

**EFFECTS OF SODIUM CHLORIDE ON THE RHEOLOGICAL PROPERTIES,
SETTING TIME, SELF-DESICCATION AND STRENGTH OF CEMENTED PASTE
BACKFILL**

ELIZABETH ALEXANDRA CARNOGURSKY

Thesis submitted to the University of Ottawa
in partial fulfilment of the requirements for the
Degree of Master of Applied Science in Civil Engineering

Under the supervision of
Dr. Mamadou Fall

Department of Civil Engineering
Faculty of Engineering
University of Ottawa
July 2023

© Elizabeth Alexandra Carnogursky, Ottawa, Canada, 2023

Abstract

Cemented paste backfill (CPB) is a highly advantageous method of backfill that has been increasing in use in recent decades as it provides many environmental, economic, and practical benefits. When combined with cement and water, it recycles a portion of the dewatered tailings produced from mines as backfill for underground stopes. CPB is transported from the plant on the surface through pipes to the stopes, sometimes over several kilometers, and then placed in underground mining cavities (stopes) to support the ground or rock mass. Therefore, it must meet certain rheological, setting time, and strength gain performance requirements. Additionally, as many mines around the world are located in areas of freshwater scarcity, and societies are holding corporations to ever higher standards for humanitarian and environmental responsibility, many mines are seeking to utilize locally available, saline groundwater or seawater as mixing water in backfill. The impacts of this decision on the rheological, setting, and strength properties of CPB must be better understood to allow for the confident selection of this convenient solution, as the risks associated with improper design include huge costs due to pipeline clogging and death or injury due to backfill failure and ground subsidence.

NaCl is a contributor to natural groundwater and seawater salinity and may be present in concentrations of up to 300 g/L. An additional cost-saving measure favoured by mines is to replace some of the costly Portland cement with much cheaper supplemental cementitious materials such as blast furnace slag. Therefore, this thesis examines the impacts of NaCl concentration and binder composition on the yield stress, viscosity, initial and final setting time, and strength development of CPB. A robust experimental program has been undertaken in which CPB was subjected to the above-mentioned tests in addition to pH and MIP testing, SEM, TG/DTG, XRD, and zeta potential analyses, and electrical conductivity, suction, and water

content monitoring. CPB samples were made with synthetic silica tailings, Portland cement, and water with NaCl concentrations of 0 g/L, 10 g/L, 35 g/L, 100 g/L, and 300 g/L and CPB made with 35 g/L and slag replacement percentages of 0%, 25%, 50%, and 75%. Additional samples tested were made with natural gold tailings, Portland cement, and NaCl concentrations of 0 g/L and 35 g/L for verification. Rheological testing was conducted at 0 minutes, 15 minutes, 1 hour, and 2 hours after mixing, and UCS testing was conducted after 1 day, 3 days, 7 days, 28 days, and 60 days of curing. Additional tests or analyses were performed on selected mixes and curing times for optimum insight and monitoring was conducted from 0 to 28 days after curing.

It was found that low concentrations of NaCl (10 g/L and 35 g/L) generally had favourable impacts on the UCS and setting times of CPB, while higher concentrations had negative impacts.

The impacts of slag replacement on UCS development of saline CPB were also generally favourable. However, the impacts of slag replacement on initial setting time were generally negative, and favourable at higher replacements (50% or more) for final setting time. Low NaCl concentration led to slightly negative impacts on yield stress, especially at longer curing times (1-2 hours), but high concentrations greatly reduced the yield stress. NaCl concentration had minor impacts to viscosity, with any concentration leading to a slightly higher initial viscosity but slightly lower viscosity at longer curing times. Slag replacement content had negligible effects on yield stress, but led to favourable decreases in viscosity over longer curing times.

The combination of positive and negative impacts indicates that care must be taken to knowledgably prioritize or balance critical properties in mix design, though there is indication of opportunities for overall improvement. Supplemental testing provided useful information to explain the mechanics behind the results which will allow designers to carefully select the required components for the desired properties.

Dedication

To my daughter, Emmanuelle, for whom I do everything.

To my husband, Joseph, without whose patience, support, advice, and encouragement this would not have been possible.

Thanks be to God.

Acknowledgments

I am sincerely grateful to my supervisor, Dr. Mamadou Fall, for providing me with this opportunity to learn and for his invaluable guidance, advice, and encouragement during this research.

I would also like to thank Dr. Sada Haruna for his practical assistance, mentorship, and support as I learned to navigate our lab and the world of research. I also thank my lab mates: Zubaida, Aparna, and Shuaigang for their assistance.

I must also thank Jean-Claude Celestin for his assistance in procuring, coordinating, and trouble-shooting the multitude of needs and challenges that were faced in this research.

Finally, I thank my family for their love and encouragement. Most especially, I thank Joseph for doing more than words can express to facilitate my studies, and my mother, Gabrielle Leblanc, for her patience, support, and childcare during the most stressful times in this past year.

Table of Contents

Abstract.....	ii
Dedication.....	iv
Acknowledgments.....	v
Table of Contents	vi
Table of Figures	x
Table of Tables	xii
Table of Equations	xiii
List of Symbols and Abbreviations.....	xiv
Chapter 1: General Introduction	1
1.1 Background and Problem Statement.....	1
1.2 Objectives	4
1.3 Research Approach and Methods.....	4
1.4 Thesis Outline	6
1.5 References.....	7
Chapter 2: Background and Literature Review	9
2.1 Mining.....	9
2.1.1 Mining in Arid Regions	9
2.1.2 The Mining Process	12
2.2 Backfill in Mines.....	14
2.2.1 Cemented Paste Backfill.....	15
2.2.2 Design Requirements – Rheology	16
2.2.3 Design Requirements – Strength Gain.....	18
2.3 Cement and Cement Hydration.....	22
2.3.1 Supplementary Cementitious Materials and Pozzolanic Reactions.....	25
2.3.2 Admixtures.....	26

2.4	Literature Review of Previous Studies on Rheology, Setting Time and Strength of Saline CPB	28
2.4.1	Rheology and Setting Time of Saline CPB.....	28
2.4.2	Strength Gain of Saline CPB	35
2.5	References.....	40
Chapter 3:	Technical Paper 1 – Strength Development and Self-Desiccation of Saline Cemented Paste Backfill	46
3.1	Abstract.....	46
3.2	Introduction.....	47
3.3	Materials and Methodology	50
3.3.1	Materials and CPB Sample Preparation.....	50
3.3.2	UCS Testing.....	52
3.3.3	Monitoring Program	52
3.3.4	SEM	53
3.3.5	MIP	53
3.3.6	TG/DTG.....	53
3.3.7	XRD	54
3.4	Results and Discussion	54
3.4.1	Effect of Salt Concentration on the Strength Development and Self-Desiccation of CPB with Portland Cement.....	54
3.4.2	Effect of Binder Type on the Strength Development of Saline CPB.....	65
3.5	Summary and Conclusions	72
3.6	References.....	73
Chapter 4:	Technical Paper 2 – Rheology and Setting Time of Saline Cemented Paste Backfill	80
4.1	Abstract.....	80
4.2	Introduction.....	81
4.3	Materials and Methodology	84

4.3.1	Materials and Sample Preparation	84
4.3.2	Yield Stress	86
4.3.3	Viscosity.....	86
4.3.4	Initial and Final Setting Time	87
4.3.5	Monitoring Program	88
4.3.6	XRD	88
4.3.7	TG/DTG.....	88
4.3.8	Zeta Potential	89
4.3.9	pH Testing.....	89
4.4	Results and Discussion	89
4.4.1	Effect of Salt Concentration on the Rheology and Setting Time.....	89
4.4.1.1	Yield Stress	89
4.4.1.2	Viscosity.....	96
4.4.1.3	Setting Time.....	99
4.4.2	Effect of Binder Type on the Rheology and Setting Time of Saline CPB ..	102
4.4.2.1	Yield Stress	102
4.4.2.2	Viscosity.....	105
4.4.2.3	Setting Time.....	108
4.5	Summary and Conclusions	110
4.6	References.....	112
Chapter 5:	Synthesis of Results	120
5.1	Summary of Investigations	120
5.2	Effect of NaCl Concentration	121
5.2.1	On Rheology	121
5.2.2	On Setting Time	122
5.2.3	On Strength Gain	123

5.3	Effect of Binder Type.....	124
5.3.1	On Rheology.....	124
5.3.2	On Setting Time.....	125
5.3.3	On Strength Gain.....	125
5.4	Conclusions.....	126
Chapter 6:	Conclusions and Recommendations.....	128
6.1	Conclusions.....	128
6.2	Recommendations.....	129

Table of Figures

Figure 1.1 Critical Properties of CPB During Preparation and Implementation	3
Figure 1.2 Categorization of Tests Performed	5
Figure 2.1 A Global-scale Data Set of Mining Areas (Maus et al., 2020)	9
Figure 2.2 Schematic of stope backfill dimensions (Mitchell et al., 1982)	20
Figure 3.1 Grain size distribution for ST and GT	51
Figure 3.2 Impact of NaCl concentration on UCS of CPB with Portland cement.....	54
Figure 3.3 Impact of NaCl concentration on total pore volume after 28 days of curing	56
Figure 3.4 Impact of NaCl concentration on pore size distribution after 28 days of curing	56
Figure 3.5 Impact of NaCl concentration on water content over first 28 days of curing	57
Figure 3.6 Impact of NaCl concentration on suction over first 28 days of curing	58
Figure 3.7 XRD results for non-saline CPB after 28 days of curing	59
Figure 3.8 XRD results for CPB with 35 g/L NaCl after 28 days of curing.....	60
Figure 3.9 XRD results for CPB with 100 g/L NaCl after 28 days of curing.....	60
Figure 3.10 SEM image of CPB with 35 g/L NaCl after 28 days of curing	63
Figure 3.11 SEM image of CPB with 100 g/L NaCl after 28 days of curing	63
Figure 3.12 SEM image of non-saline CPB after 28 days of curing	64
Figure 3.13 Impact of NaCl concentration on UCS of CPB made with GT.....	64
Figure 3.14 Impact of slag replacement on UCS of saline CPB (NaCl content: 35 g/L)	65
Figure 3.15 Impact of slag replacement on pore size distribution after 28 days of curing.....	66
Figure 3.16 Impact of slag replacement on total pore volume after 28 days of curing	66
Figure 3.17 Impact of slag replacement on water content over first 28 days of curing.....	67
Figure 3.18 Impact of slag replacement on suction over first 28 days of curing.....	68
Figure 3.19 XRD results for saline CPB with 50% slag replacement after 28 days of curing	69
Figure 3.20 XRD results for saline CPB with 100% PC after 28 days of curing (Figure 3.8)	69
Figure 3.21 TG/DTG results for saline CPB with 100% PC and 50% slag replacement after 28 days of curing.....	70
Figure 3.22 SEM image of saline CPB with 50% slag replacement after 28 days of curing	72
Figure 4.1 Grain size distribution for ST and GT	86
Figure 4.2 Impact of NaCl concentration on yield stress of CPB over first 2 hours of curing.....	90
Figure 4.3 Impact of NaCl concentration on zeta potential after 1 hour of curing.....	90

