PL) of 18%, and plasticity index (PI) of 4%.

Cementing materials, supplementary cementing materials, and representative and characteristically different cement kiln dusts samples used in the study were provided by Cement Association of Canada (CAC). The cementing materials complied with Canadian Standards Association (CSA) A3001-03 including CSA Type General Use hydraulic cement (GU hereafter) and CSA Type High Sulphate resistant hydraulic cement (hereafter HS). The supplementary cementing materials used were ground granulated blast furnace slag (SL hereafter) and CSA Type CI (intermediate calcium) fly ash (FC hereafter).
The particle size distributions of MT, GU, HS, SL, FC, and cement kiln dust samples (DA and DH) were obtained using a Mastersizer (Malvern Instruments) laser diffraction particle size analyzer. The MT sample contained approximately 67% fines (< 75 microns) and 33% sand size particles (> 75 microns) (Figure 4.1). Based on the Unified Soil Classification System (USCS), the tailings were classified as ‘sandy silt’ or ML (ASTM D2487). The MT sample contained approximately 25% fines (< 20 microns). MT, SL, HS, FC and GU were found to have medium grain sizes of 40.1, 10.1, 15.0, 20.0 and 14.5 μm, respectively (Figure 4.1). Additionally, the specific surface area of these materials was determined using the Braunauer, Emmett, and Teller (BET) method and the results have been tabulated in Tables 4.1-4.2. The specific gravity ($G_s$) of tailings and binders/additives used in the study were measured in accordance with ASTM D854. The results are presented in Tables 4.1-4.2.

The chemical compositions of MT, GU, HS, SL, FC, and cement kiln dusts (DA and DH) used in this study were determined by a combination of X-ray fluorescence spectroscopy (XRF) (Tables 4.1-4.2) and inductively coupled plasma-atomic emission spectrometry. The major oxides were determined by fusion XRF. MT sample was determined to contain 37.8 wt% $Fe_2O_3$ and ~12 wt% $S$ substantiating pyrite as major mineral present. A qualitative assessment of tailings mineralogy using powder X-ray diffraction (XRD) and Bruker D8 coupled with a semi-quantitative X-ray fluorescence analysis indicated the dominance of quartz (~42%) and pyrite (~40%).
Sulphate concentration in mine tailings process water was determined using an ion chromatograph (Waters® HCLP PUMP 515, Waters® 432 Conductivity meter). An injection volume of 50 mL was used for each sample with 20 minutes running time. The average of three results per sample was taken to ascertain the accuracy of each test. The process water used in the cemented paste tailings preparation had a sulphate concentration of 13,730 mg/L.

Ground granulated blast furnace slag is a nonmetallic byproduct of iron manufacturing and essentially consists of silicates and aluminosilicates of calcium and other bases, which is developed in a molten condition simultaneously with iron in a blast furnace, then water chills rapidly to form glassy granular particles, and then ground to cement fineness or finer (Bouzoubaa 2005). The slag used in the present study met the specifications of CAN/CSA A3001-03. Lea (1970) suggested that with aluminum oxide (Al₂O₃) content of less than 11 wt%, SL can aid greatly in inhibiting the detrimental effects of sulphate attack in cementitious matrices.

Fly ash, a by-product of coal burning power plants, is often composed of predominantly silt-size, spherical, amorphous ferro-aluminosilicate minerals (Sale et al. 1997). Fly ash produced from burning bituminous coal has cementitious properties in addition to its pozzolanic properties, and is capable of counteracting the acid potential of mine waste by virtue of its high Ca content (Roy and Griffin 1982). The fly ash used in the present study had a cumulative SiO₂, Al₂O₃, and Fe₂O₃ content of less than 70%. In accordance with
Canadian Standard Association (CSA A3001-03), the fly ash would be classified as CSA Type CI (medium calcium oxide contents fly ash) based on the determined chemical composition and CaO contents (16.9%).

CKD samples were obtained from cement manufacturing plants. Two different cement kiln dusts (hereafter called DA and DH). DA had a higher specific surface (1968 m²/kg) than DH (1782 m²/kg) as determined by using the Braunauer, Emmett, and Teller (BET) method. The results have been tabulated in Tables 4.2. The un-reacted or free calcium oxide CaO in DH and DA as determined by ASTM C25 was 26.3% and 22.8%, respectively. The chemical compositions and physical properties of MT, GU, HS, SL, and FC are presented in Table 4.1, whilst Table 4.2 contains the measured chemical and physical characteristics of cement kiln dusts.

4.3.2 Saturated hydraulic conductivity test specimens and apparatus

The saturated hydraulic conductivity $k_s$ of pure tailings specimens and specimens from mixtures of tailings and stabilization additives were evaluated using the fixed-wall, constant-flow-rate permeameter system (Fig. 4.3) described previously by Fernandez and Quigley (1985). The equipment generates a constant flow rate through the test specimen, and the induced head drop across the specimen is used to calculate the hydraulic conductivity, $k_s$ using Darcy’s law. The mine tailings paste mixtures (tabulated in Table 4.3) prepared for UCS testing as described in section 3.4.2.1 were cast in 5.38 cm diameter steel cylinders and sealed in plastic bags (see Appendix B.1 and B.2). The
specimens were stored in a curing chamber at 100% RH and 25°C before hydraulic conductivity testing. Each specimen in a steel cylinder was enclosed by porous disks at its ends as shown in Fig. 4.4. A filter paper was placed between the sample and the porous disk. A confining stress was applied to the sample by means of a calibrated stainless steel spring-loading mechanism to prevent swelling of the specimen during testing.

The space between the upper porous disk and the upper cap was filled with the water. Distilled water was used to simulate rain water and also to have a minimum effect on hydration products of cemented paste tailings. O-rings sealed the contact between the cell and the stainless steel end caps. Each cell was held together by four threaded rods. All steel cylinders containing samples were mounted on a frame. The syringes were filled with the water, and entrapped air was expelled out from the system by driving the plungers. A pressure transducer was attached to the syringe in each circuit. A triaxial loading frame driving piston-syringe system containing water was used to generate a constant flow rate. The motorized feed rate was adjusted to maintain a positive pressure in the chambers of the hydraulic conductivity apparatus and provide a constant flow and desired permeation rate (see Appendix B.3). The specimens were permeated with distilled water until the hydraulic conductivity stabilized. A confining stress of 30 kPa and an imposed constant flow rate of $7.4 \times 10^{-3}$ mL/s were used in the experiments. Influent pressure was monitored with a pressure transducer, while the effluent pressure was maintained at atmospheric pressure. A column of water above the specimens and constant imposed flow rate confirmed the saturated state of tested specimens (Figure 4.4).
The average result of three specimens was taken to ascertain the accuracy of each test. The homogenized mine tailings sample MT (control sample) and cured paste specimens having different percentages of binders/additives (Table 4.3) were permeated with distilled water until the saturated hydraulic conductivity $k_s$ and hydraulic gradient stabilized.

4.4 Results and discussion

4.4.1 Saturated hydraulic conductivity evolution of cemented paste tailings prepared with single and binary binders comprising DA, DH, GU and HS

A nearly constant value of saturated hydraulic conductivity for control MT sample ($5.1 \times 10^{-5}$ cm/s) suggested negligible alteration of interconnected pores within the tailings during permeation as shown in Figure 4.5. The observed hydraulic conductivity falls within the usual range ($10^{-6}$ to $10^{-4}$ cm/s) for homogenized tailings (Pettbone and Kealy 1971, Qui and Sego 2001). The uncovered sulphidic mine tailings would be expected to facilitate the ingress of moisture (water) and air (oxygen), and hence, the oxidation of pyrite present in the tailings. Thus the tailings could not be surface disposed of in an environmentally safe manner without adopting additional measure(s) since the hydraulic conductivity value is well above the permitted maximum limit of $1 \times 10^{-5}$ cm/s for wastes planned for land disposal/burial (US EPA 1986).
In Portland cement based cemented paste tailings specimens, i.e., MT+7%GU and MT+7%HS, the value of $k_s$ decreased rapidly in the first 7 days of curing from $5.1 \times 10^{-5}$ to $1.5 \times 10^{-6}$ cm/s and $1 \times 10^{-6}$ cm/s, respectively (Figures 4.5 and 4.6). This period also corresponds to the highest reduction in $k_s$ with curing time for Portland cements. According to Taylor (1990), the early hydration phase of cement corresponds to the period in which major hydration products are formed. These cement hydrates gradually fill the initial pores of the cemented paste and are responsible for the depletion of fluid transportability of the solidified matrix. After 7 days, a further decrease in saturated hydraulic conductivity occurred as evident from Figure 4.5. The observed value of $k_s$ at 28 days of curing was $8 \times 10^{-7}$ cm/s and $7 \times 10^{-7}$ cm/s (Figures 4.5 and 4.6, respectively). The reduced $C_3A$ content in Type HS cement and the resulting decreased amount of secondary gypsum and ettringite generated by the hydration of HS can be a reason for the slightly higher $k_s$ value of MT+7%HS relative to that of the MT+7%GU paste mixture. Secondary gypsum can potentially fill additional pores in the matrix such as cemented paste tailings (Fall and Benzaazoua 2005, Ercikdi et al. 2009). The data indicate that 7%GU and 7%HS contributed to a reduction in $k_s$ by at least 1½ orders of magnitude in 28 days of curing period, as shown in Figures 4.7 and 4.8.

The cured paste specimens MT+8%DA and MT+8%DH reduced hydraulic conductivity values from $5.1 \times 10^{-5}$ to $1.2 \times 10^{-5}$ and $2.7 \times 10^{-6}$ cm/s, respectively, at 28 days of curing (Figures 4.6 and 4.9). DA contributed to the reduction in $k_s$ by at least 1/2 order of magnitude, whereas, DH by approximately 1 order of magnitude during 28 days of curing. The early hydration reactions within cement kiln dust based composites, such as
cemented paste tailings, generate hydrated silicate and aluminate compounds analogous to those in the case of Portland cement. The tailings solids act as aggregates to form a low strength concrete (Conner 1993, Nehdi and Tariq 2007). DA and DH produced hydration products that filled pores within tailings material, encapsulated the tailings particles, and thus reduced the permeability of the cemented paste tailings. The production of $C-S-H$ gel is responsible for the blockage of flow paths within tailings and results in matrix densification. The $k_s$ value of the 8%DA treated sample is $1.2 \times 10^{-5}$ cm/s, which is slightly higher than the maximum hydraulic conductivity permitted by US EPA (1986); on the other hand, the paste specimen containing 8%DH achieved a $k_s$ value of $2.7 \times 10^{-6}$ cm/s, which is lower than the acceptability criterion. It is believed that the decrease in hydraulic conductivity of cement kiln dust based paste is due to the high free CaO content of the DH or DA, and to its considerable cementitious properties by virtue of the low loss on ignition values, as shown the Table 4.2.

The addition 3%GU+8%DA, 3%HS+8%DA, 3%GU+8%DH, and 3%HS+8%DH to mine tailings reduced the $k_s$ values of cemented paste tailings specimens to $1 \times 10^{-6}$, $1.2 \times 10^{-6}$, $1.4 \times 10^{-7}$, and $2 \times 10^{-7}$ cm/s, respectively, at 28 days of curing (Figures 4.5, 4.6, 4.9, and 4.10, respectively). The hydration of Portland cement and cement kiln dust generate similar hydrated phases and their collective use in an appropriate proportion can facilitate solidification processes due to the production of large amounts of $C-S-H$. These binders contributed to a reduction in $k_s$ by at least 1½ orders of magnitude, 1½ orders of magnitude, 2½ orders of magnitude, and more than 2 orders of magnitude as shown in Figures 4.7, 4.8, 4.11, and 4.12, respectively.
The reductions in saturated hydraulic conductivity for cemented paste tailings specimens containing 7%GU, 7%HS, 8%DA, 8%DH, 3%GU+8%DA, 3%GU+8%DA, 3%HS+8%DA, and 3%HS+8%DH were comparable. This group of specimens show a rapid decrease in $k_s$ during the first 7 days of curing, followed by a steady reduction up to 28 days of curing.

4.4.2 Saturated hydraulic conductivity evolution of cemented paste tailings prepared with binary and ternary binders comprising DA, DH, FC, GU, and HS

The additions of 8%FC in conjunction with 8% cement kiln dust (i.e., 8%DA+8%FC and 8%DH+8%FC) produced $k_s$ values of $4.2 \times 10^{-6}$ and $1 \times 10^{-6}$ cm/s, respectively, for 28 day cured cemented paste tailings specimens. Using these composite binders can result in monoliths with modified pore structure of the solidified matrices due to synergistic effects between the cementitious CKD, and the cementitious and pozzolanic FC. Matrix densification due to such cementitious and pozzolanic reactions lowered the saturated hydraulic conductivity of the pastes. The incorporation of Type CI fly ash alone or in combination with Portland cement triggers two important mechanisms when mixed with sulphidic tailings, the first mechanism consists of the addition of alkalinity and neutralization of acidity. The second mechanism refers to the reduction in hydraulic conductivity, which inhibited water penetration into sulphidic tailings and hence the generation of acidic drainage (Nehdi and Tariq 2007). Oxidation of tailings is caused by ingress of oxygen, which is controlled by diffusion. Water penetration can cause less
oxidation if the water is oxygenated, which is usually the case. These composite binders effectively reduced $k_s$ of the resultant monoliths.

The saturated hydraulic conductivity $k_s$ of the paste specimens produced by the addition of 3%GU+8%FC and 3%HS+8%FC at 28 days of curing was $1.6 \times 10^{-6}$ and $1 \times 10^{-6}$ cm/s, as evident from Figures 4.5 and 4.6, respectively. These additions contributed to a reduction in $k_s$ by at least 1½ orders of magnitude in 28 days of curing, as shown in Figures 4.7 and 4.8. In Portland cement-fly ash systems, fly ash reacts with calcium hydroxide generated from Portland cement hydration to produce stable calcium silicate and aluminate hydrates. These hydration products possess the capability of filling the voids within the solidified matrix such as cemented paste tailings. Additionally, the reduction in the amount of lime remaining further reduces the occurrence of water soluble $Ca(OH)_2$, which improves the strength, durability, and reduced hydraulic conductivity of the resultant monolith.

The addition of 3%GU+8%DA+5%FC, 3%HS+8%DA+5%FC, 3%GU+8%DH+5%FC, and 3%HS+8%DH+5%FC contributed to the reduction in $k_s$ by at least 2½ orders of magnitude, 2½ orders of magnitude, 3 orders of magnitude, and 3 orders of magnitude, respectively, in 28 days of curing, as shown in Figures 4.7, 4.8, 4.11, and 4.12. Pozzolanic materials perform different functions when used in Portland cement based systems. They modify the properties of binders in pozzolanic reactions. The small particles of supplementary cementing materials help to eliminate pores and micro pores
by acting as filler and micro fillers, resulting in increased density of the hardened composite. They also fill the voids between the fine cement grains that would otherwise be occupied by water within the matrix, thereby improving particle packing effect. The cumulative physical and chemical effects may generate denser and stronger hardened cement paste in interfacial transition zone encapsulating aggregate particles such as tailings grains (Brandt 2009).