Figure 4.4 Impact of NaCl concentration on pH over first 2 hours of curing.....	91
Figure 4.5 Comparison of XRD peaks for CPB with and without NaCl after 1 hour of curing...	92
Figure 4.6 Comparison of XRD peaks for CPB with and without NaCl after 2 hours of curing .	93
Figure 4.7 Impact of NaCl concentration on electrical conductivity over first 24 hours of curing	93
Figure 4.8 TG/DTG results for CPB with and without NaCl after 1 hour of curing	94
Figure 4.9 TG/DTG results for CPB with and without NaCl after 2 hours of curing.....	94
Figure 4.10 Impact of NaCl concentration on yield stress of CPB made with GT.....	95
Figure 4.11 Impact of NaCl concentration on pH of CPB made with GT	96
Figure 4.12 Impact of NaCl concentration on viscosity of CPB over first 2 hours of curing	96
Figure 4.13 Impact of NaCl concentration on suction for first 24 hours of curing	98
Figure 4.14 Impact of NaCl concentration of viscosity of CPB made with GT	99
Figure 4.15 Impact of NaCl concentration on initial setting time of CPB	99
Figure 4.16 Impact of NaCl concentration on final setting time of CPB	100
Figure 4.17 Impacts of NaCl concentration on the setting times of CPB made with GT.....	101
Figure 4.18 Impact of slag replacement on yield stress of saline CPB (NaCl content: 35 g/L) over first 2 hours of curing.....	102
Figure 4.19 Impact of slag replacement on zeta potential after 1 hour of curing	103
Figure 4.20 TG/DTG results for saline CPB with 100% PC and 50% slag after 2 hours of curing	103
Figure 4.21 Impact of slag replacement on electrical conductivity over first 24 hours of curing	104
Figure 4.22 Impact of slag replacement on pH over first 2 hours of curing.....	105
Figure 4.23 Impact of slag replacement on viscosity of saline CPB (NaCl content: 35 g/L) over first 2 hours of curing.....	106
Figure 4.24 Comparison of XRD peaks for CPB with and without slag after 1 hour of curing.	107
Figure 4.25 Comparison of XRD peaks for CPB with and without slag after 2 hours of curing	107
Figure 4.26 Impact of slag replacement on initial setting time of saline CPB (NaCl content: 35 g/L).....	108
Figure 4.27 Impact of slag replacement on final setting time of saline CPB (NaCl content: 35 g/L).....	109

Table of Tables

Table 2.1 Ranges of Groundwater Salinity	11
Table 2.2 Cement Composition Phases.....	22
Table 3.1 Mix Design Parameters	51
Table 3.2 Chemical Composition of PC and Slag.....	51
Table 4.1 Mix Design Parameters	85
Table 4.2 Chemical Composition of PC and Slag.....	85
Table 5.1 Parameters studied in this thesis	120
Table 5.2 Tests conducted in this thesis	120

Table of Equations

Equation 1: Bingham Model of flow	17
Equation 2: Pumping pressure of cementitious materials	17
Equation 3: Pumping flow where $\tau_{0t} > \tau_0$	18
Equation 4: Pumping pressure for Q_1	18
Equation 5: Factor of Safety for CPB (Mitchell et al., 1982)	19
Equation 6: Cohesion of CPB for FS=1 (Mitchell et al., 1982)	19
Equation 7: UCS for CPB (Mitchell et al., 1982)	20
Equation 8: Factor of Safety for CPB (Modified Mitchell)	21
Equation 9: Cohesion of CPB (Modified Mitchell)	21
Equation 10: UCS of CPB for FS=1 (Modified Mitchell)	21
Equation 11: Factor of Safety for CPB with low aspect ratio (Modified Mitchell)	21
Equation 12: Cohesion for CPB with low aspect ratio (Modified Mitchell)	21

List of Symbols and Abbreviations

‰	permille
$^{\circ}\text{C}$	degrees Celcius
α	angle of sliding plane
$\dot{\gamma}$	Shear rate
γ	unit weight
η	viscous constant
η_s	shear viscosity
μ	plastic viscosity
μm	micron or micrometre
μS	microsiemens
σ	shear stress
τ	shear stress
τ_0	apparent yield stress
τ_{0t}	interface yield stress
φ	friction angle
AFm	monosulphate
AFt	ettringite
ASTM	American Society of Testing and Materials
c	cohesion
c_b	cohesion of backfill
C_2S	dicalcium silicate, belite
C_3A	tricalcium aluminate
C_3AF	tetracalcium aluminoferrite
C_3S	tricalcium silicate, alite
CAD	Canadian Dollars
CH	calcium hydroxide, Portlandite
cm	centimetre
CPB	Cemented paste backfill
C-S-H	calcium silicate hydrate
CSR	constant shear rate

CTF	cemented tailings fill
EC	Electrical conductivity
FC	flow curve
FS	Factor of Safety
g	grams
GCPB	gangue-cemented paste backfill
GDP	gross domestic product
GT	Gold tailings
hr(s)	hour(s)
IEP	isoelectric point
kPa	kilopascal
k_r	filling factor
L	litre
mg	milligrams
MIP	Mercury intrusion porosimetry
NRCAN	Natural Resources of Canada
OPC	Ordinary Portland Cement
P_0	surcharge
Pa	pascal
PC	Portland Cement
PCI	Portland Cement Type I
ppm	parts per million
psi	pounds per square inch
RPM	rotations per minute
s	second
SCM	Supplementary cementitious material
SEM	Scanning electron microscopy
ST	Silica tailings
TDS	Total dissolved solids
TG/DTG	Thermogravimetric/Differential thermogravimetric
UCS	uniaxial compressive strength or unconfined compressive strength

VWC	Volumetric water content
w/c	water to cement ratio
WC	water content
XRD	X-Ray Powder Diffraction

Chapter 1: General Introduction

1.1 Background and Problem Statement

Mining is a major global industry, bringing in approximately 1.25 trillion CAD in revenue in 2021 (Garside, 2016), with Canada contributing 55.5 billion CAD and having assets of approximately 273 billion CAD (Natural Resources of Canada (NRCAN), 2022). Mining was Canada's third largest industry by national GDP in 2020 (Statistics Canada, 2023). Canada is the world leader in potash production and among the top five producers for diamonds, gold, indium, niobium, platinum group metals, titanium concentrate, and uranium (NRCAN, 2022).

Mining is also one of the world's oldest industries, long providing many raw materials necessary for life and other industries. However, its history is blighted by a reputation for environmental destruction and danger for miners. In recent times, Canada and many other nations have made a strongly concerted effort to eliminate safety hazards and reduce environmental damage (Berbner, et al., 2022; Hart, et al., 2022), with initiatives such as TSM (Towards Sustainable Mining), MSHA (Mine Safety and Health Administration), and the Green Mining Initiative (NRCAN, 2018).

As part of the mining process, large voids are formed in the ground through the removal of ore (stopes). These voids must be backfilled in order to prevent ground collapse, ensure worker safety, and allow continued efficient extraction of mineral resources. The type and quality of backfill has numerous productivity and safety implications (de la Vergne, 2003). Additionally, the removed ore presents a significant environmental liability after it has been processed (tailings), as it can cause acid mine drainage, environmental disruption, or slope instability if improperly stored. The costs of properly storing it are significant (de la Vergne, 2003).

In recent years, cemented paste backfill (CPB) has emerged as a novel form of backfill that offers a multitude of benefits for all aspects: environmental, geotechnical, and economical (Grice, 1998; Ghada, 2019; Bull, 2019; Pokharel, 2008). It consists of utilizing a portion of the solid waste from mineral processing as the primary component for mine backfill, which simultaneously reduces costs associated with sourcing backfill material and reduces demand for surface storage of tailings. CPB has also been shown to provide good stability (Grice, 1998; Ghada, 2019; de la Vergne, 2003; Belem, et al., 2000), and research is ongoing.

The successful implementation of CPB in a mine is dependent on how well it meets the requirements of the project, namely: to be economically and easily prepared with readily available materials, be transported to the stope, and develop sufficient strength quickly enough to allow operations to continue efficiently.

Therefore, CPB needs to have adequate flowability (rheological properties) to be transported from the plant on the surface to the stope via pipes, to have a reasonably fast setting time to allow bulkheads to be removed and minimize risk of liquefaction, and to have sufficient strength gain to safely allow mining of adjacent stopes while minimizing costs associated with ore dilution. CPB consists of tailings, cement, and water. The tailings are readily and cheaply available, being a waste product of normal operations. However, cement is costly and is often replaced in part with supplemental cementitious materials (SCMs) such as slag, fly ash, or natural pozzolans. These are typically inert materials that become cementitious under certain conditions and are typically much cheaper than cement. Finally, cement mixing water is conventionally of a certain quality and free of significant impurities (ASTM Standard C1602), but this is not always readily available at all mining locations around the world, especially in arid climates. In these locations, local groundwater may contain a significant quantity of dissolved

salts, sometimes reaching total dissolved solids (TDS) concentrations of up to 300 g/L (Van Weert, 2009). Additionally, mines may be located in coastal regions where the most readily available source of water is seawater, such as in Chile (Cisternas and Galvez, 2018) and China (Wang et al., 2018), and the use of seawater in mine operations is being considered. In these situations, the ability to reliably use mixing water of substandard quality and still achieve the rheological, setting time, and strength requirements given above is crucial to the practical and economic implementation of CPB.

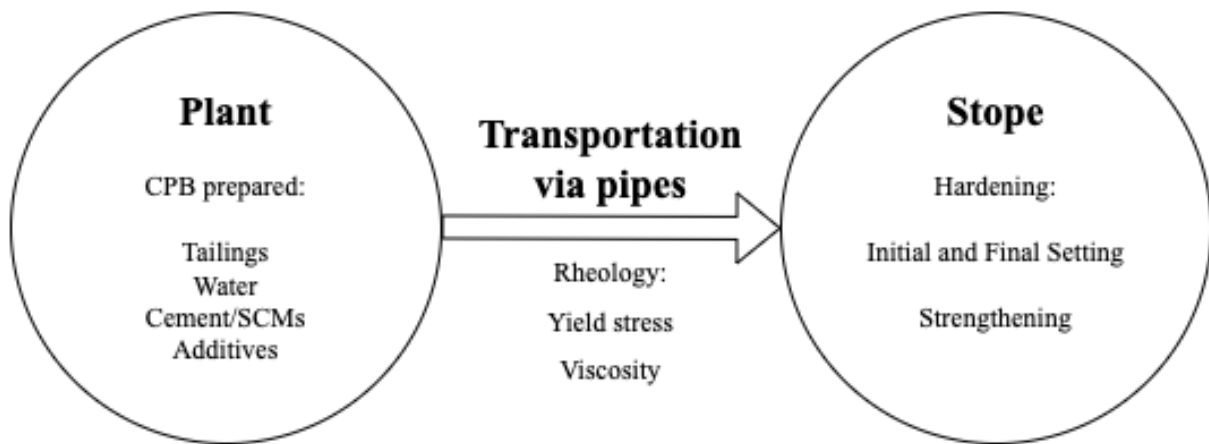


Figure 1.1 Critical Properties of CPB During Preparation and Implementation

While significant research has been conducted on various aspects of CPB there has been insufficient research into the effects of NaCl which systematically encompassed both fresh and hardened properties and provided supplemental information on microstructure and suction development.

Therefore, the problem statement of this research is the need for better understanding of the impacts of poor water quality (namely NaCl concentration) on the rheological, setting time, and strength gain properties of CPB made with cement and varying quantities of slag.

1.2 Objectives

The objective of this thesis is to investigate the effects of NaCl concentration on the rheological properties, setting time, and strength gain of CPB. The experimental program consists of uniaxial compressive strength (UCS), setting time, yield stress, and viscosity testing, as well as microstructural analyses, pH and zeta testing, and a monitoring program. The objective of these experiments is to investigate:

1. The effect of varying concentrations of NaCl on the rheological properties of CPB up to two hours of curing.
2. The effect of varying quantities of slag replacement of PC on the rheological properties of saline CPB up to two hours of curing.
3. The effect of varying concentrations of NaCl on the initial and final setting times of CPB.
4. The effect of varying quantities of slag replacement of PC on the initial and final setting times of saline CPB.
5. The effect of varying concentrations of NaCl on the strength gain of CPB from one to sixty days of curing.
6. The effect of varying quantities of slag replacement of PC on the strength gain of CPB that contains NaCl from one to sixty days of curing.