The akin reduction pattern in $k_s$ for cemented paste tailings specimens prepared with $8\%$DA+$8\%$FC, $8\%$DH+$8\%$FC, $3\%$GU+$8\%$FC, $3\%$GU+$8\%$DA+$5\%$FC, $3\%$GU+$8\%$DH+$5\%$FC, $3\%$HS+$8\%$FC, $3\%$HS+$8\%$DA+$5\%$FC, $3\%$HS+$8\%$DH+$5\%$FC can be readily observed in Figures 4.5, 4.6, 4.9, and 4.10. It is evident that these binders caused the hydraulic conductivity values to reach a plateau after 14 days of curing.

### 4.4.3 Saturated hydraulic conductivity evolution of cemented paste tailings prepared with binary and ternary binders comprising DA, DH, SL, GU, and HS

The addition of $8\%$DA+$8\%$SL and $8\%$DH+$8\%$SL to MT lowered the $k_s$ of hardened mine tailings paste specimens from $5.1\times10^{-5}$ cm/s to $6\times10^{-7}$ and $1.1\times10^{-7}$ cm/s, respectively, after 28 days of curing (Figures 4.5 and 4.9). The incorporation of $8\%$DA+$8\%$SL and $8\%$DH+$8\%$SL contributed to the reduction in $k_s$ by approximately 1½ orders of magnitude and 2 orders of magnitude as shown in Figures 4.7 and 4.11, respectively. The decrease in the saturated hydraulic conductivity can be attributed to the activation of SL by the total alkalis ($Na_2O_{eq}$) present in DA and DH (Table 4.2) at the
later ages of hydration, resulting in the formation of secondary $C\text{-}S\text{-}H$ filling up more available pore volume within cemented paste tailings matrix in hardened state (Shoaib et al. 2000). The filler effect of SL may also have played a role.

The observed value of saturated hydraulic conductivity produced by the composite containing 3%GU+8%SL at 28 days of curing was $5.1 \times 10^{-7}$ cm/s, which is lower than that of paste specimen made with 7%GU alone ($8.0 \times 10^{-7}$ cm/s). This can be attributed mainly to the effect of fine supplementary cementing material addition such as ground granulated blast furnace slag capable of producing filler effect in addition to the binder hydration products. Bakker (1983) conducted permeability experiments on hardened cement pastes made with Portland cement alone and in amalgamation with blast furnace slag. It was observed that the precipitation of calcium hydroxide in Portland cement based mixes can be inadequate for the total blocking of pores within the cement paste, while in Portland cement-slag mixes, $Al_2O_4$ and $SiO_3$ delivered by the hydration of slag can meet the released calcium hydroxide from Portland cement clinker. It was concluded that the precipitation of calcium silicate hydrate ($C\text{-}S\text{-}H$) and calcium aluminate hydrate ($C_4AH_{13}$) in cement-slag mix can fully block the pores of the hardened paste, resulting in much reduced permeability.

The observed 28 day $k_s$ value for the paste specimen produced with 3%HS+8%SL is $5.3 \times 10^{-7}$ cm/s, as shown in Figure 4.8. Pozzolanic materials such as slags contribute to refinement of the pore structures when used in conjunction with Portland cement.
(Manmohan and Mehta 1981). The pozzolanic reactions of slag with calcium hydroxide in cemented matrix generate additional calcium silicate hydrate ($C-S-H$) gel. These result in additional hydration products that favour enhanced pore refinement and densification of the cemented matrix. This, in turn, can reduce the transportability of fluids through the cemented paste tailings. It can be seen in Figures 4.5, 4.6, 4.9, and 4.10 that the $k_5$ values for cemented paste tailings containing slag are lower than GU based pastes, since the hydration mechanisms of GU-slag binder systems are delayed later than those of Portland cement alone (Demirboga 2007).

The paste specimens containing ternary binder blends, i.e., 3%GU+8%DA+8%SL, 3%HS+8%DA+8%SL, 3%GU+8%DH+8%SL, and 3%HS+8%DH+8%SL achieved 28-day $k_5$ values of $4.7 \times 10^{-8}$, $4 \times 10^{-8}$, $1 \times 10^{-8}$, and $1.6 \times 10^{-8}$ cm/s, respectively (Figures 4.5, 4.6, 4.9, and 4.10, respectively). When slag starts to dissolve in alkaline pore solution resulting from cement hydration in a cement-slag binder system, it forms secondary $C-S-H$, which fills the capillary pore space left by the prior hydration of the Portland cement fraction. This implies that the hydration of slag can make capillary pores discontinuous by providing secondary discrete blockages of $C-S-H$ across pores. Slag is also known for enhancing the bond and reducing the porosity of cement-aggregate interfaces in mortars and concretes (Hooton 2000).

The incorporation of 3%GU+8%DA+8%SL, 3%HS+8%DA+8%SL, 3%GU+8%DH+8%SL, and 3%HS+8%DH+8%SL as binders in cemented paste tailings
formulations contributed to the reduction in saturated hydraulic conductivity by more than 3 orders of magnitude in 28 days of curing period as evident from Figures 4.7, 4.8, 4.11, and 4.12.

Figures 4.5, 4.6, 4.9, and 4.10 illustrate similar trends in $k_s$ reduction for mine tailings paste specimens made with 8%DA+8%SL, 8%DH+8%SL, 3%GU+8%SL, 3%HS+8%SL, 3%GU+8%DA+8%SL, 3%GU+8%DH+8%SL, 3%HS+8%DA+8%SL, 3%HS+8%DH+8%SL. These figures demonstrate that binary and ternary binders containing SL continue to generate considerable hydration products and result in substantially reduced water percolation up to 28 days of curing.

The above discussion substantiates the influence of binder type on the evolution of saturated hydraulic conductivity. The cement kiln dust-slag based binders have a greater effect on saturated hydraulic conductivity than the cement kiln dust-fly ash binders. In the case of the latter binders, the hydraulic conductivity values reach a plateau after 14 days of curing, whereas the former binders continue to generate considerable hydration products and result in substantially reduced water percolation until 28 days of curing.
4.4.4 Saturated hydraulic conductivity evolution of cemented paste tailings with quaternary binders containing DA, DH, SL, FC, GU and HS

The cemented paste tailings specimens formulated by the addition of quaternary binders, i.e., 3%GU+8%DA+5%FC+8%SL, 3%HS+8%DA+5%FC+8%SL, 3%GU+8%DH+5%FC+8%SL, and 3%HS+8%DH+5%FC+8%SL attained 28-day $k_s$ values of $1 \times 10^{-8}$, $1.2 \times 10^{-8}$, $3.2 \times 10^{-9}$, and $2.7 \times 10^{-9}$, respectively (Figures 4.5, 4.6, 4.9, and 4.10). These quaternary blends contributed to reduction in $k_s$ by at least $3 \frac{1}{2}$, $3 \frac{1}{2}$, 4, and more than 4 orders of magnitude, respectively (Figures 4.7, 4.8, 4.11, and 4.12). The paste specimens containing quaternary binder blends demonstrated exceedingly low $k_s$ values than mixtures containing single, binary, and ternary binders/additives.

When Portland cement hydrates in mortars and concretes, sulphaaluminate and calcium hydroxide are found throughout the bulk paste. The large size crystals become available in the transition zone (porous area in the paste around aggregate/tailings grains) since relatively large pore spaces are available for the crystals to grow. The fine particles of pozzolanic materials such as slag and fly ash near these transition zones react with the local calcium hydroxide crystals to form more $C-S-H$. This additional $C-S-H$ (often called secondary ($C-S-H$)) growth is principally responsible for filling the weak and permeable transition zones, improving matrix strength and reducing permeability along the pathways (Hooton 2000). A combination of several mechanisms, such as cementitious and pozzolanic reactivity, particle packing effect and densification of the interfacial transition zone between tailings particles and the cementing paste, can radically reduce
the permeability of cement-based materials (Brandt 1995, Nehdi and Mindess 1999). The enhanced activation of pozzolanic materials by high calcium cement kiln dusts (DH and DA), improved particle packing density by virtue of blending coarser tailings, fine SL, Type CI fly ash (FC), and micro-structural synergistic action in blended cementing materials can contribute to the decrease in the saturated hydraulic conductivity of the resultant matrices. The resistance to external sulphate attack is greatly dependent on the hydraulic conductivity of the cement paste or cement based composite (Baker 1983, Roy and Idorn 1982). According to Mehta (1981), the chemical resistance of blended cements originates principally from the process of pore refinement associated with the pozzolanic reactions involving the removal of calcium hydroxide. The quaternary binder blends effectively reduced the saturated hydraulic conductivity of the resultant monoliths, turning them into effective barriers against water percolation.

It can be seen from Figures 4.5, 4.6, 4.9, and 4.10 that cemented paste tailings specimens composed of quaternary binders, i.e., 3%GU+8%DA+5%FC+8%SL, 3%HS+8%DA+5%FC+8%SL, 3%GU+8%DH+5%FC+8%SL, and 3%HS+8%DH+5%FC+8%SL, produced reductions in $k_s$ values in a similar fashion. The reduction in $k_s$ occurs quickly in the first 14 days of curing and decreases at a slower rate for the next 14 days.

Replacing GU by HS in ternary and quaternary binders did not produce significant difference in $k_s$ values except the case when HS was used alone as a sole binder. In this
case, slightly higher values of MT-HS paste saturated hydraulic conductivity at 7 and 14 days of curing were observed. However, on the 28th day, $k_s$ values for MT-GU and MT-HS were not rationally differentiable.

### 4.4.5 Comparison of saturated hydraulic conductivity between early and later ages of curing

Figures 4.13 to 4.16 show the comparison of saturated hydraulic conductivity values between 28-day and 120-day cured cemented paste tailings specimens. A slight increase in $k_s$ (with respect to 28th day) was observed in Type GU based cemented paste tailings specimens at 120th day of curing. A closer examination of Figures 4.13 and 4.14 reveals that the increase in $k_s$ was greater in specimens containing GU followed by those made with DH or DA, FC, SL, and HS. The contributing hydration products associated with internal sulphate attack mechanisms in Type GU cement based matrices are the monosulphate hydrate, calcium aluminate hydrate, and calcium hydroxide. This effect is intimately related to the sulphate concentration, curing time and the amount and chemical composition of the binder. If the sulphate contents exceed 10,000 ppm (13,730 ppm in the present case), detrimental precipitation of swelling secondary gypsum may be expected, which can be a source for an internal sulphate attack in cementitious matrix (Belem and Benzaazoua 2008). The generated volume of hydration products can be far in excess of the available pore volume, thereby creating internal stresses that can lead to expansion and, subsequently, micro-cracking. The slight increase in saturated hydraulic conductivity of the specimen incorporating a higher percentage of GU (7%) as a binding
agent may be attributed to the formation and propagation of connected networks of micro-cracks over time resulting from sulphate attack (Fall et al. 2009). Moreover, the observed increase in saturated hydraulic conductivity was proportional to the dosage of GU in sulphidic cemented paste tailings made with both single binders and composite binders.

Figures 4.15 and 4.16 show slightly reduced hydraulic conductivity values at 120th day of curing with respect to 28th day for cemented paste tailings specimens containing ternary and quaternary binders, i.e., 3%HS+8%DA+5%FC, 3%HS+8%DA+8%SL, 3%HS+8%DA+5%FC+8%SL, 3%HS+8%DH+5%FC, 3%HS+8%DH+8%SL, and 3%HS+8%DH+5%FC+8%SL. The addition of SL, DH or DA, and FC to HS-tailings mixtures reduced the availability of calcium aluminate compounds susceptible to sulphate attack and provided better long-term water retention capabilities for the hardened composites as shown in Figures 4.15 and 4.16.

No significant difference was found between the measured values of $k_s$ for cemented paste tailings specimens at 120th day and 360th day of curing.
4.5 Conclusions

The present study was carried out to determine the effect of enhanced Pozzolanic reactivity of ground granulated blast furnace slag and Type C fly ash using calcium and alkali rich cement kiln dusts in reducing the saturated hydraulic conductivity of sulphidic cemented paste tailings. Based on the results, the following is concluded:

- The evolution of saturated hydraulic conductivity with respect to curing time for the cured mine tailings-binder amalgamations showed an overall trend of decrease in $k_s$ with curing time. The delineation of $k_s$ evolution trends were predominantly based on the hydration mechanisms of a specific binder or binder-additive amalgamation used to formulate a particular paste material.

- The precipitation of calcium hydroxide in Type GU based cemented paste tailings can be inadequate for total blocking of pores within cemented paste tailings matrix. Slag and Type C fly ash perform different beneficial functions when used as a partial replacement of Portland cement. However, sufficient quantity of cement can only ensure complete hydration of SL and/or FC.

- By virtue of its highly alkaline soluble fraction, high calcium CKD can successfully be used as activating agent for SL and FC in cemented paste tailings, since its principal constituents contain enough calcium to trigger the reactivity of aluminosilicate glass contained in such Pozzolanic materials. The enhanced pozzolanic reactivity of SL and FC with additional calcium hydroxide produced by the incorporation of high calcium and alkali rich cement kiln dust in mine tailings cemented matrices generated additional calcium silicate hydrate ($C-S-H$).
calcium hydroxide crystals to form more $C$-$S$-$H$, improving particle packing effect. The secondary $C$-$S$-$H$ growth is considered to be principally responsible for filling the weak and permeable transition zones. The improved pozzolanic reactions resulted in additional hydration products, favoring enhanced pore refinement and densification, which, in turn, reduced the transportability of fluid through the hardened matrices.

- The slag-cement kiln dust based binders have more pronounced affect on saturated hydraulic conductivity than the Type CI fly ash based binders. In the case of the latter binders, the saturated hydraulic conductivity values reach a plateau after 14 days of curing, whereas the former binders continue to generate considerable hydration products and result in reduced water percolation up to 28 days of curing. A combination of several mechanisms, such as enhanced cementitious and pozzolanic reactivity, particle packing effect and densification of the interfacial transition zone between tailings particles and the cementing paste, can radically reduce the permeability of cemented paste tailings considerably.

- In cemented paste tailings formulated with quaternary binders, the enhanced activation of pozzolanic materials by high calcium cement kiln dusts (DH and DA), improved particle packing density by virtue of blending coarser tailings, slag, Type CI fly ash, and micro-structural synergistic action contributed to a decrease in the saturated hydraulic conductivity of the resultant cemented matrices. Consequently, the precipitation of calcium silicate hydrate ($C$-$S$-$H$) and calcium aluminate hydrate in such mixes served to fully block the pores of the
hardened cemented paste tailings, resulting in significantly reduced saturated hydraulic conductivity.

- The cemented paste tailings containing Type GU cement as binder are susceptible to formation and propagation of connected network of micro-cracks due to sulphate attack at later ages since a slight increase in $k_s$ has been observed in such specimens. This can be overcome by using ternary and quaternary binders in sulphidic cemented paste tailings formulations that contain a small amount of Portland cement in combination with selective cement kiln dust and slag.
4.6 References


<table>
<thead>
<tr>
<th>Chemical characteristics</th>
<th>Mattabi Mine Tailings</th>
<th>Ground granulated blast furnace slag</th>
<th>High sulphate resistant hydraulic cement</th>
<th>Type CI fly ash</th>
<th>General Use hydraulic cement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MT</td>
<td>SL</td>
<td>HS</td>
<td>FC</td>
<td>GU</td>
</tr>
<tr>
<td>Major oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>31.60</td>
<td>34.98</td>
<td>22.03</td>
<td>42.37</td>
<td>19.87</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.29</td>
<td>0.25</td>
<td>0.18</td>
<td>0.81</td>
<td>0.24</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>7.03</td>
<td>9.11</td>
<td>3.57</td>
<td>18.66</td>
<td>4.93</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>37.83</td>
<td>1.86</td>
<td>3.67</td>
<td>5.75</td>
<td>2.38</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.85</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.22</td>
<td>9.37</td>
<td>2.87</td>
<td>3.54</td>
<td>2.77</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14</td>
<td>38.56</td>
<td>63.36</td>
<td>16.90</td>
<td>65.37</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.22</td>
<td>0.51</td>
<td>0.42</td>
<td>1.18</td>
<td>0.44</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.27</td>
<td>1.22</td>
<td>0.00</td>
<td>2.53</td>
<td>0.00</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>L.O.I</td>
<td>19.41</td>
<td>0.43</td>
<td>1.03</td>
<td>5.06</td>
<td>1.93</td>
</tr>
<tr>
<td>Total</td>
<td>97.09</td>
<td>97.14</td>
<td>97.20</td>
<td>97.13</td>
<td>98.00</td>
</tr>
<tr>
<td>Physical characteristics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity (Gs)</td>
<td>3.88</td>
<td>2.86</td>
<td>3.12</td>
<td>2.43</td>
<td>3.13</td>
</tr>
<tr>
<td>Specific surface area BET (m$^2$/kg)</td>
<td>322</td>
<td>1983</td>
<td>1070</td>
<td>852</td>
<td>1190</td>
</tr>
<tr>
<td>D$_{50}$ (microns)</td>
<td>40.1</td>
<td>10.1</td>
<td>15.0</td>
<td>20.0</td>
<td>14.5</td>
</tr>
</tbody>
</table>

$^1$CAN/CSA A3001-03 Type CI (Intermediate calcium content fly ash); ($SiO_2+Al_2O_3+Fe_2O_3$) min % > 50% [SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ = 66.78%]; CaO < 20%

$^2$CAN/CSA A3001-03 Type GU: General use hydraulic cement (equivalent to ASTM Type I)

$^3$CAN/CSA A3001-03 Type HS: High sulphate resistant cement (equivalent to ASTM Type V)

$^4$CAN/CSA A3001-03 Type S: Ground granulated blast furnace slag
Table 4.2 Chemical and physical properties of cement kiln dusts

<table>
<thead>
<tr>
<th>Chemical characteristics</th>
<th>DA</th>
<th>DH</th>
<th>Range for major oxides 63 different CKDs†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major oxides (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>18.6</td>
<td>18.40</td>
<td>2.2-34.3</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.73</td>
<td>3.91</td>
<td>1.1-10.5</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.30</td>
<td>3.41</td>
<td>0.2-6.0</td>
</tr>
<tr>
<td>CaO</td>
<td>52.4</td>
<td>57.8</td>
<td>19.4-61.3</td>
</tr>
<tr>
<td>MgO</td>
<td>2.56</td>
<td>1.31</td>
<td>0.5-3.5</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.14</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>8.62</td>
<td>4.32</td>
<td>0.02-17.4</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4.40</td>
<td>4.91</td>
<td>0.1-15.3</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.71</td>
<td>0.81</td>
<td>0.0-6.3</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.10</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>’L.O.I</td>
<td>5.12</td>
<td>4.80</td>
<td>4.2-42.4</td>
</tr>
<tr>
<td>‡† Total oxides</td>
<td>99.68</td>
<td>99.98</td>
<td></td>
</tr>
<tr>
<td>*Free CaO</td>
<td>22.80</td>
<td>26.3</td>
<td>0-27.2</td>
</tr>
<tr>
<td>**Total alkalis=(Na&lt;sub&gt;2&lt;/sub&gt;O)eq(%)</td>
<td>3.60</td>
<td>4.04</td>
<td>0.14-11.42</td>
</tr>
<tr>
<td>***Total reactive oxides (TRO) (%)</td>
<td>44.73</td>
<td>48.60</td>
<td>1.86-56.08</td>
</tr>
<tr>
<td>Specific gravity (Gs)</td>
<td>2.86</td>
<td>2.81</td>
<td>‡†† 2.48-2.96</td>
</tr>
<tr>
<td>Specific surface area</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET (m&lt;sup&gt;2&lt;/sup&gt;/Kg)</td>
<td>1968</td>
<td>1782</td>
<td></td>
</tr>
<tr>
<td>D&lt;sub&gt;50&lt;/sub&gt; (microns)</td>
<td>10.4</td>
<td>15.2</td>
<td></td>
</tr>
</tbody>
</table>

*Loss on ignition determined at (950±50°C)

††XRF sum of total oxides

*Analysis carried out in accordance with ASTM C25-06

**Total alkalis= (Na<sub>2</sub>O)eq = (Na<sub>2</sub>O+0.658K<sub>2</sub>O) (Wang et al. 2007)

*** Total reactive oxide content=TRO= [(CaO+MgO)−LOI]−[K<sub>2</sub>O+Na<sub>2</sub>O] (Collins and Emery 1983)

†Statistics on composition of 63 different cement kiln dusts from various sources (Sreekrishnavilasam et al. 2006)

†††(Peethamparan et al. 2008, Collins and Emery 1983)
Table 4.3 Mixture proportions of mine tailings and binder reagents

<table>
<thead>
<tr>
<th>DA based binders containing SL, FC, GU and HS</th>
<th>DH based binders containing SL, FC, GU and HS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT+8%DA+8%FC</td>
<td>MT+8%DH+8%FC</td>
</tr>
<tr>
<td>MT+8%DA+8%SL</td>
<td>MT+8%DH+8%SL</td>
</tr>
<tr>
<td>MT+3%GU+8%DA</td>
<td>MT+3%GU+8%DH</td>
</tr>
<tr>
<td>MT+3%HS+8%DA</td>
<td>MT+3%HS+8%DH</td>
</tr>
<tr>
<td>MT+3%GU+8%DA+5%FC</td>
<td>MT+3%GU+8%DH+5%FC</td>
</tr>
<tr>
<td>MT+3%HS+8%DA+5%FC</td>
<td>MT+3%HS+8%DH+5%FC</td>
</tr>
<tr>
<td>MT+3%GU+8%DA+8%SL</td>
<td>MT+3%GU+8%DH+8%SL</td>
</tr>
<tr>
<td>MT+3%HS+8%DA+8%SL</td>
<td>MT+3%HS+8%DH+8%SL</td>
</tr>
<tr>
<td>MT+3%GU+8%DA+5%FC+8%SL</td>
<td>MT+3%GU+8%DH+5%FC+8%SL</td>
</tr>
<tr>
<td>MT+3%HS+8%DA+5%FC+8%SL</td>
<td>MT+3%HS+8%DH+5%FC+8%SL</td>
</tr>
</tbody>
</table>

*Binders for comparative assessment*

| MT+7%GU                                      | MT+7%HS                                      |
| MT+8%DA                                      | MT+8%DH                                      |
| MT+3%GU+8%FC                                 | MT+3%HS+8%FC                                 |
| MT+3%GU+8%SL                                 | MT+3%HS+8%SL                                 |
Figure 4.1 Particle size distributions of MT, GU, HS, SL, and FC

Figure 4.2 Particle size distributions of cement kiln dusts (DA and DH)
Figure 4.3 Schematic diagram of fixed wall constant flow rate hydraulic conductivity apparatus (After Fernandez and Quigley 1985)

Figure 4.4 Schematic of one-permeameter cell of fixed wall hydraulic conductivity apparatus (After Fernandez and Quigley 1985)
Figure 4.5 Saturated hydraulic conductivity \( (k_s) \) evolution of cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and GU

Figure 4.6 Saturated hydraulic conductivity \( (k_s) \) evolution of cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and HS
Figure 4.7 Saturated hydraulic conductivity ($k_s$) of control MT sample and 28-day cured cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and GU

Figure 4.8 Saturated hydraulic conductivity ($k_s$) of control MT sample and 28-day cured cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and HS
Figure 4.9 Saturated hydraulic conductivity ($k_s$) evolution of cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and GU

Figure 4.10 Saturated hydraulic conductivity ($k_s$) evolution of cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and HS
Figure 4.11 Saturated hydraulic conductivity ($k_s$) of control MT sample and 28-day cured cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and GU

Figure 4.12 Saturated hydraulic conductivity ($k_s$) of control MT sample and 28-day cured cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and HS
Figure 4.13 Saturated hydraulic conductivity ($k_s$) of 28-day and 120-day cured cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and GU

Figure 4.14 Saturated hydraulic conductivity ($k_s$) of 28-day and 120-day cured cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and GU
Figure 4.15 Saturated hydraulic conductivity ($k_s$) of 28-day and 120-day cured cemented paste tailings prepared with MT and binders comprising DA, SL, FC, and HS.

Figure 4.16 Saturated hydraulic conductivity ($k_s$) of 28-day and 120-day cured cemented paste tailings prepared with MT and binders comprising DH, SL, FC, and HS.
CHAPTER 5

METAL IMMOBILIZATION IN CEMENTED PASTE TAILINGS USING SLAG AND TYPE C FLY ASH ACTIVATED BY HIGH AND LOW CALCIUM CEMENT KILN DUSTS

5.1 Introduction

Metal mining is vital for the economy of many countries endowed with natural resources, and in some cases, it can be the dominant source of international revenue. Today's increased demand for metals has led to accumulation of substantial amounts of metal mining wastes that must be managed carefully since heavy metals and arsenic contained in such materials pose a risk to human and ecosystem health because of their non-degradability and environmentally persistent characteristics. In the absence of effective intervention measures, such mineral production operations can produce significant pollution in the form of acid mine drainage, which can threaten ground and surface water (Yanful and St-Arnaud 1992, Yanful and Orlandea 2000). This, in turn, can adversely affect the health of communities that rely on such water resources for drinking or agricultural purposes. Other manufacturing and industrial processes generate byproducts such as cement kiln dust, blast furnace slag, and fly ash which, in the past, were merely either disposed of in a manner that paid little attention to environmental protection or recycled to a limited extent. Today, efforts to recycle/reuse, or to minimize such byproducts and industrial wastes are necessary based on economic and environmental imperatives.
A variety of environmentally problematic/chemically hazardous wastes can be incorporated into a cementitious waste system using solidification/stabilization (S/S) (Conner 1990, Spence and Shi 2005). In particular, the inorganic suspended contaminants can be incorporated into a final hardened concrete matrix such as cemented paste tailings since S/S is highly effective for waste rich in inorganic contaminants. In the solidification process, the monolith binds and strengthens the mass and coats and incorporates pollutants in the siliceous solids. Physical entrapment or encapsulation can be achieved by generating a solidified monolith, whereas, chemical assimilation may be attained by incorporation metals and metalloid elements in binder hydration products such as calcium silicate hydrate (C-S-H).

Cemented paste tailings has been considered a viable option to manage heavy metal-bearing waste for surface and underground disposal scenarios. Ordinary Portland cement is the most adaptable binder currently available for the immobilization of heavy metals. The alkaline environment created by Ca(OH)$_2$ and cement are commonly used in acidic waste conditioning because of relatively low operating cost. These systems readily incorporate wet wastes such as mine tailings and their alkalinity prevent or reduces the solubility of many toxic metals. The mechanisms for metal stabilization involve pH control and buffering, speciation/precipitation/re-precipitation, oxidation/reduction, and sorption/ion exchange. Owing to the fact that the metals are not often present as simple compounds in such matrices, a combination of mechanisms is presumed to be active in cementitious systems containing metallic elements (Spence and Shi 2005).
5.2 Portland cement, ground granulated blast furnace slag, and cement kiln dust based remediation systems for wastes containing metals

The dominant phases generated by Portland cement hydration are (a) 60-70% of calcium silicate hydrate \((3CaO \cdot 2SiO_2 \cdot 3H_2O)\), a gel of variable stoichiometry abbreviated as \(C-S-H\) (b) 20-25% of calcium hydroxide \([Ca(OH)_2]\) or portlandite.. Bhatty (1987) investigated the interaction of cadmium, chromium, lead, mercury and zinc in Portland cement based metallic waste matrices and argued that the mechanism of fixation of metallic ion in such systems may take place in several ways including: (a) fixation of metal by addition reaction in which metallic ion is taken up in the structure of \(C-S-H\), (b) fixation by substitution of metallic ion by calcium \((Ca ^{+2})\) in the structure of \(C-S-H\) (c) fixation by formation of a new compound which is normally insoluble in a system such as \(C_3S-CaSO_4\), (d) fixation by multiple mechanisms rendering such systems more complex to evaluate.

Ordinary Portland cements alone have been broadly used for stabilization/solidification of metallic wastes; however, their effectiveness to adequately stabilize or fix metals such as \(Hg, Pb\) and \(Cu\) is uncertain (Conner 1990, Spence and Shi 2005, Shi and Fernández-Jiménez 2006). Researchers have noted that the pH of interstitial pore solution in a hydrated cement paste is often above 12, which is not ideal for complete stabilization of some metals. In Portland cement based solidified/stabilized metallic waste, the high pH of fresh cement constituents favours the precipitation of many metals as hydroxide, hydrous oxide, or carbonates. However, only surface substitution occurs when metals are
present as aqueous ions, and no incorporation takes place if the metals exist as insoluble chemical compounds. In the latter case, ettringite and monosulphate phases of hydrated cement paste can accommodate more metals within their structure (Bonan and Sarkar 1994).

Cement and/or pozzolan-based stabilization of mine tailings containing metallic and metalloid elements owe its effectiveness to the formation of calcium silicate hydrates (C-S-H) (Conner 1990). In such systems, heavy metals can interact in a number of ways including adsorption, chemical precipitation, ion exchange, surface complexation, micro-encapsulation, chemical incorporation in the hydrated new phases, diadochy and isomorphous substitution (Trussel and Spence 1994, Glasser 1997, Nehdi and Tariq 2007). The principal hydration product of a lime-pozzolan mixture is C-S-H. The aluminates in the pozzolan generate a variety of hydrates including: calcium aluminate hydrate \( (C_4AH_{19}) \), gehlenite hydrate \( (C_2ASH_8) \), AFt \( (C_3A\cdot3CaSO_4\cdot32H_2O) \), and AFm \( (C_3A\cdotCaSO_4\cdot12H_2O) \) (Spence and Shi 2005). The resulting pozzolanic reactions can be generally enunciated as follows,

\[
\begin{align*}
\text{Ca(OH)}_2 + \text{SiO}_2 + (n-1) \text{H}_2\text{O} & \rightarrow x \text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O} \quad (1.1) \\
\text{Ca(OH)}_2 + \text{Al}_2\text{O}_3 + (n-1)\text{H}_2\text{O} & \rightarrow x \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O} \quad (1.2) \\
\text{Ca(OH)}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + (n-1)\text{H}_2\text{O} & \rightarrow 3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O} \quad (1.3) \\
(1.5-2.0) \text{CaO} \cdot \text{SiO}_2\text{aq} + \text{SiO}_2 & \rightarrow (0.8-1.5) \text{CaO} \cdot \text{SiO}_2\text{aq} \quad (1.4)
\end{align*}
\]
5.2.1 Ground granulated blast furnace slag

Ground granulated blast furnace slag (SL hereafter) is classified as latent hydraulic cement with composition broadly intermediate between pozzolanic material and Portland cements (Taylor 1990). Iron slags possess ion-exchange and sorption properties along with an acid-neutralizing capacity by virtue of higher surface area and higher porosity (Feng et al. 2004). According to Dimitrova and Mehanjiev (2000) absorption of metal ions by blast furnace slag occurs principally by an ion exchange mechanism which involves partial dissolution and subsequent hydrolysis of calcium silicates and aluminosilicates contained in slag. The process involves a non-equivalent exchange and replacement of the calcium in the slag by the metal ions sorbed from the solution. Slag based binder can be effective in waste S/S operations owing to several technical reasons including: (a) lower diffusivity of such matrix due to improved binding and finer pore microstructure that promotes physical retardation for leaching (Spence et al. 1989, Roy and Parker 1983), (b) lower redox potential of pore solution which creates a reducing environment contrary to the Portland cement and Portland cement-fly ash binders that establish oxidizing environments (Glasser 1991), (c) enhanced durability as compared to Portland cement based matrices (Talling and Brandstetr 1989). Blast furnace slag tends to raise the pH to some extent (favoring both sorption and hydrolysis of metals to form hydroxide solids (Younger et al. 2003).