1.3 Research Approach and Methods

The research approach used consisted of two testing phases: primary testing and supplemental testing (Figure 1.2). Primary testing sought to determine the direct effects of the objectives listed in Section 1.2, while supplemental testing sought to uncover the mechanisms

behind those effects and provide explanations for them. The primary testing can be further broken down into two categories: fresh properties and hardened properties.

Primary fresh properties testing included yield stress, viscosity, and setting time testing.

Primary hardened properties testing consisted of UCS testing.

Supplemental testing included XRD spectroscopy, TG/DTG analyses, MIP, pH testing, zeta potential testing, SEM imaging, and a monitoring program which included suction, electrical conductivity, and water content monitoring. Due to costs and logistical impracticalities, not all supplemental tests were performed on all sample mixes, but were strategically selected to provide the best value of information. The term “microstructure” in this study refers to all structures and characteristics in the microscale, that is, from approximately 0.1-100 μ m.

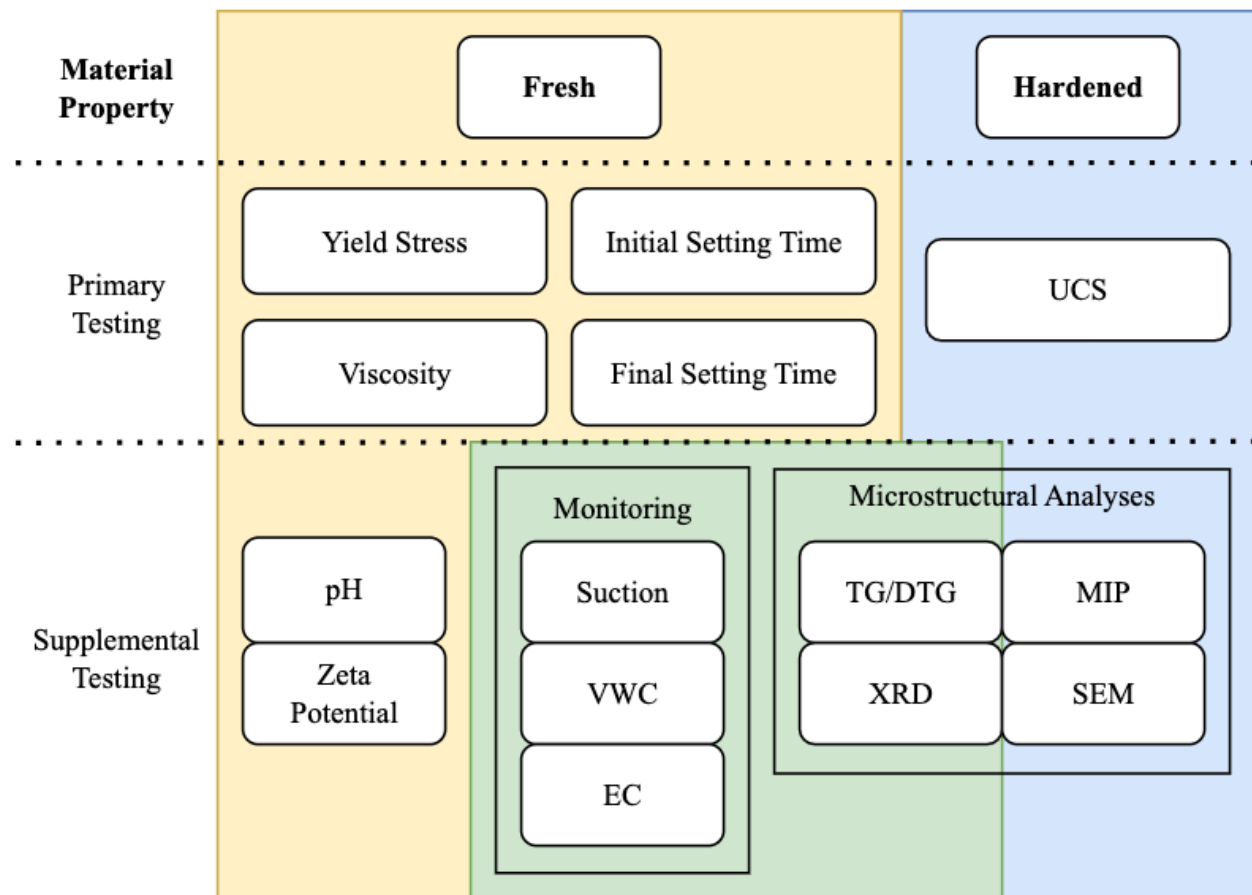


Figure 1.2 Categorization of Tests Performed

1.4 Thesis Outline

This thesis consists of six chapters including two technical papers.

Chapter 1: provides a general introduction to the importance, benefits, use, and requirements of CPB, as well as some challenges to its successful implementation. The problem statement, research objectives, approach, and structure of this thesis are stated.

Chapter 2: provides a detailed background on mining in arid regions and the availability of fresh or saline groundwater, as well as the technical aspects of mine backfill, including CPB and its rheological, setting time, and strength requirements. An overview of cement and SCM hydration is also provided. Finally, a detailed review of existing literature on the rheology, setting time, and strength properties of saline CPB is undertaken and discussed.

Chapter 3: discusses the impacts of NaCl concentration on the strength gain of CPB and the impacts of slag replacement quantity on the strength gain of saline CPB (Technical Paper I).

Chapter 4: discusses the impacts of NaCl concentration on the yield stress, viscosity, and setting time of CPB and the impacts of slag replacement quantity on the same of saline CPB (Technical Paper II).

Chapter 5: synthesizes the results of the two technical papers and literature review.

Chapter 6: presents thesis conclusions and recommendations for future study.

It should be noted that a technical paper-based format is used for this thesis and that some repetition of content is to be expected as each technical paper must independently contain necessary information for publication.

1.5 References

- ASTM Standard C1602. 2023. *Standard specification for mixing water used in the production of hydraulic cement concrete*. ASTM International, West Conshohocken, PA, 1936, DOI: 10.1520/C1602_C1602M-22, www.astm.org
- Belem, T., Benzaazoua, M., & Bussi re, B. (2000). Mechanical behaviour of cemented paste backfill. In *Proc. of 53rd Canadian Geotechnical Conference, Montreal* (pp. 373-380).
- Berbner, J., Lath, V., and Maksimainen, J. (2022). Navigating a decade of challenges: five winning initiatives for mining CEOs. *Mckinsey & Company*.
<https://www.mckinsey.com/industries/metals-and-mining/our-insights/navigating-a-decade-of-challenges-five-winning-initiatives-for-mining-ceos>
- Bull, A. J. (2019). *Temperature dependence of the leachability of cemented paste backfill* [MAsc thesis, Ottawa, ON: University of Ottawa]. <http://dx.doi.org/10.20381/ruor-23118>
- Cisternas, L. A., & G lvez, E. D. (2018). The use of seawater in mining. *Mineral Processing and Extractive Metallurgy Review*, 39(1), 18-33.
<https://doi.org/10.1080/08827508.2017.1389729>
- de la Vergne, J. N. (2003). *Hard rock miner's handbook* (3rd ed.) McIntosh Engineering.
- Garside, M. (2016). *Mining industry worldwide* [Data set]. Statista.
<https://www.statista.com/topics/1143/mining/#dossier-chapter1>
- Ghada, A. A. (2019). *Temperature dependency of the rheological properties and strength of cemented paste backfill that contains sodium silicate* [MAsc thesis, Ottawa, ON: University of Ottawa]. <http://dx.doi.org/10.20381/ruor-26207>
- Grice, A. (1998). Underground mining with backfill. *2nd Annual Summit   Mine Tailings Disposal Systems, Brisbane, Nov, 24-25*.

- Hart, T., Wetmore, K., Harridge, N., Fernandes, M., and Metzner, R. (2022). *Global mining outlook*. KPMG International. <https://home.kpmg/xx/en/home/insights/2022/04/global-mining-outlook-2022.html>
- Natural Resources of Canada. (2022). *Minerals and the economy*. Government of Canada. <https://www.nrcan.gc.ca/our-natural-resources/minerals-mining/minerals-metals-facts/minerals-and-the-economy/20529#production>
- Natural Resources of Canada. (2018). *Green mining innovation*. Government of Canada. <https://www.nrcan.gc.ca/our-natural-resources/minerals-mining/mining-resources/green-mining-innovation/8178>
- Pokharel, M. 2008. *Geotechnical and environmental responses of paste tailings systems to coupled thermo-chemical loadings*. MASc thesis, Ottawa, ON: University of Ottawa. <http://dx.doi.org/10.20381/ruor-18910>
- Statistics Canada. (2023). *Table 36-10-0434-03 Gross domestic product (GDP) at basic prices, by industry, annual average (x 1,000,000)*. Government of Canada. <https://doi.org/10.25318/3610043401-eng>
- Wang, K., Yang, P., Lyu, W., & Lin, Z. (2018). Research of Cemented Paste Backfill in Offshore Environments. *IOP Conference Series: Earth and Environmental Science*, 108(4), 042082. IOP Publishing. doi :10.1088/1755-1315/108/4/042082
- Van Weert, F., Van der Gun, J., & Reckman, J. (2009). Global overview of saline groundwater occurrence and genesis. *International Groundwater Resources Assessment Centre*.

Chapter 2: Background and Literature Review

2.1 Mining

Mines are located in every corner of the globe, except Antarctica (discovering Antarctica website, Maus et al., 2020, World Gold Council, 2022) (Figure 2.1). Some of the world leaders in mining are Australia, China, Russia, and the United States of America (Maus et al., 2020). Other countries with notable mining industries are Canada, Chile, India, and South Africa. Most of these countries also have significant arid regions, where mines are frequently located.

2.1.1 Mining in Arid Regions

An arid region is defined by the water balance concept: if inputs from precipitation are less than losses due to evapotranspiration and changes in the local water storage regions, then the region has a water deficit and may be considered “arid” (Goudie, 2013). A slight deficit may qualify a region as only being semi-arid, while regions with very significant deficits are considered to be extremely arid (Goudie, 2013). Dry lands cover one third of the globe, including significant regions of the above-listed mining countries (Goudie, 2013).

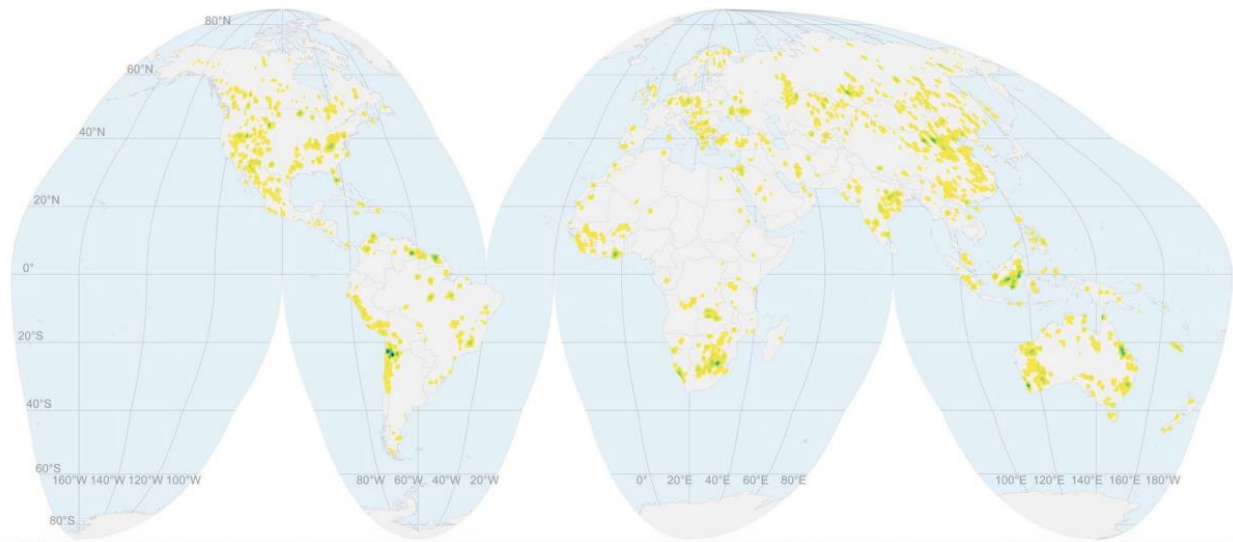


Figure 2.1 A Global-scale Data Set of Mining Areas (Maus et al., 2020)

Some examples of arid mining regions are: the Great Basin Desert and Mojave Desert in the USA, the Chilean Andes, most mining in Australia, Gujarat and Rajasthan in India, the Gobi Desert in Mongolia, and most mines in Syria and Saudi Arabia.