Slag exhibits very low hydration on its own in comparison with Portland cement; therefore, chemical activation can promote hydration. Activators can be alkaline
activators such as soda, lime, sodium carbonate, sodium silicate, and calcium sulphate (Regourd 1987). Portland cement and lime are commonly used as alkaline activators (Nidzam and Kinuthia 2010). The major hydration product of alkali-activated cements is calcium silicate hydrate \((C-S-H)\) without readily soluble compound such as \(Ca(OH)_2\) (Wang and Scrivener 1995, Shi and Fernández-Jiménez 2006). Alkali activated blast furnace slag possesses reducing and sulphide precipitation properties which are not usually found in other alkali-activated systems such as Portland cement-fly ash systems (Spence et al. 2002). Some studies highlight the mechanisms of slag hydration by alkali activation using Portland cement and lime (Kogbara et al. 2011, Nidzam and Kinuthia 2010). The hydraulic conductivity of contaminated soils in a slag-cement based solidified/stabilized system has also been found to decrease significantly (Allan and Kukacka 1995).

Researchers have demonstrated stabilization of \(Zn^{2+}\), \(Pb^{2+}\), \(Cd^{2+}\) and \(Cr^{6+}\) in \(NaOH\), \(Na_2CO_3\) and sodium silicate-activated slag cements (Malolepszy and Deja 1995, Deja 2002), and \(Pb\) stabilization using \(NaOH\) activated fly ash (Palacios and Palomo 2004). De Korte and Brouwers (2009) used a blend of lime and slag-cement and demonstrated significant decrease in the leachabilities of \(Cd\), \(Pb\), \(Zn\), and \(Ni\). Much conjecture remains about the metal immobilization mechanism, since it involves either physical entrapment or chemical stabilization, or a combination of both mechanisms. This lack of understanding is impeding the wider application of the technology.
5.2.2 Cement Kiln Dust

Cement kiln dust (CKD) is the fine-textured particulate material removed from cement kiln exhaust gas by air pollution control systems and contains considerable amounts of silica, alumina, ferric oxide; and varying quantities of sulphur and alkalis, which tend to be higher than those found in Portland cement (Pavia and Regan 2010). A significant portion of the dust is soluble in water and the resulting solutions are highly alkaline and caustic (Dyer et al. 1999). The variability of CKD composition from one cement plant to another can be ascribed to differences in the type of kiln operations, dust collection facility, location within the system where the dust is collected, the fuel used in operation processes (Klemm 1980).

Mohamed (2002) outlined the processes involved in the hydration of individual components of CKD and the nature of bonds between hydration products in stabilized soils. The hydration phases of CKD are similar to those of Portland cement and include tricalcium silicate ($C_3S$), dicalcium silicate ($C_2S$), tricalcium aluminate ($C_3A$), and tetracalcium alumino-ferrite ($C_4AF$). In S/S processes of industrial wastes, CKD generally acts as an absorbent or bulking agent, and particularly as a neutralizing agent for acidic wastes. The calcium oxide ($CaO$) content of CKD provides high alkalinity and the ability to remove free water through its hydration to $Ca(OH)_2$. The cementing ability of CKD allows it to be a partial or full substitute for cement in various S/S applications (Conner 1990).
The free lime \((CaO)\) of cement kiln dust has been found to be the most effective predictor of the reactivity of a particular cement kiln dust and the amount and nature of the hydration products generated (Bhatty 1984, Konsta-Gdoutos and Shah 2003). The quantity of free or available lime as well as alkalis \((Na_2O, K_2O)\) varies broadly between cement kiln dusts, which makes some cement kiln dusts more reactive than others. The loss on ignition (LOI) is also a controlling parameter in the reactivity of cement kiln dusts. Higher LOI indicates that a particular CKD is high in slow-reacting calcium carbonate and low in reactive free lime. In addition to the above mentioned factors governing the chemical (richness in sulphates, alkalis, chlorides, etc.) and physical makeup of cement kiln dusts, its storage or disposal scenarios can have pronounced effect on reactivity. Long-term landfilled cement kiln dusts can be less reactive and, therefore, less cementitious due to the loss of free lime as a result of carbonation.

Millions of tons of cement kiln dust are generated annually from cement manufacturing facilities in North America alone (Smith and Campbell 2000). CKD is not listed as hazardous material under US EPA regulation, however, due to the presence of metals, such as \(Pb, Zn, Ni, Pb, As,\) and \(Cd\) at trace concentrations, its emission and disposal corresponding to massive cement production is a significant environmental concern. (El-Absaawy et al. 2011). Utilization of cement kiln dust has been investigated in previous studies for heavy metal removal mainly from synthetic solutions (El-Awady and Sami, 1997, Zaki et al. 2007, Taha et al. 2010) and treatment of effluent from mining waste (Doye and Duchesne 2003, Mackie et al. 2010). Taha et al. (2010) carried out heavy metal removal assessment from waste water using CKD and concluded that in such
systems the removal of the metals was mainly accomplished by adsorption mechanisms. With the increase in pH of the pore solution, CKD surface becomes more negatively charged. Consequently, cationic metal ion adsorption capability increases due to enhanced electrostatic attraction forces. However, the dependence of heavy metal adsorption on pH was different for each metal.

The chemical environment provided in a cement-based product (such as cemented paste tailings), which dictates contaminant solubility can be adjusted to some degree by formulation optimization (Spence and Shi 2005). In the present study, we investigated contaminant containment capabilities of cemented paste tailings samples formulated by using blast furnace slag and fly ash activated by cement kiln dust. It is expected that the addition of calcium and alkali rich cement kiln dust in Portland cement-slag and Portland cement-fly ash binder systems can function as an alkali activator and accelerator in promoting the hydration mechanisms within cemented paste tailings formulations. Since the alkali bearing phases are primarily alkali sulphates, the system may become sufficiently alkaline when mixed with water. Free lime (CaO) present in cement kiln dust can readily provide cementitious properties and contribute to the total alkalinity of cemented paste tailings. Additionally, some sulphides contained inheritably in slag may develop some metal sulphides at the same time. As a result, production of low solubility metal sulphides can substantially reduce the phenomenon of metal leaching from cemented paste tailings.
5.3 Leaching tests

Leaching tests are indispensible characterization tools to evaluate the effectiveness of solidified/stabilized systems. Immobilization of waste constituents by the cementitious binders occurs due to both chemical and physical effects, and the effectiveness of the containment capability is assessed through relatively short-term leaching tests (Conner 1990, Means et al. 1995). A range of leaching tests has been developed to assess the leaching of target pollutants under a variety of set of conditions.

A cement solidified waste provides a dense physical matrix of low permability, which also constitutes a physical barrier to leaching (Spence and Shi 2005). The leachant may flow through the contaminated material/waste, maximizing contact between permeant and the material and washing out of contaminant, or flow around the solidified/stabilized waste, minimizing contact between the leachant and waste, such that leaching occurs by diffusion of contaminants through the connected porosity of the waste material (Poon and Chen 1999). Leaching propensity tests for cement based solidified/stabilized waste are conducted to investigate mass transfer from the material to a liquid, termed leachant or permeant before contact with a solid, and leachate afterwards) (Al Tabbaa and Perera 2006). According to Bishop (1988), Batchelor (1990) and Van der Sloot (2002), factors that can affect leaching of pollutants from cement-based solidified waste include: (a) acid neutralization capacity of waste product and the system (b) system pH (c) porosity of the resultant monolith (d) leachant characteristics, and (e) ratio of solidified/stabilized material to volume of leachant.
Leaching mechanisms in cemented paste tailings may involve transport of contaminants from the solidified/stabilized monolith to the contact waters by diffusion dominated processes (Asavapisit 2003, Singh and Pant 2006, Choi et al. 2009). Molecular diffusion is the process by which dissolved ions migrate from high to lower concentrations in order to relax existing concentration gradients (Conner 1990). Given the reasonably low hydraulic conductivity of mine tailings cemented paste, it is expected that release of chemical species from paste will be governed by diffusion-dominated processes.

5.3.1 Limitation of the Toxicity Characteristic Leaching Procedure (US EPA Method 1311) for mineral processing waste

Among the other leaching tests, the Toxicity Characteristic Leaching Procedure (TCLP) (US EPA Method 1311) is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. A number of researchers have employed TCLP for evaluating metals and metalloid elements from solidified/stabilized mining waste (Stouraiti et al. 2002, Yukselen and Alpasalan 2001).

The TCLP approach has been a matter of debate because of the inability of the test to estimate leaching propensity under a range of actual waste management scenarios (US EPA 1991, US EPA 1999). The procedure was originally developed to simulate the worst-case scenarios for managing waste in co-disposal landfills. In a court proceedings titled 'Columbia Falls Aluminum vs. US EPA', it was argued that the TCLP did not consider the influential technical aspects that are typical of cement based
stabilized/solidified waste, for example, the high alkalinity of wastes, low liquid to solid ratios, and disposal of waste to monofill systems (Halim et al. 2005). Moreover, the binder characteristics are not taken into account in TCLP (Bishop 1988, Bonen and Sarkar 1994). Mineral processing waste is not typically disposed in municipal landfills and, therefore, should not be subjected to organic acidic (acetic acid) leaching conditions. Such leaching media can overestimate leaching propensity in comparison with the relatively neutral to alkaline leachates in monofill disposal systems, rendering incorrect classification of waste and, therefore, leading to unnecessary treatment. The use of the TCLP for classifying monolithic wastes, such as those produced from the mineral processing industries, may also lead to the overestimation of contaminants (US EPA 1995, Halim et al. 2005).

5.3.2 Synthetic Precipitation Leaching Procedure (US EPA Method 1312)

According to US EPA (2003), for Bevill-exempt waste such as mining waste or treated mining waste (cemented paste tailings) destined for a monofill, the Synthetic Precipitation Leaching Procedure (US EPA Method 1312) can be a method of choice to evaluate the leaching potential due to rainfall or surface and ground water (Lapakko 2002, Paria and Yuet 2006). The EPA Method 1312 has been designated as American Society for Testing and Materials (ASTM) method D 6234-98, Standard Test Method for Shake Extraction of Mining Waste by the Synthetic Precipitation Leaching Procedure, and significant data on adopting SPLP for mine wastes have been generated (Lappako 2002, Smith 1997, Hammarstrom and Smith 2000). The synthetic precipitation leaching procedure (SPLP) is very similar to TCLP, except that the samples are leached with
inorganic acids (a combination of sulphuric and nitric acids) analogous to those that would be generated under oxidizing conditions such as acid rain. The method has been used by researchers (for example, Grubb et al. 2009) to evaluate metal leaching in S/S processes.

5.4 Materials and methods

5.4.1 Mine tailings and binder reagents/additives

The tailings used in the study were obtained from Mattabi mine located in Ignace, Ontario. The material was transported in a sealed container to prevent further oxidation. The physical, chemical, and mineralogical characteristics of mine tailings (hereafter MT) were determined by preparing subsamples in accordance with the relevant standards, methodologies, and test procedure.

All the cementing materials, supplementary cementing materials, and representative and characteristically different cement kiln dust samples used in the present study were provided by Cement Association of Canada (CAC). The cementing materials complying with Canadian Standards Association (CSA) A3001-03 included CSA Type General Use hydraulic cement (GU hereafter). The supplementary cementing materials used were ground granulated blast furnace slag (SL hereafter) and CSA Type CI (intermediate calcium) fly ash (FC hereafter).
The chemical compositions of MT, GU, SL, FC, and cement kiln dust samples used in the study were determined by a combination of X-ray fluorescence spectroscopy (XRF) (Tables 5.1-5.2) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). The major oxides were determined by fusion XRF, while trace elements were analyzed by pressed powder pellet XRF. Additional trace elements were determined using mixed acid digestion (extraction) followed by ICP-AES analysis. MT sample was determined to contain 37.8 wt% Fe$_2$O$_3$ and ~12 wt% S substantiating pyrite as major mineral present. The high loss on ignition value of tailings (19.41%) is due to the loss of sulphur in the analysis, as pyrite is burned off in LOI determination. A qualitative assessment of tailings mineralogy using powder X-ray diffraction (XRD) and Bruker D8 coupled with a semi-quantitative X-ray fluorescence analysis indicated the dominance of quartz (~42%) and pyrite (~40%). The other minerals identified were ~5% changoite (Na$_2$Zn(SO$_4$)$_2$·4H$_2$O), ~5% linarite (PbCuSO$_4$(OH)$_2$), ~4% lanarkite (Pb$_2$(SO$_4$)O), and ~4% sidorenkite (Na$_3$Mn(PO$_4$)(CO$_3$)).

Ground granulated blast furnace slag is a nonmetallic byproduct of iron manufacturing consisting essentially of silicates and aluminosilicates of calcium and other bases, and is developed in a molten condition simultaneously with iron in a blast furnace, then water chilled rapidly to form glassy granular particles, and then ground to cement fineness or finer (Bouzoubaa 2005). The slag used in the present study met the specification requirements of CAN/CSA A3001-03.
Fly ash, a by-product of coal burning power plants, is often composed of predominantly silt-sized, spherical, amorphous ferro-alumino-silicate minerals (Sale et al. 1997). The fly ash produced from burning bituminous coal has cementitious properties in addition to its pozzolanic properties, and is able to counteract the acid potential of mine waste by virtue of its high Ca content (Roy and Griffin 1982). The fly ash used in present experimental work had a cumulative value for $SiO_2$, $Al_2O_3$, and $Fe_2O_3$ of less than 70%. In accordance with Canadian Standard Association, CSA A3001-03, the fly ash was designated as CSA Type CI (medium calcium oxide contents fly ash) based on the determined chemical composition.

CKD samples were obtained from cement manufacturing plants to be used in the present experimental program. Two distinctly different cement kiln dusts were chosen in order to cover the range of high to low CaO, as well as high to low loss on ignition (LOI). High calcium dust (DH hereafter) had a high CaO content (57.8%), whereas, low calcium dust (DL hereafter) had a low CaO (31.8%). DH had low LOI (4.8%) and DL had high LOI (31.1%). The un-reacted or free calcium oxide CaO (lime) in DH was 26.3%, whereas, DL had 1.33% free lime, as determined by ASTM C25 (2006). The chemical compositions and physical properties of MT, GU, SL, and FC have been recorded in Table 5.1, whilst Table 5.2 contains the chemical and physical characterization determined for the two cement kiln dusts, i.e., DH and DL.
5.4.2 Determination of paste pH

Paste pH tests were also performed on MT-binder mixtures (Table 5.3) to obtain information on the immediate reactivity of constituents present in each mixture in accordance with Sobek et al. (1978). Approximately 10 g of the representative dry mixture from each binder combination was saturated with 10 mL of de-ionized water (solid:liquid ratio of 1:1) to make a homogenous paste. Measurements of paste pH was conducted according to ASTM D4972 using an ORION® Model 410A pH meter and electrode and appropriate buffer solutions for calibration. The results have been recorded in Table 5.3.