Mines require significant quantities of water for operation. Water is used for dust suppression, mineral processing including chemical separation of ore from waste, material and backfill transportation, cooling systems around power generation, and human consumption and hygiene, and may be sourced from local municipalities or water resources (Prosser, 2011).

While global or national water consumption of the mining industry does not usually constitute a significant portion of the total freshwater usage, even in arid countries such as Australia, mining water usage can be stressful on a local level (Meissner, 2021; Prosser, 2011). Mining may occur in localities that, while not meeting the definition of “arid”, only have sufficient freshwater resources to support the local human and agricultural demands. As mines are limited in choice of location to the natural location of the valuable deposit, they are also limited in the water environment they must operate in. In some cases, mining could induce significant water stress on a local environment due to groundwater pumping drawdown, which results in diminished recharge to local streams and water bodies (Prosser, 2011; Khaltar, 2020). The scarcity of freshwater resources may be accompanied by either heavy water-use regulation or conflicts and public dissent. In either case, mines must be exceptionally responsible with their water usage and recycling strategies (Meissner, 2021; Prosser, 2011). One way of achieving this is by utilizing water for which there is little other demand. Arid regions may feature seawater or groundwater that is non-potable due to high salt or dissolved solids content, which could provide the needed water source without stressing local communities and environments. Indeed, some mine processes are more effective using saline water (Prosser, 2011).

Groundwater quality can be described using concentration of total dissolved solids (TDS) (mg/L), chloride content (mg Ch/L), or electrical conductivity (EC) ($\mu\text{S}/\text{cm}$) (Van Weert et al., 2009). For future purposes in this thesis manuscript, concentration (g/L) of NaCl have also been calculated and provided. Groundwater can then be broken down into categories based on the intensity of the parameter being used. Table 2.1 provides the ranges for each category.

Table 2.1 Ranges of Groundwater Salinity

Category	TDS (mg/L)	Chloride Content (mg/L)	EC ($\mu\text{S}/\text{cm}$)	NaCl concentration (g/L)
Fresh	0 - 1,000	0 - 556	0 - 1,429	0 - 0.9
Brackish	1,000 - 10,000	556 - 5,556	1,429 - 14,286	0.9 - 9.2
Saline	10,000 - 100,000	5,556 - 55,556	14,289 - 142,857	9.2 - 91.6
Brine	>100,000	>55,556	>142,857	>91.6

(modified from Van Weert et al., 2009, after Freeze and Cherry, 1979)

For the purposes of this manuscript, all non-fresh water will be referred to as “saline”.

Saline groundwater contains highly variable dissolved contents depending on location and origin. It may contain solutes of halite, anhydrite, carbonates, gypsum, fluoride-salts, and/or sulphate-salts, in varying concentrations. In general, fresh water sources are relatively young, shallow, and frequently replenished by the water cycle, while saline water sources are deeper, older, and more stagnant, as these factors allow for more mineral dissolution (Van Weert et al., 2009).

While groundwater can have highly variable components, seawater has been found to contain essentially the same inorganic components, in similar ratios, though in different concentrations around the world (Millero et al., 2008, Le Menn et al., 2018). There has been much confusion and investigation over the past 150 years, leading to more recent attempts to clarify definitions and establish a standard composition and correlations between the results from different measurands under different conditions of temperature and pressure (Millero et al., 2008). Typical measurands are chlorinity, density, electrical conductivity, and salinity, each of

which has multiple methods of testing, and associated advantages and disadvantages (Millero et al., 2008, Le Menn et al., 2018). A very brief description of each follows:

Chlorinity – theoretically the chlorine mass fraction of a sample, which is now simple to measure, though it has been subject to numerous testing errors and biases over history

Density – represented by the thermodynamic properties of seawater such as heat capacity, sound speed, and refractive index

Conductivity – how readily a sample conducts electricity, is often converted to Practical Salinity by the use of empirical equations and consideration of temperature and pressure

Absolute Salinity – the mass fraction of dissolved material, based on composition, is often the desired measurand for which others are a proxy, as it is very difficult to measure

The major components include: Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Sr^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , Br^- , CO_3^{2-} , $\text{B}(\text{OH})_4^-$, F^- , OH^- , $\text{B}(\text{OH})_3$, CO_2 (Millero et al., 2008., Le Menn et al., 2018). A historical value that has frequently been matched for ease of research continuity is a chlorinity value of 35 g/kg, or 35 g/L (Millero et al., 2008., Le Menn et al., 2018). Though conductivity cells are more favoured now due to their ability to precisely profile salinity in-situ, chlorinity will be used in this manuscript due to its experimental simplicity.

2.1.2 The Mining Process

Mines remove large quantities of ore from the earth from which to extract valuable minerals. In underground mines, the resulting voids in the ground have the potential to collapse and cause subsidence at the surface or to endanger the lives of miners. Additionally, the voids can prevent access to other stopes, and therefore need to be backfilled to provide stable working surfaces for further operations. This should be done with a considerably less valuable material that allows the removal of ore to be profitable. The factors and requirements that go into backfill

selection and design will be discussed in a following section. When placing backfill, the stope to be filled is sealed at the bottom with a bulkhead or barricade. The bulkhead can only be removed once the fill in the stope has gained sufficient strength to maintain its shape and stability.

Additionally, adjacent secondary stopes can only be mined once the backfill in the primary stope has gained enough strength to be self-supporting and withstand blasting and excavation in the secondary stope. When backfill sheds into the secondary stope while it is being mined, it is known as ore dilution and it reduces the profitability of the mine operations due to the same material being transported multiple times unnecessarily. The faster the backfill attains the required strength, the sooner mining can progress and more profit be generated (de la Vergne, 2003; Grice, 1998; Belem, et al., 2000).

Meanwhile, the extracted ore is taken to the mine processing plant, which is usually located at the ground surface near the mine. Here, the ore is crushed and processed to separate the valuable minerals from the waste rock. Water is commonly used to transport the material and as a medium through which the mineral separating processes are conducted. The waste is called tailings and typically contains fine rock particles, water, and various chemicals depending on the processes used. The tailings must be disposed of, but due to their sulphide and chemical content, they pose a serious environmental hazard if not properly contained. Typically, they are stored in large man-made ponds on the ground surface. These tailings ponds require a lot of land and careful engineering to build and manage, at great expense, and the dams can still fail causing enormous environmental damage for which the mining company is responsible. Mines use tailings ponds to separate the fine particles from the water, which they endeavour to reuse, however, the production of tailings still constitutes a significant financial risk.

2.2 Backfill in Mines

There are several common forms of backfill that are in use in mines. They are rock fill, cemented rock fill, hydraulic fill, cemented hydraulic fill, concrete fill, paste fill, and ice fill (permafrost regions) (de la Vergne, 2003). Of these, the most commonly used are cemented rock fill, hydraulic fill, and paste fill, and each will be described in turn.

Cemented rock fill is more commonly used than rock fill alone due to its increased stability, which allows it to be used in the backfill of primary stopes and to contribute to ground support. It typically consists of waste rock that is mixed with a cement slurry before or during placement in the stope. Rock may be quarried from the ground surface for this purpose or selected from broken ore (de la Vergne, 2003).

Hydraulic fill consists of 55% to 75% mill tailings with water added to allow the mixture to be transported to the stopes. However, once in the stope, the water must be removed so that the mixture hardens sufficiently for mining purposes. To achieve this, the tailings are deslimed (cycloned to remove the fines) prior to being transported to the stopes, which allows the water to drain and the backfill to consolidate (Grice, 1998). If the mine tailings are too fine, then alluvial sand is used instead (sand fill). Cement or pozzolans are frequently added to the hydraulic fill to increase its stability and decrease the time to solidification. However, the water that drains from hydraulic fill can collect fines or contain unhydrated cement and transport them to the mine sump, where they can cause clogging and other issues. Various manufactured additives have been developed to address this issue by decreasing the quantity of water required to be added for transportation or that needs to be drained (de la Vergne, 2003).

Paste fill is similar to hydraulic fill, however it contains less water and the full tailings gradation, which gives it the physical properties of a semi-solid or non-Newtonian fluid (Belem

and Benzaazoua, 2004). This causes the fill to be more difficult to pump, but it also improves the final stability and time to achieve the required strength and decreases the drainage requirements. Cement, pozzolans, or other additives are also commonly added prior to being transported to the stope (de la Vergne, 2003). When cement is included, the material is known as cemented paste backfill (CPB) or cemented tailings fill (CTF). A typical mix will consist of 70-85% solids, 2-9% binder (by weight of solids), and a water-to-cement (w/c) ratio of 5.5 to 9.6 (Ghada, 2019). CPB will be discussed in greater detail in the following section.

2.2.1 Cemented Paste Backfill

CPB was invented in the 1980's in a German mine and has rapidly gained in popularity worldwide (Ghada, 2019). It has numerous advantages over other popular backfill alternatives:

- Diverts tailings from above-ground tailings dams
 - o Reduces environmental risks associated with acid mine drainage and tailings dams failures.
 - o Reduces engineering and land costs associated with constructing tailings dams.
- Reuses mine waste for backfill
 - o Reduces or eliminates need for quarrying rock or sand and associated costs.
 - o Does not require desliming like hydraulic fill.
- Uses less water than hydraulic fill.
 - o Less drainage reduces stress on mine sumps.
 - o Reduces water demand on local environment and communities.
 - o Higher solids content increases strength and tailings usage.
- Increases mine productivity and profitability
 - o Transforms liabilities into resources.

- Readily available.

However, it does have a few drawbacks, such as being the least “user-friendly” of the backfill options and requiring at least some cement to prevent liquefaction in the case of an earthquake (de la Vergne, 2003). Additionally, not all the tailings produced are able to be reused as backfill so some surface management is still necessary (de la Vergne, 2003), but this is still a significant improvement over other backfill options.

CPB is typically mixed in a plant on the mine site at the ground surface and then transported to the stopes via pipes, either by gravity and/or pumping.

2.2.2 Design Requirements – Rheology

Rheology is the study of the flow and deformation of materials (Banfill, 2000). In particular, it examines the relationships between stress, strain, rate of strain, and time. In response to a shear stress, parallel planes of movement within the fluid form, which creates a velocity gradient along the planes (Banfill, 2000). This gradient is sometimes known as the shear rate or strain rate (Banfill, 2000). There are two important concepts that are frequently used to describe the rheological behaviour of a material: the yield stress and the viscosity. Yield stress (typically measured in Pa) is often conceptualized as the stress required to initiate flow, which by definition would need to be measured at zero shear rate and is not practically possible (Simon and Grabinsky, 2013). There are a few ways of working around this, including extrapolation of stress measurements at different shear rates to the expected stress at a shear rate of zero, or various experimental techniques. However, the apparent yield stress is the measured yield stress at a low, non-zero shear rate (Chen, N.D.), and this is sufficient for most practical purposes. This may even be a more appropriate concept in general, as it has been argued that the yield stress of a fluid does not truly exist and is the erroneous conclusion of the typical measurement ranges of

most lab equipment and the practice of linearly extrapolating incomplete flow curves (Barnes, 2000; Chen, N.D.). Nonetheless, it is generally agreed that the apparent yield stress provides useful information in describing the flow behaviour of various fluids and has been very widely studied. The viscosity of a fluid can be conceptualized as its resistance to flow, or its internal friction. Shear viscosity is the ratio of the shear stress to the shear rate: $\eta_s = \frac{\sigma}{\dot{\gamma}}$ [Pa.s]. In Newtonian fluids, the viscosity may vary with temperature or pressure, but does not vary with deformation rate or time. In non-Newtonian fluids, the shear viscosity is shear rate dependent (Barnes, 2000).