5.4.3 Leaching test procedure

Metal leaching was measured by following the Synthetic Precipitation Leaching Procedure (SPLP) US EPA (Method 1312) for the 120-day cured cemented paste tailings samples. The specimens were cast by pouring the MT-binder mixtures (Table 5.3) into cylindrical plastic moulds as described in section 3.4.2.1. The specimens were crushed in UCS tests and the central core of each specimen was further crushed to reduce the particle size to less than 9.5 mm (see Appendix C.1). A 40 g portion was sampled and transferred to the extraction vessel. The extract was 60/40 w/w mixture of sulphuric and nitric acids made by using de-ionized water (pH 4.2±0.05) (Fey et al. 2000, Grubb et al. 2009), which was added at a solid to liquid ratio of 1:20 by weight. The vessel was agitated using a Burell® wrist-action shaker for 18 hours. The leachates were then pressure filtered through a 0.7 micron glass fiber filter (US EPA 1994) before analysis by
ICP-AES for the target elements (see Appendix C.2). The average of three sample results was taken to ascertain the accuracy of each test.

5.5 Results and discussion

Leaching tests were performed on the control mine tailings sample (without binder/additive) (hereafter MT) and the 120-day cured MT-additive mixtures as indicated in Table 5.3. The SPLP applied to MT revealed that the concentrations of Pb, Cd, Cu, Zn, Hg and As in the leachate were 4.3, 1.2, 22.7, 62.1, 0.4, and 35.6 mg/L, respectively. These values are well above the regulatory limits set exclusively for US EPA Method 1312 (SPLP) regarding remediation of polluted soil, surface and ground water (Remediation Standard Regulations 1996). The oxidation of sulphidic tailings during collection from the site, air drying, and laboratory testing can reduce its pH and cause some dissolution of metallic and metalloid elements. The paste pH of MT was determined to be 3.15.

5.5.1 Immobilization of Pb in cemented paste tailings containing slag and/or fly ash activated by high and low calcium cement kiln dusts

The leaching tests performed on cemented paste tailings samples containing mine tailings, Portland cement, and high calcium and low calcium cement kiln dusts, namely, MT+11%GU, MT+3%GU+8%DH and MT+3%GU+8%DL revealed that the concentration of Pb was reduced from 4.3 mg/L for the control mine tailings sample M100 to 0.035, 0.009, and 0.023 mg/L, respectively, as depicted in Figure 5.1.
Leaching of lead from Portland cement based solidified/stabilized waste forms has been reported to be complex. Some researchers have postulated that Pb is fixed by chemical alteration forming a metallic C-S-H, while others claim that lead hydroxide is formed which is encapsulated in a silicate matrix (Conner 1990). Lead concentrations in leachate decrease with corresponding increase in pH and become extremely low when the pH is between 9 and 11 due to the formation of insoluble hydroxide as shown in Figure 5.2, but again increases at and above pH 12 due to the formation of amphoteric Pb hydroxide complexes (Alpaslan and Yukselen 2002). The dissolved species for Pb in solution can be \( Pb^{2+} \), \( PbOH^+ \), \( Pb(OH)\text{\textsubscript{2}} \), and \( Pb(OH)_3 \). \( PbOH^+ \) is the dominant dissolved Pb species at low pH (Cartledge et al. 1990). In highly alkaline conditions, Pb precipitates as a hydroxide, \( Pb(OH)\text{\textsubscript{2}} \) and then become insoluble. Pb can also be adsorbed on the calcium hydrate or C-S-H phase (Li et al. 2001).

Akhter et al. (1990) studied the immobilization of Pb contaminated soil by using cement and pozzolanic agents. According to their conclusion, Pb is precipitated in an alkaline medium in the form of a number of mixed salts and principally on the surfaces of the solids present. These salts dissolve and re-precipitate throughout the entire course of the cement hydration process, giving rise to a monolith with high surface concentration of Pb species. These surface Pb species are more accessible to a leaching medium under a favourable leaching environment at certain pH of solution. The observed concentration of
Pb from Portland cement based cemented paste tailings is 0.035 mg/L, which is above the regulatory level of 0.015 mg/L.

The pH of interstitial pore solution in a cement paste is often above 12; control of pH is an important factor in improving Pb retention (Wiles and Barth 1992). The amphoteric nature of Pb makes it difficult to immobilize it adequately in cement-based waste forms such as MT+11%GU. Butler et al. (1990) also proposed a hypothesis elucidating the poor retention of lead from cement based systems in leaching tests. According to their observation, there are consecutive crystallizations and dissolutions of lead salts within the matrices, which are more accessible to the leachate solution. A number of authors (Alpaslan and Yukselen 2002, Halim et al. 2003) have noted that Pb fixation is not only due to physical encapsulation, but also occurs as a result of development of new phases with Al and Si-rich species; therefore, chemical stabilization is a dominant mechanism in Pb fixation in cementitious matrices such as cemented paste tailings.

Bishop (1988) showed that in a Portland cement based matrix containing Pb, leaching of Pb at certain pH is accompanied by Si leaching at the same pH. It can be inferred that Pb is primarily incorporated in the C-S-H matrix, and as the matrix begins to dissolve, and the Si is released, Pb is also released. The precipitation of Pb as a Pb silicate compound in cement has also been observed by Bhatty (1987).
Figure 5.1 shows that the $\text{Pb}$ concentration (0.009 mg/L) in the leachate from the matrix containing high calcium dust MT+3%GU+8%DH was lower than the $\text{Pb}$ value (0.023 mg/L) in leachates obtained from the matrix containing low calcium dust MT+3%GU+8%DL. This could be either due to the incorporation of $\text{Pb}$ in the undissolved $\text{C-S-H}$ matrix (Cocke 1990), or the precipitation of $\text{Pb}$ as $\text{Pb}$ silicate compounds (Bishop 1988). Moreover, some calcium hydroxide precipitate can also be incorporated or adsorbed onto the $\text{C-S-H}$ structure, resulting in a lower $\text{Pb}$ concentration in the leachate.

CKD creates alkaline conditions just like Portland cement since its hydration products are also similar to those of Portland cements. It is worth mentioning that high calcium cement kiln dust (DH) produced slightly higher paste pH (10.41) than low calcium dust (DL) with (paste pH 10.13). The observed $\text{Pb}$ concentrations in the leachate from MT+11%GU and MT+3%GU+8%DL were above the regulatory limit of 0.015 mg/L. The mixture MT+3%GU+8%DH with $\text{Pb}$ concentration of 0.009 mg/L in the leachate and paste pH of 10.41 was successful in attaining the required control over $\text{Pb}$.

The $\text{Pb}$ concentrations in the leachate from samples containing mine tailings, fly ash, high calcium and low calcium cement kiln dust, namely, MT+3%GU+8%FC, MT+8%DH+8%FC, MT+3%GU+8%DH+5%FC and MT+3%GU+8%DL+5%FC based on SPLP were 0.213, 0.423, 0.01, and 0.02 mg/L, respectively.
In stabilized/solidified material containing Portland cement-fly ash as binder, Pb may be adsorbed onto the Ca hydrate or C-S-H phase (Li et al. 2001). However, fly ash combined with Portland cement is generally considered unsuitable for adequate fixation of Pb in stabilization/solidification operations (Thevenin and Pera 1999). In the present study, the results showed that the combinations containing mine tailings-fly ash (MT+3%GU+8%FC) or mine tailings-cement kiln dust (MT+8%DH+8%FC) alone reduced the concentrations of Pb in the leachates but may not provide the required fixation of Pb within the matrix below regulatory level.

The SPLP-Pb concentrations form mixtures containing high calcium dust (MT+3%GU+8%DH+5%FC) and low calcium dust (MT+3%GU+8%DL+5%FC) in combination with fly ash were found to be very close to regulatory limits for Pb (0.015 mg/L) as shown in Figure 5.1. Palomo and Palacios (2004) studied the S/S of Pb using alkali-activated fly ash and reported that the proposed cementing system was able to treat lead, since the analyzed concentrations of Pb from leaching test were in the range of parts per billion. It was also argued that the controlling mechanism that instigated leaching of metals in those matrices was diffusion. Moreover, Van Jaarsveld et al. (1997) concluded that Pb fixation within a geopolymerized fly ash is a combination of physical encapsulation and chemical bond.

The amphoteric behaviour of Pb has been confirmed by previous research. When pH drops to ~9, Pb begins to leach significantly. The observed concentrations of Pb in
leachates from samples MT+8%DH+8%FC is 0.423 mg/L as shown in Figure 5.1, which is in harmony with the reported amphoteric characteristics of Pb.

The leaching test performed on samples containing mine tailings in combination with slag, and high and low calcium cement kiln dust, namely, MT+8%DH+8%SL, MT+3%GU+8%DH+8%SL, MT+3%GU+8%DL+8%SL, MT+3%GU+8%SL and MT+3%GU+5%FC+8%SL showed that the concentrations of Pb in the leachate solution are significantly reduced compared with those obtained from the control sample (4.3 mg/L) and were 0.007, 0.005, 0.023, 0.008 and 0.009 mg/L, respectively.

When cement kiln dust was added to slag in cemented paste tailings formulations, the activation of alumino-ferrite-tricalciumsulphate \( (Al_2O_3\cdotFe_2O_3\cdot3CaSO_4) \) and alumino-ferrite-monocalciumsulphate \( (Al_2O_3\cdotFe_2O_3\cdotCaSO_4) \) phase generation occurred. Those phases caused densification of the microstructure of cemented paste tailings.

When fly ash was incorporated in cemented paste tailings containing slag, Pb ions were mostly stabilized through physical encapsulation by the hardened slag matrix and results in exceedingly decreased concentrations in the leachate as shown in Figure 5.1. Thevenin and Pera (1999) also investigated the interactions between lead nitrate and ordinary Portland cement (Type GU) and with Portland cement in combination with blast furnace slag. They concluded that fly ash alone was not favourable toward lead fixation and the best retention of lead was obtained with slag-based cements. The present findings are in agreement with these previous research results.
The observed SPLP-Pb concentrations form the mixtures MT+3%GU+8%DH+5%FC+8%SL, MT+3%GU+8%DL+5%FC+8%SL were 0.010 and 0.132 mg/L, and corresponding paste pH 11.03 and 10.87, respectively. Thus, the addition of alkaline activator such as CKD to a pozzolanic material like slag can be effectively used to consume free $Ca(OH)_2$, which results in a lower pH and precipitation of heavy metals.

5.5.2 Immobilization of Zn

The leaching test performed on stabilized tailings samples MT+11%GU, MT+3%GU+8%DH, and MT+3%GU+8%DL, showed that the concentrations of Zn in the leachate solution were significantly reduced compared with those obtained from the untreated mine tailings. The concentration of Zn in cemented paste tailings sample MT+11%GU dropped from 62.10 mg/L for the control sample to 1.220 mg/L. Figure 5.3 shows that Zn concentration decreased to 2.887 and 3.195 mg/L in case of cemented paste tailings mixtures containing high calcium dust MT+3%GU+8%DH and low calcium dust MT+3%GU+8%DL, respectively.

Mollah et al. (1992) argued that Zn in a Zn-spiked Portland cement solidified/stabilized matrix is primarily fixed by the formation of calcium zincate precipitate $[CaZn_2(OH)_6·2H_2O]$ that swathe cement grains and inhibit their further hydration (Cocke
and Mollah 1993). Moulin et al. (1999) further confirmed that the substitution of Zn in a cement based matrix is possible either by replacement of $Ca^{+2}$ or by direct linkage to the end of silicate chains through $Zn-O-Si$ bonds. The replacement of $Ca^{+2}$ by $Zn^{+2}$ in the ettringite crystal structure also has been reported (Poon et al. 1985, Bonen and Sarkar 1994). Rose et al. (2001) conducted X-ray Absorption Spectroscopy study of immobilization processes for Zn in calcium silicate hydrates and provided evidence that Zn ions were only incorporated in the $C-S-H$ framework without any precipitation products. According to Mulligan et al. (2001), Zn hydrolyzes above pH 8, forming $Zn(OH)_2$. Under the highly alkaline environment created by calcium rich cement or cement kiln dust, the formation of hydroxy-complexes, $Zn(OH)_4^{2−}$ and $Zn(OH)_5^{3−}$ is likely, although, their anionic characteristics hinder their adsorption onto the negatively charged surface of $C-S-H$. However, they may form calcium zinc complex hydrated compound, such as $CaZn_2(OH)_6\cdotH_2O$ (Mollah et al. 1992, Li et al. 2001).

When the pH of a solution containing Zn is above 12, such as in cemented paste tailings containing Portland cement alone, $Zn(OH)_3^{−}$ and $Zn(OH)_4^{2−}$ tend to be the dominant anionic species. These negatively charged zinc hydroxy ions are again not expected to adsorb on the negative $C-S-H$ surface. The negative surface is however balanced by $Ca^{+2}$ ions forming an electrical layer (Mollah et al. 1995). Cemented paste tailings formulated with Portland cement alone and in combination with high calcium dust can immobilize Zn in stabilized/solidified matrix and the observed Zn concentration in the leachate from Portland cement based cemented paste tailings sample MT+11%GU is 1.225 mg/L,
which is below the permissible value for SPLP test (5 mg/L), which is concordant with the results of previous research.

SPLP-Zn concentrations obtained from cemented paste tailings mixtures MT+8%DH+8%SL, MT+3%GU+8%DH+8%SL, MT+3%GU+8%DL+8%SL, MT+3%GU+8%SL, and MT+3%GU+5%FC+8%SL were 3.558, 0.112, 0.524, 0.058, and 0.094 mg/L, respectively (Figure 5.3).

Qian et al. (2003) studied the behaviour of zinc immobilized in an alkali-activated slag using sodium silicate activator matrix. They concluded that the chemical fixation mechanisms for immobilizing Zn ions may involve: (a) the development of insoluble zinc silicate gel; (b) the formation of less or insoluble calcium zincate precipitate; and (c) the incorporation of metal ions in the lattice of C-S-H. The significantly reduced Zn concentrations in the leachates from cemented paste tailings formulations containing slag and fly ash are due to the synergistic effect of the cementitious properties of the individual constituents and their activation by calcium rich cement kiln dust. However, the efficiency of high calcium dust in Zn immobilization is higher than that of low calcium dust as evident from Figure 5.3. The structural retention of Zn and Pb by C-S-H further suggests that leaching of the hydrated products from cemented paste tailings will be controlled by the dissolution of C-S-H (Rose et al. 2001).
Cemented paste tailings formulations (MT+3%GU+8%DH+5%FC+8%SL and MT+3%GU+8%DL+5%FC+8%SL) reduced the SPLP-Zn concentrations in the leachate from 62.10 mg/L to 0.321 and 0.677 mg/L, respectively. The paste pH for the two formulations was 11.03 and 10.87, respectively, as shown in Table 5.3. The composites containing slag and fly ash in combination with Portland cement or cement kiln dust have lower pH in comparison with the cemented paste containing Portland cement as sole binder (Spence and Shi 2005) favouring better immobilization of some metals such as Zn in S/S processes.