CPB exhibits non-Newtonian behaviour above a certain solids content (Boger et al., 2006; Bull, 2019). The model most commonly used to describe the flow behaviour of CPB is the Bingham Model (Cooke, 2006; Slatter, 2005), which incorporates apparent yield stress, viscosity, and shear rate:

Equation 1: Bingham Model of flow

$$\tau = \tau_0 + \mu\dot{\gamma}$$

Where τ is the shear stress (Pa), τ_0 is the apparent yield stress (Pa), μ is the plastic viscosity (Pa.s), and $\dot{\gamma}$ is the shear rate (s^{-1}) (Mai et al., 2014; Banfill, 2003).

When the yield stress is less than interface shear stress, the pumping pressure can be represented as:

Equation 2: Pumping pressure of cementitious materials

$$P = \frac{2L}{R} \left(\frac{Q}{3600\pi R^2 k_r} \eta + \tau_{0t} \right)$$

Where P is the pumping pressure (bar), L is the length of pumping pipe (m), R is the radius of the pumping pipe (m), Q is the pumping flow (m^3/h), k_r is the filling factor (which is

dependent on the type of pump: 0.7 for automatical and 0.8 for stationary), η is the viscous constant (Pa.s/m), and τ_{0t} is the interface yield stress (Mai et al., 2014).

In some cases, the pumping flow is high enough (Q_1) to result in an interface shear stress that is higher than the shear stress. In this case, the pumping flow is:

Equation 3: Pumping flow where $\tau_{0t} > \tau_0$

$$Q_1 = 3600 \frac{\tau_0 - \tau_{0t}}{\eta} \pi R^2 k_r$$

And the pumping pressure is:

Equation 4: Pumping pressure for Q_1

$$P = \frac{2L}{R} \left[\frac{Q/3600\pi R^2 k_r - (R/4\mu)\tau_{0t} + (R/3\mu)\tau_0}{1 + R/4\mu} \eta + \tau_{0t} \right]$$

Where μ is the plastic viscosity and τ_0 is the concrete yield stress (Mai et al., 2014).

The rheology of CPB is complex and influenced by numerous factors. It has been found to be influenced by water quality, w/c ratio, solids content, tailings fineness, hydration age, cement type and content, temperature, additives, and numerous other factors (Fall et al., 2005; Bull, 2019; Ghada, 2019; Taylor, 1997; Qi and Fourie, 2019). As mentioned above, CPB is typically transported to the stopes via pipes. Systems can be designed to minimize the transportation costs of the CPB by utilizing gravity or minimal pumping, but these require coordination with the CPB mix design and rheological properties. CPB that has higher solids or binder content will also have higher yield stress and viscosity and will be more difficult to transport by gravity and require more pumping energy (Belem and Benzaazoua, 2004; Ghada, 2019; Niroshan et al., 2017).

2.2.3 Design Requirements – Strength Gain

The primary purpose of mine backfill is to provide ground support, by which hazardous working conditions are mitigated and operations able to be continued, as good backfill practice

has been found to improve the ground stability of the whole mine site (Xu et al., 2021). For this, the ultimate strength properties are absolutely crucial. Secondly, backfill must gain strength quickly enough to allow bulkheads to be removed and adjacent operations to continue within a reasonable time frame, or the efficiency and profitability of the mine will be reduced (Belem et al., 2000; Fall et al., 2007). Finally, the design must consider the durability of CPB over time as adjacent excavations will eventually take place around the backfill and any exposed backfill faces must be self-supporting.

The mechanical stability of CPB is often evaluated using its uniaxial compressive strength (UCS) (Fall et al., 2005). Mitchell et al. (1982) provided the most commonly used method for evaluating the required UCS for mine design, which is given below.

The dimensions of the stope are as shown in the figure below (Figure 2.2). Mitchell et al. assumed no surcharge ($p_0=0$), and that friction along the rock-backfill interface and cohesion in the backfill could be ignored. The factor of safety becomes:

Equation 5: Factor of Safety for CPB (Mitchell et al., 1982)

$$FS = \frac{\tan(\phi)}{\tan(\alpha)} + \frac{2cL}{H^*(\gamma L - 2c_b) \sin(2\alpha)}$$

Where H^* is the equivalent height of the wedge given by: $H^* = H - \frac{\tan(\alpha)}{2}$, γ is the unit weight of the backfill, and c_b is the bound cohesion along the interface between the sidewalls and the backfill.

For a factor of safety of 1, a stope with a high aspect ratio such that $B \ll H \cong H^*$, and $c=c_b$, the required cohesion is:

Equation 6: Cohesion of CPB for FS=1 (Mitchell et al., 1982)

$$c = \frac{\gamma H}{2(H/L + \tan(\alpha))}$$

When $\phi=0$, this becomes the commonly used equation:

Equation 7: UCS for CPB (Mitchell et al., 1982)

$$UCS = \frac{\gamma H}{1 + H/L}$$

Given many of the assumptions stated, this solution is considered to be very conservative, and is commonly used in practice (Li and Aubertin, 2012). However, Li (2013) has observed that the cohesion between the fill and the sidewalls is typically much lower than the cohesion within the fill, not equal as the method assumes, indicating that the solution is not conservative. He also pointed out that the effective friction angle of the backfill is typically $35^\circ - 40^\circ$, not 0° as assumed by Mitchell's Method.

The layout and dimensions used in Mitchell's calculations are shown in Figure 2.2.

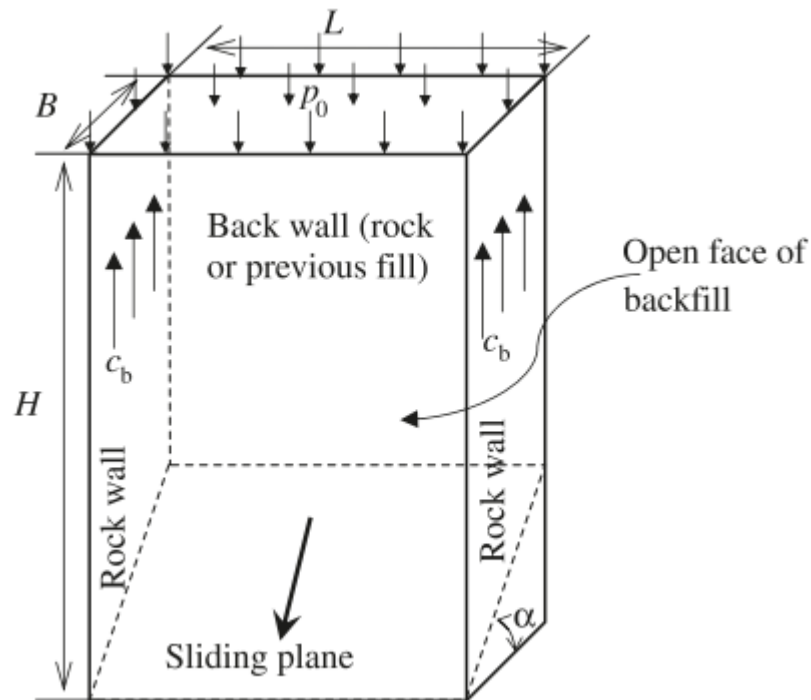


Figure 2.2 Schematic of slope backfill dimensions (Mitchell et al., 1982)

Li and Aubertin (2012) proposed a modified Mitchell (MM) solution that considers the application of a surcharge ($p_0 \neq 0$) but not the friction between the rock-backfill interfaces, as follows:

Equation 8: Factor of Safety for CPB (Modified Mitchell)

$$FS = \frac{\tan(\phi)}{\tan(\alpha)} + \frac{2c}{\sin(2\alpha)(p_0 + H^*(\gamma - \frac{2c_b}{L}))}$$

Where $c_b \neq c$, it can be written as $c_b = r_b c$, where $r_b = c_b/c$ and is between 0 and 1. This gives a required backfill cohesion of:

Equation 9: Cohesion of CPB (Modified Mitchell)

$$c = \frac{p_0 + \gamma H^*/2}{[(FS - \frac{\tan\phi}{\tan\alpha})\sin(2\alpha)]^{-1} + r_b H^*/L}$$

and strength of:

Equation 10: UCS of CPB for $FS=1$ (Modified Mitchell)

$$UCS = 2c \tan(45^\circ + \phi/2).$$

They also provided a solution for slopes with a low aspect ratio:

Equation 11: Factor of Safety for CPB with low aspect ratio (Modified Mitchell)

$$FS = \frac{\sin\phi}{\sin\alpha} + \frac{2c}{[p_0 + H(\frac{\gamma}{2} - \frac{r_b c}{L})]\sin(2\alpha)}$$

or

Equation 12: Cohesion for CPB with low aspect ratio (Modified Mitchell)

$$c = \frac{p_0 + \gamma H/2}{2[(FS - \frac{\tan(\phi)}{\tan(\alpha)})\sin(2\alpha)]^{-1} + \frac{r_b H}{L}}$$

The UCS of CPB is affected by curing time, temperature, initial water content, additives, cement content and type, and numerous other factors. These factors have also been found to influence the rate of strength development and the durability of the CPB and have been the subject of much research. More detailed discussion of other evaluation methods can be found in Belem and Benzaazoua, 2004, which have been omitted here for brevity.

2.3 Cement and Cement Hydration

Though some tertiary stopes can be filled with uncemented paste backfill, cement is a crucial component in CPB as its hydration reactions are primarily responsible for the strength of the CPB and its ability to support the underground mine workings. Therefore, it is helpful to elaborate on the properties of cement and its hydration.

Portland cement (PC) is formed by superheating limestone and clay until partial fusion occurs and nodules of clinker are formed. This clinker is mixed with a small amount of gypsum or other source of calcium sulphate and finely ground, resulting in cement. Since cement is of natural origin, its mineral and chemical makeup is variable, but it consists primarily of 4 major phases, in addition to the added gypsum, which are described in Table 2.2. There are a variety of specialty cement mixes, but the most commonly use in CPB is Ordinary Portland Cement (OPC), also known as Portland Cement type I (PCI). In this thesis, all references to PC, PCI, or OPC will be assumed to be equivalent.

Table 2.2 Cement Composition Phases

Chemical Name	Phase Name	Cement Chemist Notation	Chemical Notation	% Makeup of Cement
Tricalcium Silicate	Alite	C ₃ S	Ca ₃ SiO ₅	45 - 60
Dicalcium Silicate	Belite	C ₂ S	Ca ₂ SiO ₄	15 - 30
Tricalcium Aluminate	Aluminate	C ₃ A	Ca ₃ Al ₂ O ₆	6 - 12
Tetracalcium Aluminoferrite	Ferrite	C ₃ AF	Ca ₂ AlFeO ₅	6 - 8
Calcium Sulphate	Gypsum	-	CaSO ₄	5 - 6

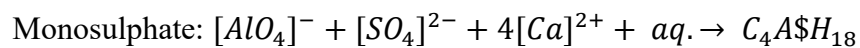
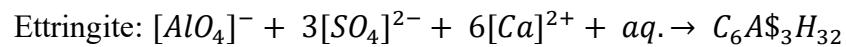
These basic components react with water to form the various hydrates that make up hardened cement. The hydration of each phase plays numerous roles in the overall hydration of Portland Cement (PC), many of which are still poorly understood and being actively studied. A general overview will be provided shortly. The hydration products formed are: calcium silicate hydrate (C-S-H), calcium hydroxide (CH, also known as Portlandite), and calcium

sulphoaluminate (including ettringite and monosulphate) (Mehta and Monteiro, 2001).

Additionally, Friedel's Salt forms when the cement paste contains salts.

Immediately upon mixing of the water and anhydrous cement, cement components begin to dissolve, which creates a highly ionic solution that spurs (or hinders) further dissolution, precipitation, and reactions. It can be generally stated that early-age reactions occur through solution while later-stage reactions are generally solid-state (Mehta and Monteiro, 2001). Additionally, the components involved do not dissolve at similar rates, nor do hydration products form at similar rates or even remain stable after initial formation. This complex flux of products and rates is what makes cement research so challenging and opaque.

First to hydrate is C₃A. Its hydration and the formation of associated products are so rapid that cement would be unusable unless slowed down long enough to be transported and formed. For this reason, gypsum is added to the clinker, as it retards the hydration of C₃A. The faster dissolution of gypsum reduces the solubility of the C₃A (Mehta and Monteiro, 2001). The hydration products formed are ettringite (C₆A₃H₃₂ or high-sulphate) and monosulphate (C₄AH₁₈ or low-sulphate).



Next to hydrate is C₃AF, which produces similar hydration products as C₃A: C₆A(F)₃H₃₂ and C₄A(F)H₁₈. AFt and AFm are now frequently used to designate the products that are structurally similar to ettringite and monosulphate, respectively, but have variable chemical compositions (Mehta and Monteiro, 2006). Whether AFt or AFm forms depends on the balance of aluminate or sulphate ions in the solution: at higher concentrations of sulphate, AFt forms, while at lower concentrations, AFm forms. Thus, in the very early stages, ettringite tends to

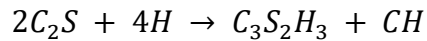
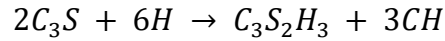
form, due to the high sulphate concentration from the gypsum, which is primarily responsible for the initial setting and early strength gain of young cement. However, the C_3A and C_3AF later undergo renewed hydration, which causes an increase in aluminate ions while the sulphate ions are depleted. This causes the needle-like ettringite to convert to plate-like monosulphate (Mehta and Monteiro, 2006).

Conversion of ettringite to monosulphate: $C_6A_3H_{32} + 2C_3A + 22H \rightarrow 3C_4AH_{18}$

Next to hydrate is the C_3S , followed by the C_2S , both of which are accelerated by the presence of gypsum in the mixture. Both of these form two hydration products: calcium-silicate-hydrate and calcium hydroxide, which play pivotal roles in the strength development and properties of concrete. Calcium-silicate-hydrate is actually a family of hydrates that shares a similar poorly crystalline structure and has varying ratios of silica to calcium. It has been found that the influence of the rigid, porous, gel-like structure far outweighs the influence of the composition on the properties of the hydrate (Mehta and Monteiro, 2006). Thus, it is convenient to simply identify this family of hydration products as C-S-H, wherein the dashes indicate variability in the ratios between the components. The C-S-H has been identified as contributing the most to the overall strength gain of the concrete mixture.

Calcium hydroxide, also called Portlandite, is frequently abbreviated as CH. This product does contribute to the strength of the concrete mixture, but it is also more vulnerable to acidic and sulphate environments over long times, which can reduce the long-term durability of the concrete (Mehta and Monteiro, 2006). As will be discussed in greater detail in a following section, CH is also a reactant in further hydration reactions, so its presence is highly variable throughout the curing process.

Assuming full reaction of all C_3S and C_2S , the following idealized equations give the hydration equations that form C-S-H (assumed as $C_3S_2H_3$ when fully hydrated) and CH (Mehta and Monteiro, 2006):

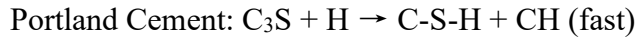


* Cement chemist notation is based on the oxides of minerals rather than the minerals alone, where: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, \$ = SO₃, H = H₂O

2.3.1 Supplementary Cementitious Materials and Pozzolanic Reactions

The high cost of cement has motivated many cement users, especially mines, to reduce their cement demand, though their strength requirements may be little changed (Mehta and Monteiro, 2006; Jiang and Fall, 2017b; Ghada, 2019). An effective means of achieving this is through the use of supplementary cementitious materials (SCMs), which include fly ash, metakaolin, and ground/granulated blast-furnace slag. These are materials that are either non-reactive with water or are too weakly cementitious to serve the required purposes (Mehta and Monteiro, 2006). However, in the presence of calcium hydroxide and water they react to produce C-S-H and other hydration products and can significantly contribute to the strength gain of a concrete mixture (Roy and Idorn, 1982; Daube and Bakker, 1986; Gruskovnjak et al. 2006; Kolani et al., 2012). The reactions are known as pozzolanic reactions, which tend to be slower and have lower heats of hydration than the reactions involved in ordinary Portland cement. They also consume CH which can improve the durability of concretes (Taylor, 1997; Mehta and Monteiro, 2006). Other than the reduced quantity of CH, it has been found that the principal hydration products of Portland cement with slag are essentially the same as plain Portland cement without slag (Taylor, 1997; Mehta and Monteiro, 2006). Typically, these materials are

used to replace a quantity of cement in the mix and are specified by the percentage of cement replacement by mass. The pozzolanic reaction can be compared to the plain Portland cement reaction as such (Mehta and Monteiro, 2006):



Slag was selected for this study due to its popularity as an SCM, low cost, and availability. It is a by-product of iron production and its reuse is environmentally beneficial. Though fly ash is also an industrial by-product, it is produced from the burning of coal in power plants (Kosmatka and Wilson, 2011). Canada, among other nations, has committed to phasing out coal electricity so the production of fly ash will diminish with time and eventually become inaccessible (Government of Canada, 2023). Therefore, it offers limited value for study. Metakaolin is a processed natural material that is used in the production of high-performance or specialty concretes and is often used as an additive rather than a replacement for cement; as such, it may be more costly and it can be less readily available than slag (Kosmatka and Wilson, 2011).

2.3.2 Admixtures

Concrete and other cementitious materials (e.g., CPB) are used for a vast variety of purposes and in many different environments and circumstances, as such, the specific requirements for each use are different and the mixes for each application must be carefully designed to ensure the requirements are met. As has been touched on already, the hydration dynamics are highly complex and strongly influenced by the presence and quantities of different components. It has long since been discovered that the addition of non-cementitious components can influence the behaviour and properties of concrete or cementitious materials in numerous

ways. ASTM C494 - Standard Specification for Chemical Admixtures for Concrete identifies seven types:

A - Water reducing

B - Retarding

C - Accelerating

D - Water reducing and retarding

E - Water reducing and accelerating

F - Water reducing, high range

G - Water reducing, high range, and retarding

Which are defined as:

Water reducing - an admixture that reduces the quantity of mixing water required to produce concrete (or cementitious material) of a given consistency. These are often referred to as “plasticizers” because they increase the plasticity of a cement mixture when used with the same quantity of mixing water.

High range - an admixture that reduces the quantity of mixing water required to produce concrete (or cementitious material) of a given consistency by 12% or greater.

Retarding - an admixture that retards the setting of concrete (or cementitious material).

Accelerating - an admixture that accelerates the setting and early strength development of concrete (or cementitious material).

As will be seen in the following chapters, chlorides, especially NaCl, can act as a water reducer and as either an accelerator or retarder depending on concentration.

2.4 Literature Review of Previous Studies on Rheology, Setting Time and Strength of Saline CPB

2.4.1 Rheology and Setting Time of Saline CPB

Many studies have been conducted on various rheological properties of cement, concrete, and cement paste backfill, but very few have been conducted on specifically saline cement paste backfill. To allow for a greater focus, only the most relevant studies will be discussed below.

Simon and Grabinsky (2013) studied the effects of binder content on the apparent yield stress of CPB made with natural mine tailings, as well as the effects of hydrochloric acid and NaCl on the pH of said CPB. They also studied the effects of fly ash replacement and superplasticizers, but these will not be discussed here. Zeta potential measurements of the natural mine tailings suspended in deionized water were also taken. They found that a mixture of tailings and PC had a higher yield stress than either tailings or PC alone and attributed this to the mixture of different sized particles having a higher particle packing density than the components alone. They concluded that the difference in electrostatic repulsion (as measured by the zeta potential) between the tailings and PC particles promoted a closer packing density than could be achieved in a solution of a single component. In the two-component solution, the differently charged particles would have been attracted to each other and packed more densely, while in the single-component solutions, the similarly charged particles would have been repulsed and had a greater particle spacing, leading to a lower yield stress. They concluded that the increase in yield stress during the first two hours of curing was due to consolidation of particles under self-weight, rather than cement hydration reactions, as the cement was still in the dormant phase of hydration. It was found that an increase in HCl (decrease in pH) led to a decrease in yield stress and that the pH of the solution remained constantly neutral with the addition of NaCl. It was also found that

an increase in the concentration of any ion, regardless of type, increased the zeta potential (less negative). From this, it was concluded that cations such as Na^+ are a potential determining ion for mine tailings, which is to say that the adsorption of these ions reverses the sign of the particle surface charge from negative to positive. It was also concluded that the maximum apparent yield stress occurs near the isoelectric point (IEP), which is the pH at which the zeta potential is zero. This is because a zeta potential of zero represents the minimum of interparticle electrostatic dispersion forces in the mixture, which allows other interparticular forces such as Van der Waals forces to contribute to interparticular attraction and further increase the packing density and the yield stress.

Klein and Simon (2006) studied the effects of binder content, pH, and electrolytes on setting time and strength development of CPB made with natural mine tailings. They also studied the effects of fly ash replacement and superplasticizers, but these will not be discussed here. They found that a decrease in PC led to an increase in setting time, and that an increase in initial water content also led to an increase in both initial and final setting times. The addition of 3% NaCl by mass of PC (0.066 mol/L) led to a decrease in initial and final setting times by about 7% and the addition of 3% NaCl by mass of solids (1.313 mol/L) led to an even further decrease in both initial and final setting times. They also found that increasing the acidity by the addition of HCl led to significant increases in the initial and final setting times, while increasing the alkalinity by the addition of NaOH led to notable decreases in the initial and final setting times. This was believed to be due to a low pH hindering the dissolution of the silicate phase in the PC. NaCl was found to increase the UCS of the CPB compared to the control by 30% after 28 days and by 9.3% after 6 months, while the 1-year strengths were similar.

Zhao et al. (2020) studied the effects of mine processed water and binder content and type on the yield stress of CPB made with natural mine tailings. The binders studied were PC and Minecem, which is a slag-based cement used in mines. They also studied the effects of temperature and fly ash but these will not be discussed here further. They used constant shear rate (CSR) method of yield stress to measure the yield stress required to initiate flow prior to the breakdown of the CPB's hydration product structure. They also used flow curve (FC) to measure the dynamic yield stress required to maintain or terminate flow. They pointed out that the static yield stress and viscosity was higher than the dynamic because the undisturbed structure of hydration products required additional stress to break down. They found that CPB made with 3% of Minecem as a binder produced a higher UCS after 28 days than 3% or 4% of PC, and that 3% of Minecem also had a lower yield stress than 4% of PC, which is also more favourable. They also found that using mine-processed water generally resulted in a higher yield stress than using tap or fresh water, and that this was due to the presence of some elements such as Ca and Mg in the mine-processed water, which thickened the CPB and made it require more energy to transport. They also found that using Minecem in combination with mine-processed water mitigated some of the negative impacts on yield stress that using mine-processed water caused, when compared against using mine-processed water and PC.