5.5.3 Immobilization of Cd

SPLP applied to solidified/stabilized tailings samples MT+11%GU, MT+3%GU+8%DH, and MT+3%GU+8%DL showed substantial reduction of Cd concentrations in the leachates. Cd concentrations in the leachate form cemented paste tailings sample containing Portland cement alone MT+11%GU was reduced from 1.21 mg/L (control sample) to 0.002 mg/L (Figure 5.4). Cadmium has been reported to be fixed efficiently in cement-based waste forms. The cadmium-cement system generates \( \text{Cd(OH)}_2 \), precipitates, which provide sites for the nucleation of hydrated cement phases: C-S-H and \( \text{Ca(OH)}_2 \), (Butler et al. 1990, Brown and Bishop 1985).

Halim et al. (2004) observed that in a Portland cement based matrix containing cadmium, \( \text{Cd(OH)}_2 \) precipitates are not homogeneously distributed in the C-S-H matrix. Akhter et al. (1990) also reported that \( \text{Cd} \) precipitates as \( \text{Cd(OH)}_2 \) in Portland cement based matrix
at early stage in the process of cement hydration and that it serves as nuclei for crystallization of calcium silicate hydrate gel (C-S-H). Cocke and Mollah (1993) examined the surface species in a cadmium doped Portland cement system and confirmed the presence of two primary Cd species, i.e., \( \text{Cd(OH)}_{2} \) precipitate, and \( \text{Cd(OH)}_{4}^{2-} \). According to the researchers, the latter species formed at the high pH within the cement medium and was sturdily sorbed to surface calcium. Bhatyy et al. (1999) have noted that cadmium is the less soluble of the two metals, \( \text{Pb} \) and \( \text{Cd} \), at high pH but becomes soluble at pH values ~ 9. Moreover, it becomes soluble at a point where there is still a significant amount of C-S-H left in the pore solution.

Cemented paste tailings samples containing high calcium dust (MT+3%GU+8%DH), and low calcium dust (MT+3%GU+8%DL) along with 3% Portland cement decreased \( \text{Cd} \) concentrations to 0.020 and 0.053 mg/L, respectively. These concentrations are above the permissible value of 0.005 mg/L, however, high calcium dust performed better than the low calcium dust in \( \text{Cd} \) fixation within the solidified monolith. It may be inferred that upon reacting the cemented paste tailings samples with the leaching fluid, the \( \text{Cd(OH)}_{2} \) solubilised in the acidic medium of the leachant (pH 4.2). Additionally, as the portlandite was released from the cement matrix and the C-S-H disintegrated, the entrapped \( \text{Cd} \) was released. Bishop (1988) also confirmed that the breakdown of C-S-H matrix in cement solidified waste can terminate physical confinement of \( \text{Cd} \) within the monolith.
The leaching test performed on solidified/stabilized tailings samples MT+8%DH+8%SL, MT+3%GU+8%DH+8%SL, MT+3%GU+8%DL+8%SL, MT+3%GU+8%SL, and MT+3%GU+5%FC+8%SL delivered leachates with \( Cd \) concentrations of 0.004, 0.003, 0.082, 0.012, and 0.002 mg/L, respectively, as shown in Figure 5.4.

Akhter et al. (1990) stabilized contaminated soil containing \( Cd \) (10,000 mg/L) and reported that \( Cd \) can be effectively immobilized within the matrix by using a combination of Portland cement and blast furnace slag. Addition of 10% Portland cement and 10% slag reduced the concentration of \( Cd \) in the leachate to 0.48 mg/L. The use of blast furnace slag in combination with Portland cement and high calcium dust results in a more refined porosity and exceedingly low hydraulic conductivity compared to the Portland cement when used alone in cemented paste tailings, resulting in a lower level of contaminant leaching. It is evident from Figure 5.4 that the leachate \( Cd \) concentration delivered by the sample containing low calcium dust (MT+3%GU+8%DL) was above the regulatory level of 0.005 mg/L.

SPLP-\( Cd \) concentration obtained from MT+3%GU+8%DH+5%FC+8%SL and MT+3%GU+8%DL+5%FC+8%SL was 0.002 mg/L (Fig. 5.4). With a higher binder dosage in those composites, more \( Cd(OH)_2 \) precipitate may be incorporated or absorbed into the calcium silicate hydrate (C-S-H) structure of the cementitious matrix resulting in a lower \( Cd \) concentration in the leachate. This observation is consistent with the previous
work carried out by Kogbara et al. (2011). They used higher binder dose (20% lime-slag) to immobilize Cd and found exceedingly low Cd concentrations in the leachate.

### 5.5.4 Immobilization of Cu

SPLP applied to cemented paste tailings mixtures MT+11%GU, MT+3%GU+8%DH and MT+3%GU+8%DL which contained Portland cement in combination with high and low calcium dusts produced leachates whose Cu concentrations were significantly lower than those from the control mine tailings sample (22.660 mg/L). Fig. 5.5 shows that the concentrations of Cu in leachate from MT+11%GU, MT+3%GU+8%DH, and MT+3%GU+8%DL were 1.830, 2.778, and 3.866 mg/L corresponding to the paste of pH 12.21, 10.41, 10.13, respectively.

The precipitation of certain elements to form insoluble phases can also modify the initial porosity of the composites such as mine tailings cemented paste. Thus, the chemical alterations can be mainly explained by the chemical equilibrium evolution between the soluble and insoluble fractions within the hardened mass of cemented paste (Benzaazoua et al. 2004). Solubility behaviour within pore water of cemented material such as cemented paste tailings is a complex interaction between calcium oxides, silicates, and water (Thomas et al. 2003). Leachability of metals and pH of cemented paste tailings are essentially functions of available portlandite, gypsum, and several calcium aluminosilicates and sulphates within the solidified/stabilized matrix.
Roy and Cartledge (1997) investigated the speciation of Cu in electroplating sludge solidified with Portland cement. The principal copper-bearing phase was a hydrated copper phase (\(CuO\cdot3H_2O\)), however, according to the researchers Cu in such solidified/stabilized systems can also exist as hydroxides or react with calcium to form complex compounds. Polettini et al. (2004) investigated the remediation of heavy metal contaminated soil by Portland cement agglomeration and observed that in cementitious waste containing copper, \(Cu(OH)_2\) was the controlling phase at pH values above 7. It was reported that the principal immobilization mechanism for Cu within the matrix was related to the precipitation/dissolution and was predominantly dependent on the pH of the leachate. Fig. 5.5 shows that Cu in Portland cement based cemented paste tailings is not adequately fixed since the observed concentration in the leachate was 1.83 mg/L (above the regulatory level of 1.3 mg/L) corresponding to paste pH 12.2.

SPLP-Cu concentrations in leachates obtained from MT+3%GU+8%FC, MT+8%DH+8%FC, MT+3%GU+8%DH+5%FC, and MT+3%GU+8%DL+5%FC were 0.813, 0.667, 0.866, and 1.211 mg/L, respectively (Fig. 5.5). Cemented paste tailings containing fly ash in combination with Portland cement and high calcium cement kiln dust showed better performance in Cu fixation. Fly ash combined with Portland cement is suitable for the immobilization of copper (De Korte and Brouwers 2009). Shi and Fernández-Jiménez (2006) have argued that the efficiency of immobilization of metals in geopolymeric matrices such as alkali activated fly ash is dominated by physical micro-encapsulation mechanisms and its permeability characteristics.
SPLP-Cu concentrations in leachate from cemented paste tailings samples MT+8%DH+8%SL, MT+3%GU+8%DH+8%SL, and MT+3%GU+8%SL, MT+3%GU+8%DL+8%SL, MT+3%GU+5%FC+8%SL, MT+3%GU+8%DH+5%FC+8%SL and MT+3%GU+8%DL+5%FC+8%SL were 0.557, 0.014, 0.625, 0.897, 0.125, 0.011, and 0.12 mg/L, respectively (Fig. 5.5).

The hydration of slag in a matrix in the presence of metal ions such as Cu is accompanied by sorption of metal ions by the slag (Dimitrova and Mehandjiev 2000). It has been reported that sorption of metal ions on alumino-silicates is very effective under alkaline conditions (Huang and Rhoads 1989). Utilization of slag in Portland cement based S/S of wastes can have several advantageous functions including (a) decrease in the pH of initial pore solution to ~11, thereby increasing the precipitation of selected heavy metals such as Cu, (b) reduction in oxidation-reduction potential which further reduces the solubility of most radionuclides; (c) precipitation of some metals as sulphides which are more insoluble than their corresponding hydroxides, (d) considerable reduction in the permeability of the solidified/stabilized matrices (Spence and Shi 2005).

The observed concentrations of Cu in leachates from samples MT+8%DH+8%SL, MT+3%GU+8%DH+8%SL, MT+3%GU+8%DL+8%SL, MT+3%GU+8%SL, MT+3%GU+5%FC+8%SL, MT+3%GU+8%DH+5%FC+8%SL and MT+3%GU+8%DL+5%FC+8%SL with paste pH of 10.54, 10.76, 10.66, 9.92, 11.03, and 10.87, respectively, were all below the regulatory limit of 1.30 mg/L.
5.5.5 Immobilization of $Hg$

Leaching tests performed on cured cemented paste tailings samples MT+11%GU, MT+3%GU+8%DH, and MT+3%GU+8%DL, produced concentrations of 0.071, 0.178 and 0.226 mg/L for $Hg$ in the leachate, respectively. The control sample had SPLP-$Hg$ concentration of 0.425 mg/L as shown in Fig. 5.6.

Elemental mercury is volatile, therefore, retention of this species by chemical stabilization in cement-based waste forms is not considered very effective since mercury does not exist as a strong surface-absorbing species (Mattus and Gilliam 1994). Roy et al. (1992) studied the microstructure and chemistry of heavy metals sludge solidified/stabilized by Portland cement using a combination of scanning and transmission electron microscopy, optical microscopy, energy-dispersive X-ray microanalysis, and X-ray diffractometry. The authors concluded that physical encapsulation was the principal mechanism for the immobilization of $Hg$. Bricka and Cullinane (1990) used Portland cement as the sole binders for the fixation of 25,900 mg/L of mercury contained in a waste composite along with other metals. The concentration of $Hg$ in the TCLP leachate of the raw waste was 0.1 mg/L. After treatment with Portland cement, the TCLP concentration of mercury increased to 28.6 mg/L instead of decreasing. It was concluded that cement solidification may not be the best stabilization method for mercury.
Although metal concentrations from cemented paste tailings samples containing 11% Portland cement alone and in combination with high and low cement kiln dust were reduced in comparison to the control sample (0.425 mg/L), but these concentrations were above the regulatory limit for $Hg$ (0.002 mg/L).

Fig. 5.6 shows that SPLP-$Hg$ concentrations obtained from $MT+8\%DH+8\%SL$, $MT+3\%GU+8\%DH+8\%SL$, $MT+3\%GU+8\%DL+8\%SL$, $MT+3\%GU+8\%SL$, $MT+3\%GU+5\%FC+8\%SL$, $MT+3\%GU+8\%DH+5\%FC+8\%SL$, and $MT+3\%GU+8\%DL+5\%FC+8\%SL$ were 0.057, 0.001, 0.062, 0.011, 0.001, 0.002, and 0.021 mg/L, respectively. Studies suggest that $Hg$ is predominantly encapsulated physically in the solidified/stabilized matrix; therefore, mercury ion leachability would be sensitive to the permeability of the solidified waste form alone (Mattes and Gilliam 1994). In cement kiln dust activated slag based mine tailings cement paste, the contribution of physical entrapment is derived from the refined pore structure and densification due to amorphous metal silicate precipitation in the pore structure. Such an environment prevented the low solubility compound, mercuric oxide ($HgO$) from leaching (McWhinney et al. 1990). Additionally, Mattus and Gilliam (1994) have confirmed that this precipitate is retained in the matrix by physical retardation and not by chemical sorption. Qian et al. (2003) studied the immobilization of $Hg$ in alkali activated slag systems. They claimed that $Hg$ ions could be effectively immobilized in alkali solution-slag systems; however, the immobilizing efficiencies of such systems on $Hg$ ions were stronger than on $Zn$ ions.
Cemented paste tailings formulated with high calcium cement kiln dust activated slag (MT+3%GU+8%DH+8%SL), and slag in combination with fly ash (MT+3%GU+8%DH+5%FC+8%SL) possessed exceedingly low hydraulic conductivity (section 4.4.3), which acts as a physical barrier to contaminants and thereby prevents \(Hg\) leaching. Notably, the physical encapsulation mechanism, coupled with chemical fixation mechanisms, worked together in the operative immobilization of \(Hg\) ions.

5.5.6 Immobilization of As

SPLP was applied to the control mine tailings sample MT and cemented paste tailings samples MT+11%GU, MT+3%GU+8%DH, and MT+3%GU+8%DL. The concentrations of As in the leachates decreased from 35.55 mg/L for MT to values 0.02, 0.21, and 0.35 mg/L for MT+11%GU, MT+3%GU+8%DH, and MT+3%GU+8%DL, respectively as shown in Fig. 5.7.

Portland cement, quick lime, and hydrated lime in sufficient quantities have been demonstrated to be effective in As fixation in waste stabilization/solidification processes. According to Benzaazoua et al. (2002), the dissolution of portlandite (in lime rich mixtures) is associated with the precipitation of arsenic compounds, thus limiting As mobility. The calcium content of the binding agent has been found to be the main factor in arsenic fixation. A cemented paste tailings rich in portlandite establishes pH conditions and calcium activity favourable for the inhibition of arsenopyrite oxidation (Dutre and Vandecasteele 1996 and 1998, Bothe and Brown 1999, Benzaazoua et al. 2004). Arsenic
compounds formed in Portland cement based cemented paste tailings are a combination of calcium arsenates, iron-arsenic compounds and calcium arsenates (Coussy et al. 2011). Akhter et al. (1990) had to deal with a concentration of 12,200 mg/L arsenic contained in contaminated soil. Among the different types of admixtures tested, only the one containing 44% ordinary Portland cement was successful in reducing the concentration of As in the Extraction Procedure (EP) toxicity leachate below the regulatory limit of 5 mg/L.

Figure 7 shows that 11% Portland cement mixed with mine tailings was able to reduce As concentration in the leachate below the regulatory level (0.05 mg/L). The binder containing high calcium CKD (MT+3%GU+8%DH) effectively reduced As concentration to 0.21 mg/L in comparison with the binder containing low calcium dust (MT+3%GU+8%DL), i.e., 0.35 mg/L, but those values were still above the regulatory limit (0.05 mg/L).

SPLP-As concentrations observed in the leachates from samples containing fly ash, high and low cement kiln dust, and Portland cement, i.e., MT+3%GU+8%FC, MT+8%DH+8%FC, MT+3%GU+8%DH+5%FC, MT+3%GU+8%DL+5%FC were 0.05, 0.115, 0.02, and 0.093 mg/L, respectively. Moon and Dermatas (2007) investigated Class C fly ash-based (S/S) techniques in remediating field soil samples contaminated with arsenic (As) and lead (Pb). A semi-dynamic leaching test was used to evaluate the effectiveness of the S/S treatment. The authors observed 98.3% reduction in the release
of As upon addition of 25% fly ash. The reduction was probably due to the formation of a Ca-As compound and lead silicate or pozzolanic reaction products, or both. Vandecasteele et al. (2002) also found very little As leachabilities in Portland cement-fly ash systems.