Zhou and Fall (2022) studied the effects of chloride bearing anti-freezes, including NaCl, and slag replacement on the viscosity and yield stress of CPB made with PC, and synthetic (silica) tailings at sub-zero temperatures. They also collected data on the impacts of NaCl on zeta potential, electrical conductivity, and water content. The effects of binder content, temperature, and CaCl₂ were also studied, but these will not be discussed further here. The addition of NaCl led to a reduction in yield stress at all times compared to the control. This was concluded to be

caused by chloride ion adsorption on the surfaces of the unhydrated PC particles and hydration particles, which led to a decrease in zeta potential, increase in repulsive forces between the particles, and decrease in yield stress. It was also found that the zeta potential decreased (became more negative) with an increase in pH, due to the increase in hydroxyl concentration. It was also found that the samples with chloride-bearing additives had more hydration products than the samples without additives, including Friedel's Salt and precipitated NaCl. Since the presence of these additional products was expected to lead to an increase in interparticular friction and yield stress, it can be concluded that this effect was more than compensated for by the effects of the increase in zeta potential. Thus, the net change in yield stress is due to the balance between competing effects of NaCl in CPB. It was also found that the addition of NaCl led to an increase in the viscosity over all curing times when compared against the control. This was believed to be due to the increased particle-particle interactions from the additional hydration products. Additionally, as the concentration of NaCl increased, the yield stress after 1 hour decreased and the viscosity increased. It was concluded that the increased magnitude of the zeta potential controlled the impacts to yield stress, while the acceleration of hydration product formation (and increased solid volume fraction) controlled the impacts to viscosity. All of these conclusions were supported by TG/DTG, XRD, and zeta testing, as well as electrical conductivity monitoring. Finally, it was found that as the replacement of PC with slag increased, so did the yield stress, which was expected to be because the presence of slag increased the zeta potential (made it less negative) thus reducing the inter-particular repulsion. It was also found that 50% replacement of PC with slag led to a decrease in the viscosity, while 75% replacement led to an increase, for both samples with NaCl and the control. From 0% to 50% slag replacement, the slag slowed down the hydration reactions, leading to the decrease in viscosity, while at >50%

slag replacement, the small slag particles acted as a filler between cement and tailings particles and increased the inter-particle contacts, leading to the increase in viscosity. For samples including partial slag replacement, the addition of NaCl also led to an increase in viscosity and decrease in yield stress, as was the case for the PC CPB.

Xiao et al. (2021) studied the effects of sodium chloride and ground granulated blast furnace slag replacement on the yield stress and viscosity of CPB made with synthetic silica tailings, PC, and distilled water. They also studied the effects of temperature, sulphate content, and binder content, but these will not be discussed further. They also performed microstructural analyses, pH, electrical conductivity, and zeta measurements. They found that both viscosity and yield stress increased over the first two hours of curing for both the PC mix and the 50/50 PC/Slag mix, which was concluded to be due to the increase in cement hydration products and consumption of water during this time, which led to increased particle-particle friction and resistance. It was noted that the slag mix had a higher yield stress and a lower viscosity than the PC mix at all but the initial curing times. This was believed to be due to the more negative zeta potential of the PC mix than the slag mix, which indicated stronger repulsive forces and lower yield stress in the PC mix. The PC mix had a higher viscosity for two reasons: its faster hydration rate led to a higher solid volume fraction and cohesion between particles, and the lower hydration rate of the slag led to lower specific surface area and more free water which formed a water film that lubricated the particles in the slag mix. Yield stress and viscosity were found to generally increase with increasing slag content, except in the case of 100% slag. This was due to the smaller slag particles acting as filler and increasing the particle packing and inter-particle friction. The 100% slag mix did not experience any change in yield stress or viscosity, as it lacked a sufficiently alkaline environment from PC to initiate hydration reactions. When

NaCl was added to the mixes, the yield stress and viscosity of both the PC and the slag mixes decreased at all curing times. The chloride ions were adsorbed onto the surfaces of the hydration products and unhydrated cement, which led to a more negative zeta potential, greater repulsion between particles, and increased flowability. It was also found that saline CPB without slag had lower yield stress and viscosity than saline CPB with slag. This was due to two reasons: the precipitation of NaCl in the slag samples which increased particle friction and collisions and the increased chloride binding capacity of slag led to the production of Friedel's Salt which also increased inter-particle friction and collisions. These results were all validated with TG/DTG and XRD testing.

Jiang and Fall (2017a) studied the effects of various concentrations of NaCl on the yield stress and strength development of CPB made with silica tailings, and PC at sub-zero temperatures. The strength development results will be discussed in a following section. Zeta potential measurements and microstructural analyses were also conducted. It was found that an increase in NaCl concentration led to a decrease in yield stress at most curing times, which was found to be due to the increase in adsorbed chloride ions, which increased the zeta potential and repulsive forces between cement and hydration particles, and decreased the inter-particle friction. It was also found that all samples experienced a drop in yield stress from initial mixing to about one hour after, followed by a strong increase. The non-saline sample did not have data available after one hour due to partial freezing. The initial drop in yield stress was found to be caused by the low temperatures inhibiting hydration reactions, and allowing the yield stress to be dominated by the initial inter-particle forces. Additionally, cement gel formed at low temperatures has a lower specific area (coarser texture) which adsorbs more free water and reduces the lubrication between particles. The rise in yield stress after one hour was caused by

the increase in hydration products leading to increased inter-particle friction. It was also noticed that samples with higher concentrations of NaCl had higher yield stress gains after the first hour, and that this was due to the precipitation of NaCl particles which increased the friction and collisions between CPB particles.

Jiang and Fall (2017b) studied the effects of various concentrations of NaCl on the yield stress and strength development of CPB made with silica tailings, slag, and PC at sub-zero temperatures. The strength development results will be discussed in a following section. Zeta potential measurements and microstructural analyses were also conducted. It was found that the yield stress of the CPB decreased with increasing concentration of NaCl and that the cause of this was more negative zeta potential caused by the adsorption of Cl^- ions onto the surfaces of the cement particles and hydration products, which increased the fluidity. They also found that the yield stress increased slightly from 0 to 1 hour of curing and that the yield stress began to increase more strongly after 1 hour, except for the non-saline sample which was not able to be tested. This was due to the rate of hydration reactions which were slowed under colder temperatures. It was also found that saline slag-CPB experienced a slight increase in yield stress over the first hour of curing, while saline PC-CPB experienced a slight decrease during this time. In all cases, the yield stress increased significantly after 1 hour, but the slag-CPB had higher yield stress than the PC-CPB. This was found to be due to the higher precipitation of NaCl in the slag samples than the PC samples, which led to greater inter-particle friction and collisions. Additionally, the slag samples also formed more Friedel's Salt and similar products due to its higher chloride binding capacity, stemming from its higher alumina content and larger specific surface area over PC. They also found that the yield stress of both slag- and PC-CPB samples decreased as the NaCl concentration increased, but that the relative decreases (compared to non-

saline CPB) in yield stress were greater for the slag-CPB than for the PC-CPB. Again, this was found to be due to slag's much higher chloride binding ability and larger surface area, which led to a greater increase in the absolute value of the zeta potential of the slag samples than the PC samples and correspondingly, a greater drop in yield stress with the addition of more NaCl. Overall, competing factors were found that contributed to both the increase and the decrease of the yield stress of saline slag-CPB compared to saline PC-CPB, and the overall outcome depended on the slag replacement content, NaCl concentration, and curing time. These results were verified by microstructural analyses and supplemental testing.

In summary, while some research has been conducted on the impacts of NaCl on yield stress of CPB, little research has been conducted on the impacts to viscosity. In cases where the yield stress was studied, the results were only applicable to below-freezing temperatures (Jiang and Fall, 2017 a and b) (Zhou and Fall, 2022), or influenced by the use of mine water and natural mine tailings (Zhao et al., 2020), or did not explore the impact of NaCl concentration (Xiao et al., 2021). Previous studies on the influence of NaCl on viscosity also did not study the impacts of NaCl concentration and were applicable to below-freezing conditions. There has only been one study on the impacts of NaCl to setting time and it only examined two concentrations of NaCl, did not examine the effects of slag on saline CPB, and was influenced by the use of natural mine tailings. Thus, there is still a need to comprehensively study the impacts of NaCl concentration and slag replacement variations on viscosity, yield stress, and setting time at room temperature and without the variability caused by the use of natural mine tailings or mine water.

2.4.2 Strength Gain of Saline CPB

Extensive research has been conducted on the impacts of additives, including various chlorides, on the strength gain of cementitious materials. However, studies specifically on the

impacts of NaCl on CPB strength gain are relatively limited. The most relevant studies will be discussed below.

Chen et al. (2020) studied the effects of varying concentrations of NaCl in the mixing water on the strength gain of gangue-cemented paste backfill (GCPB) from 3 to 28 days of curing. GCPB is composed primarily of gangue, fly ash, and PC and is used in coal mines and under buildings, water, and railway applications. NaCl concentrations of 0‰, 5‰, 10‰, 20‰, 30‰, and 40‰ were tested, and supplemental microstructural analyses were also conducted. It was found that GCPB made with a NaCl concentration of 5‰ had the highest elastic modulus, while the 0‰, 10‰, and 20‰ samples had similar, lower moduli, and the 30‰ sample had the lowest after 3 days of curing. At 7 and 28 days, all the samples had similar moduli, except the 40‰ sample which was significantly lower. A high elastic modulus indicates a greater resistance to deformation in the elastic stage. At all curing times, only the samples with 5‰, 10‰, and 20‰ NaCl had higher peak UCS than the control samples (0‰ NaCl). The reason for this was that the chloride reacted with the C₃A in the cement to form insoluble Friedel's Salt, and reacted with CH to form an alkaline compound salt, which is insoluble in the chlorine solution. These hydration products contributed to the strength of the CPB and created a denser microstructure but did not completely fill the pore spaces. However, the samples with 30‰ and 40‰ NaCl had lower peak UCS than the control; in particular, the 30‰ samples did not experience the same strength growth rate as the other samples. It was concluded that the reason for this was excessive ettringite growth, which may have caused expansion cracking or damaged the joint skeleton of the samples, and that too much Friedel's salt reduced the UCS. Finally, the 40‰ sample was not able to be tested after only 3 days of curing because the high chloride content absorbed more water in the GCPB, increasing the liquid phase and preventing the samples from being molded.

Wang and Villaescusa (2000) studied the effects of high NaCl concentration on the UCS of cemented tailings fill and cemented aggregate fill. Only the effects on cemented tailings fill will be discussed further here. They tested concentrations of 5%, 10% and 20.8% NaCl and found that all significantly reduced the UCS at 28 days of curing when compared to the non-saline control samples.

Jiang and Fall (2017a) studied the effects of various concentrations of NaCl on the strength development and deformation behaviour of CPB made with synthetic silica tailings, distilled water, and PC at a sub-zero temperature of -6°C . Supplemental testing included XRD and DTG. They found that UCS increased over time regardless of initial saline concentration due to the increase in C-S-H and consumption of water over time. They also found that, for all curing times, an increase in NaCl concentration led to a significant decrease in UCS. This was because the higher salinity led to more water content that was not frozen, which is known to decrease the strength of soils. Another reason was that the Na^{+} from the NaCl likely replaced some of the Ca^{+} in the C-S-H which reduces the Ca/Si ratio and has been shown to reduce its UCS. The precipitation of NaCl was also found to reduce the strength of the CPB and was confirmed by TG/DTG results. Finally, the formation of Friedel's Salt causes Na^{+} ions in the pore solution to bind with the C-S-H in order to maintain a neutral charge, which was also confirmed by TG/DTG testing. Thus, the presence of NaCl reduces the activation energy for CH. Regarding the deformation behaviour, it was found that non-saline samples exhibited strain-softening, while saline samples exhibited strain-hardening. This was attributed to the increased unfrozen water content of the saline samples which has been shown to result in more ductile behaviour in frozen soils. Additionally, as curing time increased, ductility decreased, which was attributed to

increased binder hydration. Lastly, as salinity increased, the modulus of elasticity decreased due to the increased quantity of unfrozen water. Supplemental testing supported these conclusions.