SPLP-As concentrations measured in the leachate from cemented paste tailings samples containing slag in combination with high and low cement kiln dust, fly ash, and Portland cement, i.e., MT+8%DH+8%SL, MT+3%GU+8%DH+8%SL, MT+3%GU+8%DL+8%SL, MT+3%GU+5%FC+8%SL, MT+3%GU+8%DH+5%FC+8%SL, and MT+3%GU+8%DL+5%FC+8%SL were 0.03, 0.006, 0.04, 0.05, 0.006, 0.002, and 0.008 mg/L, respectively (Fig. 5.7).

Calcium arsenate (Ca-As-O) and (NaCaAsO₄•7.5H₂O) have been reported to be the major species to immobilize As(III) and As(V) and also dependent on the availability of significant sodium and calcium within cementitious matrix such as cement kiln dust based cemented paste tailings (Kundu and Gupta 2008, Moon et al. 2008, Yoon et al. 2010). Arsenopyrite grains are most probably encapsulated within the C-S-H of the cementitious matrix for cemented paste tailings containing slag, without the formation of new As-compounds (Roy and Cartledge 1992, Coussy et al. 2011). The significant reduction in As concentration in leachate can be attributed to the buffering capacity provided by high calcium cement kiln dust-slag system.
5.6 Conclusions

Much conjecture remained in the past about metal immobilization mechanisms in cementitious waste systems, since it involves either physical entrapment/encapsulation as a dominant fixation process or chemical stabilization as a principal immobilization tool, or a combination of both mechanisms for the fixation of contaminants in a given S/S system. This lack of understanding is impeding wider application of S/S technologies. This study elucidates dominating immobilization mechanisms for different contaminants contained in sulphidic cemented paste tailings. The key findings based on the laboratory investigation are as follows,

- Ordinary Portland cements alone have been broadly utilized for S/S of metallic wastes. Zn in a Portland cement solidified/stabilized matrix is fixed by the formation of calcium zincate precipitate that swathe cement grains, whereas Cd can be fixed effectively in cement-based waste system generating precipitates, which provide sites for the nucleation of hydrated cement phases. However, the effectiveness of Portland cement alone to adequately fix Hg, Pb, and Cu may be questionable; principally due to fact that the pH of interstitial pore solution in a hydrated Portland cement paste is often above 12, which is not ideal for the complete stabilization of some metals. Cu immobilization was better in blended cement systems containing high calcium dust, slag and a small amount of Portland cement. Physical encapsulation has been shown to be the principal mechanism for immobilization of Hg, but cement alone up to 11% by weight of tailings has proved to be inadequate for Hg immobilization.
In CKD activated slag based mine tailings cement paste, the contribution of physical entrapment is derived from the refined pore structure and densification due to amorphous metal silicate precipitation in the pore structure. Such an environment prevented the low solubility compound, mercuric oxide \((HgO)\), from leaching. Notably, the physical encapsulation mechanism, coupled with chemical fixation mechanisms in composite binder system containing slag worked together in the immobilization of \(Hg\). Arsenopyrite grains are most probably encapsulated within the \(C-S-H\) of the cementitious matrix for cemented paste tailings containing slag, without the formation of new As-compounds. The significant reduction in As concentration in leachate is also attributed to the buffering capacity provided by high calcium cement kiln dust-slag system. Physical entrapment/encapsulation is a dominant fixation mechanism in case of \(Hg\), \(Cu\), \(Pb\), and \(As\), whereas \(Cd\) and \(Zn\) have been postulated to be immobilized principally by chemical stabilization.

The optimized cement blend containing a small amount of Type GU cement and SL activated by high calcium CKD \((MT+3\%GU+8\%DH+8\%SL)\) offers more efficient metal fixation capacity by virtue of (a) a more favorable pore solution pH for chemical stabilization of metals as compared to Portland cement alone, (b) concomitant production of low solubility metal sulphides, and (c) densified and exceedingly refined pore structure of the resultant monolith capable of providing much improved physical barrier against contaminants leaching.
• The chemical environment provided by cementitious binders in cemented paste tailings, which dictates contaminant solubility, can be adjusted to a reasonable degree through formulation optimization.

• Different solidified/stabilized monoliths exhibit variable leachability behaviors for the contaminants primarily related to their exclusive pore solution compositions. Calcium rich CKD possesses sufficient cementitious properties in addition to alkaline characteristics. These synergistic effects can provide metal immobilization efficiencies beyond pH control by incorporating them in C-S-H structure. Contrarily, low calcium CKD (DL) promoted chemical stabilization only within the resultant composites due to lack of cementitious properties and is, therefore, incapable of providing physical encapsulation of the contaminants.

• Cemented paste tailings specimens made with composite binder containing SL and FC activated by high calcium CKD in combination with small amount of Type GU cement (MT+3%GU+8%DH+5%FC+8%SL) significantly impaired the solubility of all contaminants investigated by the SPLP and proved successful in fixing metals and arsenic within the matrices, thus satisfying the Remediation Standard Regulations (1996).


5.7 References


Table 5.1 Chemical and physical properties of MT, SL, GU, and FC

<table>
<thead>
<tr>
<th>Chemical characteristics</th>
<th>Mattabi Mine Tailings</th>
<th>Ground granulated blast furnace slag</th>
<th>Type CI fly ash</th>
<th>General Use hydraulic cement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MT</td>
<td>SL</td>
<td>FC</td>
<td>GU</td>
</tr>
<tr>
<td>Major oxides (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>31.60</td>
<td>34.98</td>
<td>42.37</td>
<td>19.87</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.29</td>
<td>0.25</td>
<td>0.81</td>
<td>0.24</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.03</td>
<td>9.11</td>
<td>18.66</td>
<td>4.93</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>37.83</td>
<td>1.86</td>
<td>5.75</td>
<td>2.38</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.85</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.22</td>
<td>9.37</td>
<td>3.54</td>
<td>2.77</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14</td>
<td>38.56</td>
<td>16.90</td>
<td>65.37</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.22</td>
<td>0.51</td>
<td>1.18</td>
<td>0.44</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.27</td>
<td>1.22</td>
<td>2.53</td>
<td>0.00</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.02</td>
<td>-</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>L.O.I</td>
<td>19.41</td>
<td>0.43</td>
<td>5.06</td>
<td>1.93</td>
</tr>
<tr>
<td>Total</td>
<td>97.09</td>
<td>97.14</td>
<td>97.13</td>
<td>98.00</td>
</tr>
<tr>
<td>Elements (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>255.88</td>
<td>32.12</td>
<td>16.10</td>
<td>13.50</td>
</tr>
<tr>
<td>B</td>
<td>81.4</td>
<td>175.33</td>
<td>1335.6</td>
<td>109.00</td>
</tr>
<tr>
<td>Ba</td>
<td>5.01</td>
<td>-</td>
<td>2883.5</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>13.36</td>
<td>n.d</td>
<td>0.13</td>
<td>5.80</td>
</tr>
<tr>
<td>Co</td>
<td>n.d‡</td>
<td>2.56</td>
<td>n.d</td>
<td>6.50</td>
</tr>
<tr>
<td>Cu</td>
<td>146.17</td>
<td>18.66</td>
<td>36.22</td>
<td>45.90</td>
</tr>
<tr>
<td>Hg</td>
<td>4.50</td>
<td>n.d</td>
<td>n.d</td>
<td>n.d</td>
</tr>
<tr>
<td>Mn</td>
<td>175.42</td>
<td>11.25</td>
<td>147.11</td>
<td>191.00</td>
</tr>
<tr>
<td>Mo</td>
<td>1.68</td>
<td>7.34</td>
<td>34.55</td>
<td>6.20</td>
</tr>
<tr>
<td>Pb</td>
<td>275.64</td>
<td>-</td>
<td>n.d</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S</td>
<td>12100.00</td>
<td>6524.00</td>
<td>5223.12</td>
<td>1.03%</td>
</tr>
<tr>
<td>Zn</td>
<td>347.33</td>
<td>65.25</td>
<td>32.13</td>
<td>101.00</td>
</tr>
</tbody>
</table>

‡n.d: Not detected
Table 5.2 Chemical properties of cement kiln dusts

<table>
<thead>
<tr>
<th>Chemical characteristics</th>
<th>High Calcium Cement Kiln Dust (DH)</th>
<th>Low Calcium Cement Kiln Dust (DL)</th>
<th>Range for major oxides 63 different Cement kiln dusts§</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major oxides (wt.%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.91</td>
<td>4.23</td>
<td>1.1-10.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>18.40</td>
<td>16.43</td>
<td>2.2-34.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.41</td>
<td>3.86</td>
<td>0.2-6.0</td>
</tr>
<tr>
<td>CaO</td>
<td>57.8</td>
<td>31.80</td>
<td>19.4-61.3</td>
</tr>
<tr>
<td>MgO</td>
<td>1.31</td>
<td>2.98</td>
<td>0.5-3.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.21</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td>SO₃</td>
<td>4.32</td>
<td>7.61</td>
<td>0.02-17.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.91</td>
<td>1.23</td>
<td>0.1-15.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.81</td>
<td>0.26</td>
<td>0.0-6.3</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.10</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>∗L.O.I</td>
<td>4.80</td>
<td>31.10</td>
<td>4.2-42.4</td>
</tr>
<tr>
<td>††Total oxides</td>
<td>99.98</td>
<td>99.82</td>
<td>-</td>
</tr>
<tr>
<td>*Free CaO</td>
<td>26.3</td>
<td>1.33</td>
<td>0.27.2</td>
</tr>
<tr>
<td>**Total alkalis=(Na₂O)ₕₑₜ (%)</td>
<td>4.04</td>
<td>1.07</td>
<td>0.14-11.42</td>
</tr>
<tr>
<td>***Total reactive oxides (TRO) (%)</td>
<td>48.61</td>
<td>2.19</td>
<td>1.86-56.08</td>
</tr>
<tr>
<td>Elements (ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>17.08</td>
<td>n.d‡</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>123.64</td>
<td>80.73</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>204.11</td>
<td>92.47</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>12.336</td>
<td>3.13</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>13.17</td>
<td>9.82</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>23.03</td>
<td>8.36</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>1.01</td>
<td>1.86</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>189.71</td>
<td>11.8</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>4.07</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>60.56</td>
<td>7.95</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>2912.36</td>
<td>15350.00</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>43.11</td>
<td>16.33</td>
<td>-</td>
</tr>
</tbody>
</table>

‡n.d: Not detected

*Loss on ignition determined at temperature 950±50°C
††XRF sum of total oxides

*Analysis carried out in accordance with ASTM C25-06

**Total alkalis= (Na₂O)ₕₑₜ = (Na₂O+0.658K₂O) (Wang et al. 2007)

*** Total reactive oxide content=TRO= [(CaO+MgO)−LOI]−[K₂O+Na₂O] (Collins and Emery 1983)

§Statistics on composition of 63 different cement kiln dusts from various sources (Sreekrishnavilasam et al. 2006)
Table 5.3 Mixture proportions of mine tailings and binder reagents/additives

<table>
<thead>
<tr>
<th>Mine tailings-binder mixture for cemented paste formulation*</th>
<th>Mixture paste pH ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT (control sample)</td>
<td>3.15</td>
</tr>
<tr>
<td>MT+8%DH+8%FC</td>
<td>9.12</td>
</tr>
<tr>
<td>MT+8%DH+8%SL</td>
<td>10.54</td>
</tr>
<tr>
<td>MT+3%GU+8%DH</td>
<td>10.41</td>
</tr>
<tr>
<td>MT+3%GU+8%DL</td>
<td>10.13</td>
</tr>
<tr>
<td>MT+3%GU+8%DH+5%FC</td>
<td>10.62</td>
</tr>
<tr>
<td>MT+3%GU+8%DL+5%FC</td>
<td>10.22</td>
</tr>
<tr>
<td>MT+3%GU+8%DH+8%SL</td>
<td>10.95</td>
</tr>
<tr>
<td>MT+3%GU+8%DL+8%SL</td>
<td>10.76</td>
</tr>
<tr>
<td>MT+3%GU+8%DH+5%FC+8%SL</td>
<td>11.03</td>
</tr>
<tr>
<td>MT+3%GU+8%DL+5%FC+8%SL</td>
<td>10.87</td>
</tr>
<tr>
<td>MT+11%GU</td>
<td>12.21</td>
</tr>
<tr>
<td>MT+3%GU+8%FC</td>
<td>9.71</td>
</tr>
<tr>
<td>MT+3%GU+8%SL</td>
<td>10.66</td>
</tr>
<tr>
<td>MT+3%GU+5%FC+8%SL</td>
<td>9.92</td>
</tr>
</tbody>
</table>

MT: Mattabi mine tailings
SL: Ground granulated blast furnace slag
DH: High calcium cement kiln dust
DL: Low calcium cement kiln dust
FC: CAN/CSA A3001-03 Type CI (Intermediate calcium content fly ash)
GU: CAN/CSA A3001-03 Type GU: General use hydraulic cement
*% by dry wt. of MT
† Determined by following the procedure by Sobek et al. (1978)
Figure 5.1 Concentrations of Pb in leachates from control MT sample and 120-day cured cemented paste tailings samples

Figure 5.2 Solubility of metal hydroxides as a function of pH (After Cullinane et al. 1986, Shi and Spence 2004, Paria and Yuet 2006)
Figure 5.3 Concentrations of Zn in leachates from control MT sample and 120-day cured cemented paste tailings samples

Figure 5.4 Concentrations of Cd in leachates from control MT sample and 120-day cured cemented paste tailings samples
Figure 5.5 Concentrations of Cu in leachates from control MT sample and 120-day cured cemented paste tailings samples

Figure 5.6 Concentrations of Hg in leachates from control MT sample and 120-day cured cemented paste tailings samples
Figure 5.7 Concentrations of As in leachates from control MT sample and 120-day cured cemented paste tailings samples
CHAPTER 6
CONCLUSIONS AND SCOPE FOR FURTHER RESEARCH

6.1 CONCLUSIONS

The present study was planned and conducted to investigate the effectiveness of using cement kiln dust as an alkaline activator and accelerator for ground granulated blast furnace slag and Type C fly ash for production of resilient and environmentally efficient sulphidic cemented paste tailings. Comparative assessment of a range of binder combinations has been carried out for cemented paste tailings formulations using performance assessment indicators such as unconfined compressive strength, saturated hydraulic conductivity, micro-structure, and contaminant containment capability (leachability). The main findings of the research are summarized below.

CHAPTER 3

- The performance evaluation of the UCS of a range of binder combinations containing different cement kiln dusts, ground granulated blast furnace slag (SL), Type C fly ash (FC), and small amount of Portland cement in formulating sulphidic cemented paste tailings was carried out over a curing period of 480 days. Strength development in all sulphidic cemented paste tailings specimens was similar in the sense that all specimens attained maximum mechanical strength at the end of an initial curing period of 56 or 90 days; thereafter, the compressive
strength of the specimens tended to decrease depending on the type and dose of binder/additive, except ternary and quaternary binder combinations containing Type HS cement. The loss of strength in the specimen with GU as a sole binder may be attributed to the sulphate attack. The presence of sulphates in ordinary Portland cement based cemented paste tailings can cause dissolution of the calcic phases of the cement hydration products and promote the formation of swelling phases, which, in turn, can induce deterioration of the cemented matrices.

- The percentage of compressive strength reduction, for paste specimens containing cement kiln dust with high CaO and low LOI value, SL (with limited aluminum oxide), and FC as mineral additives, was much lower than that of specimens prepared with Type GU cement as a sole binder. Cement kiln dust, by virtue of its highly alkaline soluble fraction, can successfully be used as an activating agent for slag and fly ash in cemented paste tailings, since its principal constituents contain enough calcium to trigger the reactivity of aluminosilicate glass contained in such pozzolanic materials. Free lime content was found to be the most effective predictor of the reactivity of a particular cement kiln dust. The total calculated alkalis (Na$_2$O$_{eq}$) present in DA (3.6%) and DH (4.0%) effectively triggered the activation mechanism of SL and FC.

- DA and DH containing high CaO content (52.4% and 57.8%, respectively) and low LOI (5.1% and 4.8%, respectively) performed best in making sulphidic cemented paste tailings, whereas the paste mixtures containing DB and DL (with very low free lime and very high LOI) as single binders in combination with MT never hardened. The LOI is a controlling parameter in the reactivity of cement
kiln dusts. High LOI substantiates that the CKD is high in slow-reacting calcium carbonate and low in reactive free lime. Moreover, high LOI dusts contain a high percentage of bound water within its chemical structure and, therefore, less free CaO is available to react. Contrarily, low LOI indicates the presence of low CaCO₃ and high free CaO content.

- The use of HS instead of GU has been found advantageous in sulphidic paste systems to mitigate sulphate attack, principally due to its reduced C₃A content. FC and SL in HS-cement kiln dust system developed compressive strength at relatively lower rate in comparison with GU-cement kiln dust systems, but attained and maintained higher UCS over long curing periods. The long-term stability was most discernible in the case of quaternary binder blends containing Type HS cement.

- The physical properties of cement kiln dust can impact the resultant paste matrix apart from chemical characteristics. The fine size distribution of DA provided a higher specific surface (1968 m²/kg) in comparison with DH (1782 m²/kg) and promoted more intense chemical reaction within the DA-MT matrix. The increase in fineness of DA contributed to a corresponding increase in reactivity, promoting a higher compressive strength. This can be a reason for comparable performance of DA and DH in UCS tests performed on cemented paste specimens despite lower free lime contents of DA as compared to DH.

- Cement kiln dust compositions vary considerably with kiln process and the raw materials used; therefore, the impact of a particular cement kiln dust as a partial replacement of Portland cements or in combination with Pozzolanic additives may
not be consistent. The quantity of free or available lime as well as alkalis ($Na_2O$ and $K_2O$) varies broadly between cement kiln dusts, which results in making some cement kiln dusts more reactive than others. The chemical and physical makeup of cement kiln dusts and their storage or disposal scenarios can have a pronounced effect on reactivity. Long-term, landfilled cement kiln dust has been found to be less reactive due to lower free lime and higher LOI.

- The addition of selective cement kiln dust, and ground granulated blast furnace slag, and/or fly ash as partial replacement for Portland cement can improve the performance of the sulphidic cemented paste tailings and alleviate the strength loss associated with ordinary Portland cement based paste. The behavior can be attributed to the latent strength acquisition of SL and FC in the blended cements containing DA and DH as a result of proliferating hydration and pozzolanic reactions.

- The high water content used in cemented paste tailings containing Type GU and Type HS cement produced hardened porous microstructures with interstices that were largely void spaces partially filled by hydration products. In cemented paste tailings, the fraction of the total void space filled by the hydration products generated by the total cementitious materials significantly influences the strength of cemented matrix. The small particles of supplementary cementing materials help to eliminate pores and micro pores by acting as filler and micro fillers resulting in increased density of the hardened composite.

- Previous studies carried out by other researchers on hardened tailings pastes containing Portland cement-pozzolans binders confirmed the possibility of the
presence of un-reacted or un-hydrated particles of slag and fly ash within hardened tailings pastes. In the present study, SEM was carried out on cemented paste tailings to investigate the effect of using calcium and alkali rich cement kiln dust on pozzolanic reactivity of binders containing SL and FC. The effect of incorporation of DA or DH in GU/HS-SL and GU/HS-FC binders was analyzed in high magnification modes. No un-reacted grain of SL or FC was found within the crushed surfaces of the matrices. It can be inferred from these observations that the glassy SL was completely disintegrated by the highly alkaline pore solution when attacked by $OH^-$ ions. As well, all the amount of FC used in composite binder system was completely exhausted by the accelerated pozzolanic activity due to the highly alkaline environment created by DH. The disappearance of SL and FC particles confirmed the augmented pozzolanic reactivity of SL and FC when used in combination with selective cement kiln dusts.

- The cumulative physical and chemical effects by virtue of composite binder systems generated denser and stronger hardened cement pastes. The structural integrity of resultant pastes agrees with the degree of densification and compactness of their microstructure. The observed microstructure delineation of selected cemented paste tailings samples was found to be consistent with their respective mechanical performance (based on the unconfined compressive strength).

CHAPTER 4

- The evolution of saturated hydraulic conductivity with respect to curing time for the cured mine tailings-binder amalgamations showed an overall trend of decrease
in $k_s$ with curing time. The delineation of $k_s$ evolution trends were predominantly based on the hydration mechanisms of a specific binder or binder-additive amalgamation used to formulate a particular paste material.

- The precipitation of calcium hydroxide in Type GU based cemented paste tailings can be inadequate for total blocking of pores within cemented paste tailings matrix. Slag and Type C fly ash perform different functions when used as a partial replacement of Portland cement. However, sufficient quantity of cement can only ensure complete hydration of SL and/or FC.

- By virtue of its highly alkaline soluble fraction, high calcium CKD can successfully be used as activating agent for SL and FC in cemented paste tailings, since its principal constituents contain enough calcium to trigger the reactivity of aluminosilicate glass contained in such pozzolanic materials. The enhanced pozzolanic reactivity of SL and FC with additional calcium hydroxide produced by the incorporation of high calcium and alkali rich cement kiln dust in mine tailings cemented matrices generated additional calcium silicate hydrate ($C-S-H$). The improved pozzolanic reactions resulted in additional hydration products, favoring enhanced pore refinement and densification, which, in turn, reduced the transportability of fluid through the hardened matrices.

- The slag-cement kiln dust based binders have more pronounced affect on saturated hydraulic conductivity than the Type CI fly ash based binders. In the case of the latter binders, the saturated hydraulic conductivity values reach a plateau after 14 days of curing, whereas the former binders continue to generate considerable hydration products and result in reduced water percolation up to 28
days of curing. A combination of several mechanisms, such as enhanced cementitious and pozzolanic reactivity, particle packing effect and densification of the interfacial transition zone between tailings particles and the cementing paste, can radically reduce the permeability of cemented paste tailings considerably.

- In cemented paste tailings formulated with quaternary binders, the enhanced activation of pozzolanic materials by high calcium cement kiln dusts (DH and DA), improved particle packing density by virtue of blending coarser tailings, slag, Type CI fly ash, and micro-structural synergistic action contributed to a decrease in the saturated hydraulic conductivity of the resultant cemented matrices. Consequently, the precipitation of calcium silicate hydrate (\(C-S-H\)) and calcium aluminate hydrate in such mixes served to fully block the pores of the hardened cemented paste tailings, resulting in significantly reduced saturated hydraulic conductivity.

- The cemented paste tailings containing Type GU cement as binder are susceptible to formation and propagation of connected network of micro-cracks due to sulphate attack at later ages since a slight increase in \(k_s\) has been observed in such specimens. This can be overcome by using ternary and quaternary binders in sulphidic cemented paste tailings formulations that contain a small amount of Portland cement in combination with selective cement kiln dust and slag.
CHAPTER 5

- Metal immobilization mechanisms involve either physical encapsulation as a dominant fixation process or chemical stabilization as a principal immobilization tool, or a combination of both mechanisms for the fixation of contaminants in a given S/S system.

- Ordinary Portland cements alone have been broadly utilized for S/S of metallic wastes. Zn in a Portland cement solidified/stabilized matrix is fixed by the formation of calcium zincate precipitate that swathe cement grains, whereas Cd can be fixed effectively in cement-based waste system generating precipitates, which provide sites for the nucleation of hydrated cement phases. However, the effectiveness of Portland cement alone to adequately fix Hg, Pb, and Cu may be questionable; principally due to fact that the pH of interstitial pore solution in a hydrated Portland cement paste is often above 12 which is not ideal for the complete stabilization of some metals. Cu immobilization was better in blended cement systems containing high calcium dust, slag and a small amount of Portland cement. Physical encapsulation has been shown to be the principal mechanism for immobilization of Hg, but cement alone up to 11% by weight of tailings has proved to be inadequate for Hg immobilization.

- In cement kiln dust activated slag based mine tailings cement paste, the contribution of physical entrapment is derived from the refined pore structure and densification due to amorphous metal silicate precipitation in the pore structure. Such an environment prevented the low solubility compound, mercuric oxide (HgO), from leaching. The physical encapsulation mechanism, coupled with
chemical fixation mechanisms in composite binder system containing slag worked together in the immobilization of $Hg$. Arsenopyrite grains are most probably encapsulated within the $C-S-H$ of the cementitious matrix for cemented paste tailings containing slag, without the formation of new $As$-compounds. The significant reduction in $As$ concentration in leachate is also attributed to the buffering capacity provided by high calcium cement kiln dust-slag system. Physical entrapment/encapsulation is a dominant fixation mechanism in case of $Hg$, $Cu$, $Pb$, and $As$, whereas $Cd$ and $Zn$ have been postulated to be immobilized principally by chemical stabilization systems.

- The optimized cement blend containing a small amount of Type GU cement and SL activated by high calcium CKD (MT+3%GU+8%DH+8%SL) offers more efficient metal fixation capacity by virtue of (a) a more favorable pore solution pH for chemical stabilization of metals as compared to Portland cement alone, (b) concomitant production of low solubility metal sulphides, and (c) densified and exceedingly refined pore structure of the resultant monolith capable of providing much improved physical barrier against contaminants leaching.

- The chemical environment provided by cementitious binders in cemented paste tailings, which dictates contaminant solubility, can be adjusted to a reasonable degree through formulation optimization.

- Different solidified/stabilized monoliths exhibit variable leachability behaviors for the contaminants primarily related to their exclusive pore solution compositions. Calcium rich CKD possesses sufficient cementitious properties in addition to alkaline characteristics. These synergistic effects can provide metal
immobilization efficiencies beyond pH control by incorporating them in C-S-H structure. Contrarily, low calcium CKD (DL) promoted chemical stabilization only within the resultant composites due to lack of cementitious properties and is incapable of providing physical encapsulation of the contaminants.

- Cemented paste tailings specimens made with composite binder containing SL and FC activated by high calcium CKD in combination with small amount of Type GU cement (MT+3%GU+8%DH+5%FC+8%SL) significantly impaired the solubility of all contaminants investigated by the SPLP and proved successful in fixing metals and arsenic within the matrices, thus satisfying the Remediation Standard Regulations (1996).

- Binder cost represents a significant fraction of the operational cost of mining operations. The utilization of industrial byproducts (cement kiln dust, slag and fly ash) in enhanced binder formulations can further reduce the overall cost of technology, thus saving on Portland cement.

6.2 SCOPE FOR FUTURE RESEARCH

Cemented paste tailings containing more efficient blended cement will continue to develop by delivering enhanced and resilient material properties over its predecessors such as cemented paste tailings using ordinary Portland cement as sole binder. Further research efforts can focus on the following topics:
• To account for change in the physical and chemical properties of the sulphidic mine tailings using tailings materials from different origins. This can be beneficial in the development of a generalized approach in predicting performance of cemented paste tailings using cement kiln dust (s) and pozzolans based binders.

• To study rheological and other early age properties of the developed cemented paste tailings and their impact on abrasion of pipelines and other transportability characteristics.

• To study the other engineering properties of cemented paste tailings in hardened state such as shear strength, etc.

• The effect of carbonation on long-term leaching propensities of metallic and metalloid elements from solidified/stabilized matrices can be investigated. Durability testing under wetting and drying, freezing and thawing cycles can be carried out for the developed composites.

• Large scale testing in the field accounting for on-site parameters that are not captured in the laboratory can be conducted to develop a ready to implement technology.

• Leachability of metals and pH of cemented paste tailings are essentially functions of available portlandite, gypsum, and several calcium aluminosilicates and sulphates within the solidified/stabilized matrix. These species/compounds can be further studied by geochemical modeling.
APPENDIX A

This appendix provides the supplemental materials to chapter 3.
A.1 Cement kiln dust samples

CKD1: DA  CKD2: DH  CKD3: DB  CKD4: DL
A.2 Cemented paste tailings specimen preparation

A.3 Electrical Hobart A200 model mixer for cemented paste tailings preparation
A.4 Mine tailings samples in humidity chamber for curing under controlled conditions
A.5 Cured cemented paste tailings specimens for UCS tests

A.6 Super ‘L’ Tinius Olsen Universal Testing Machine (UTM) for UCS tests
A.7 SEM images of crushed section of cured cemented paste tailings showing distribution of Fe, Ca, and S
A.8 SEM images of crushed section of cured cemented paste tailings showing distribution of Si, Na, and K
APPENDIX B

This appendix provides the supplemental materials to chapter 4
B.1 Steel cylinders with porous disks and rubber rings for saturated hydraulic conductivity tests

B.2 Casting of cemented paste tailings samples for saturated hydraulic conductivity tests
B.3 Fixed wall constant flow rate hydraulic conductivity apparatus for measurement of saturated hydraulic conductivity of cured cemented paste tailings samples
APPENDIX C

This appendix provides the supplemental materials to chapter 5
C.1 Crushed samples of cured cemented paste tailings for leaching tests

C.2 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) for leaching tests
CURRICULUM VITAE

NAME
Amjad Tariq

EDUCATION
May 2007 – 2012
University of Western Ontario, London, Ontario
Ph.D. Candidate (Civil and Environmental Engineering)

2004 – 2006
University of Western Ontario, London, Ontario
M.E.Sc. (Civil and Environmental Engineering)

1985 – 1991
University of Engineering and Technology, Lahore, Pakistan
B.Sc. (Civil Engineering)

PROFESSIONAL EXPERIENCE
2007-2012
University of Western Ontario, London, Ontario
Graduate Teaching Assistant & Graduate Research Assistant

2000-2002
Montgomery Watson Harza Global Inc. (Consulting Engineers)
Abu-Dhabi, United Arab Emirates (UAE).
Civil Works Inspection Officer

1994-2000
Lahore Development Authority (LDA), Lahore, Pakistan
Assistant Director Engineering (Urban Development)

1993-1994
Metropolitan Corporation Lahore, Pakistan
Assistant Municipal Engineer

Engineer

SCHOLARSHIPS AND AWARDS

• Natural Sciences and Research Council of Canada (NSERC) Postgraduate Scholarship PGS D3, University of Western Ontario, 2007-2010.

• Western Graduate Research Scholarship, University of Western Ontario.

• Western Engineering Graduate Entrance Scholarship, University of Western Ontario, 2007.

• Ontario Graduate Scholarship, University of Western Ontario, 2005-2006

• University Merit Scholarship, University of Engineering and Technology, Lahore, 1985-1991

PUBLICATIONS AND CONFERENCE PRESENTATIONS