Jiang and Fall (2017b) studied the effects of various concentrations of NaCl on the strength development and deformation behaviour of CPB made with synthetic silica tailings, distilled water, slag, and PC at a sub-zero temperature of -6°C . Supplemental testing included MIP, XRD, and DTG. They found that an increase in salinity led to a decrease in UCS due to a reduction in the bulk freezing point of the pore water. As the presence of ice contributes significantly to the strength of the matrix, the ratio of ice to water will as well, and a decrease in bulk freezing point will lead to lower ice content and lower strength. Additionally, the presence of Na^+ ions leads to some replacement of Ca^+ in the C-S-H, and a reduction in the Ca/Si ratio, which has been associated with a decrease in strength of the C-S-H. These conclusions were corroborated by the supplemental testing, which showed that the high-salinity samples actually had more hydration products than the non-saline control samples due to a greater amount of liquid water available for hydration reactions. However, the strength contribution of the additional hydration products did not make up for the strength loss of a lower ice content. It was also found that an increase in the precipitation of Friedel's Salt had a positive effect on the strength by reducing the internal porosity. They also found that all mixes experienced an increase in UCS over time due to an increase in degree of hydration and the resulting increase in hydration products and decrease in water film thickness. All non-saline slag mixes had higher UCS than the non-saline PC mixes which was due to the filler effect of the finer slag particles that contributed to a denser microstructure. The formation of secondary C-S-H from pozzolanic reactions also led to a finer pore structure, lower overall porosity, and higher UCS which was corroborated by the MIP results. They also found that the UCS of slag-CPB is more sensitive to

NaCl than PC-CPB, as most slag samples had a lower UCS than the PC sample of the same age and salinity. This was because the finer slag matrix favoured a higher degree of free water adsorption onto the surface of the slag particles, resulting in more unfrozen water in the matrix and lower UCS. Additionally, they found that the presence of slag in the CPB resulted in a lower UCS increase after 28 days, as the sub-zero conditions significantly inhibited the progression of the pozzolanic reactions. Finally, they also found that an increase in salinity led to more plastic behaviour during deformation of slag-CPB. This was due to the increased quantity of unfrozen water, which as has been previously shown, is associated with more ductile behaviour of frozen porous materials. In addition, ductility was found to decrease with an increase in curing time as the increase in hydration products led to a finer pore structure and higher strength.

In summary, studies have investigated the effects on strength gain of NaCl on gangue-CPB, CPB with PC and slag at sub-zero temperatures. The effects of high levels of salinity have been investigated on CPB at room temperatures. However, little research has been conducted into the strength gain effects of low and high NaCl concentrations on PC-CPB and slag-CPB at room temperatures, and on the effects of slag-replacement content of saline CPB. There is a need to address this knowledge gap.

2.5 References

- ASTM Standard C494. (2008). *Standard Specification for Chemical Admixtures for Concrete*.
ASTM International, West Conshohocken, PA, 1975, DOI: 10.1520/C0494_C0494M-08,
www.astm.org
- Banfill, P. F. (2003). The rheology of fresh cement and concrete-a review. In *Proceedings of the 11th international cement chemistry congress* (Vol. 1, pp. 50-62).
- Barnes, H. A. (2000). *A handbook of elementary rheology* (Vol. 1). Aberystwyth: University of Wales, Institute of Non-Newtonian Fluid Mechanics.
- Belem, T., & Benzaazoua, M. (2004). An overview on the use of paste backfill technology as a ground support method in cut-and-fill mines. *Proceedings of the Ground Support in Mining Underground Construction, Perth, Australia*, 28-30.
- Belem, T., Benzaazoua, M., & Bussi re, B. (2000). Mechanical behaviour of cemented paste backfill. In *Proc. of 53rd Canadian Geotechnical Conference, Montreal* (pp. 373-380).
- Boger, D. V., Scales, P. J., & Sofra, F. (2006). Rheological concepts. In R. Jewell & A. Fourie (Eds.), *Paste and thickened tailings - a guide*, (pp. 25-37). Australian Centre for Geomechanics.
- British Antarctic Survey & Royal Geographical Society (with IBG). (N.D.). *Mineral Resources: Cold Facts*. Discovering Antarctica.
<https://discoveringantarctica.org.uk/challenges/sustainability/mineral-resources/>
- Bull, A. J. (2019). *Temperature dependence of the leachability of cemented paste backfill* [MASc thesis, Ottawa, ON: University of Ottawa]. <http://dx.doi.org/10.20381/ruor-23118>
- Chen, S., Du, Z., Zhang, Z., Zhang, H., Xia, Z., & Feng, F. (2020). Effects of chloride on the early mechanical properties and microstructure of gangue-cemented paste

- backfill. *Construction and Building Materials*, 235, 117504.
<https://doi.org/10.1016/j.conbuildmat.2019.117504>
- Chen, T. (N.D.). *Rheological techniques for yield stress analysis*. TA Instruments.
<https://www.tainstruments.com/pdf/literature/RH025.pdf>
- Cooke, R. (2006). Thickened and paste tailings pipeline systems: design procedure—part 1. In *Paste 2006: Proceedings of the Ninth International Seminar on Paste and Thickened Tailings* (pp. 371-381). Australian Centre for Geomechanics.
- Daube, J., & Bakker, R. (1986). Portland blast-furnace slag cement: a review. *Blended Cements*. DOI: 10.1520/STP36388S
- de la Vergne, J. N. (2003). *Hard rock miner's handbook* (3rd ed.) McIntosh Engineering.
- Fall, M., Belem, T., Samb, S., & Benzaazoua, M. (2007). Experimental characterization of the stress–strain behaviour of cemented paste backfill in compression. *Journal of materials science*, 42(11), 3914-3922. <https://doi.org/10.1007/s10853-006-0403-2>
- Fall, M., Benzaazoua, M., & Ouellet, S. (2005). Experimental characterization of the influence of tailings fineness and density on the quality of cemented paste backfill. *Minerals engineering*, 18(1), 41-44. <https://doi.org/10.1016/j.mineng.2004.05.012>
- Ghada, A. A. (2019). *Temperature dependency of the rheological properties and strength of cemented paste backfill that contains sodium silicate* [MAsc thesis, Ottawa, ON: University of Ottawa]. <http://dx.doi.org/10.20381/ruor-26207>
- Goudie, A. S. (2013). *Arid and semi-arid geomorphology*. Cambridge university press.
- Government of Canada. (2023). *Coal phase-out: the Powering Past Coal Alliance*. <https://www.canada.ca/en/services/environment/weather/climatechange/canada-international-action/coal-phase-out.html>, accessed on: July 8, 2023.

- Grice, A. (1998). Underground mining with backfill. *2nd Annual Summit on Mine Tailings Disposal Systems, Brisbane, Nov, 24-25*.
- Gruskovnjak, A., Lothenbach, B., Holzer, L., Figi, R., & Winnefeld, F. (2006). Hydration of alkali-activated slag: comparison with ordinary Portland cement. *Advances in cement research, 18*(3), 119-128. <https://doi.org/10.1680/adcr.2006.18.3.119>
- Jiang, H., & Fall, M. (2017a). Yield stress and strength of saline cemented tailings in sub-zero environments: Portland cement paste backfill. *International Journal of Mineral Processing, 160*, 68-75. <https://doi.org/10.1016/j.minpro.2017.01.010>
- Jiang, H., & Fall, M. (2017b). Yield stress and strength of saline cemented tailings materials in sub-zero environments: Slag-paste backfill. *Journal of Sustainable Cement-Based Materials, 6*(5), 314-331. <https://doi.org/10.1080/21650373.2017.1280428>
- Khaltar, B. (2020, October 14). Mongolia plans river diversion as mining boom sucks Gobi dry. *The Third Pole*. <https://www.thethirdpole.net/en/regional-cooperation/mongolia-plans-river-diversion-as-mining-boom-runs-gobi-dry/> Accessed on Jan 3, 2023.
- Klein, K., & Simon, D. (2006). Effect of specimen composition on the strength development in cemented paste backfill. *Canadian geotechnical journal, 43*(3), 310-324. <https://doi.org/10.1139/t06-005>
- Kolani, B., Buffo-Lacarrière, L., Sellier, A., Escadeillas, G., Boutillon, L., & Linger, L. (2012). Hydration of slag-blended cements. *Cement and concrete composites, 34*(9), 1009-1018. <https://doi.org/10.1016/j.cemconcomp.2012.05.007>
- Kosmatka, Steven H. and Wilson, Michelle L. (2011). *Design and Control of Concrete Mixtures*, EB001, 15th edition, Portland Cement Association, Skokie, Illinois, USA.

- Le Menn, M., Albo, P. A. G., Lago, S., Romeo, R., & Sparasci, F. (2018). The absolute salinity of seawater and its measurands. *Metrologia*, *56*(1), 015005. DOI 10.1088/1681-7575/aaea92
- Li, L., & Aubertin, M. (2012). A modified solution to assess the required strength of exposed backfill in mine stopes. *Canadian Geotechnical Journal*, *49*(8), 994-1002.
<https://doi.org/10.1139/t2012-056>
- Li, L. (2014). Generalized solution for mining backfill design. *International Journal of Geomechanics*, *14*(3), 04014006. DOI: 10.1061/(ASCE)GM.1943-5622.0000329.
- Mai, C-T., Kadri, E-H., Ngo, T-T., Kaci, A., and Riche, M. (2014). Estimation of the pumping pressure from concrete composition based on the identified tribological parameters. *Advances in Materials Science and Engineering*, 2014.
<https://doi.org/10.1155/2014/503850>
- Maus, V., Giljum, S., Gutschlhofer, J., da Silva, D. M., Probst, M., Gass, S. L., ... & McCallum, I. (2020). A global-scale data set of mining areas [Data set]. *Scientific data*, *7*(1), 1-13.
<https://doi.org/10.1594/PANGAEA.910894>
- Mehta, P. K., & Monteiro, P. J. (2006). *Concrete: microstructure, properties, and materials*, 3rd ed. McGraw-Hill Education.
- Meißner, S. (2021). The Impact of Metal Mining on Global Water Stress and Regional Carrying Capacities—A GIS-Based Water Impact Assessment. *Resources*, *10*(12), 120.
<https://doi.org/10.3390/resources10120120>
- Millero, F. J., Feistel, R., Wright, D. G., & McDougall, T. J. (2008). The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep*

- Sea Research Part I: Oceanographic Research Papers*, 55(1), 50-72.
doi:10.1016/j.dsr.2007.10.001
- Mitchell, R.J., Olsen, R.S., & Smith, J.D. (1982). Model studies on cemented tailings used in mine backfill. *Canadian Geotechnical Journal*, 19 (1), 14-28. <https://doi.org/10.1139/t82-002>
- Niroshan, N., Sivakugan, N., & Veenstra, R. L. (2018). Flow characteristics of cemented paste backfill. *Geotechnical and Geological Engineering*, 36(4), 2261-2272.
- Prosser, I., Wolf, L., & Littleboy, A. (2011). Water in mining and industry. *Water: Science and Solutions for Australia*, 135-146.
- Qi, C., & Fourie, A. (2019). Cemented paste backfill for mineral tailings management: Review and future perspectives. *Minerals Engineering*, 144, 106025.
<https://doi.org/10.1016/j.mineng.2019.106025>
- Roy, D. M. (1982, November). Hydration, structure, and properties of blast furnace slag cements, mortars, and concrete. In *Journal Proceedings* (Vol. 79, No. 6, pp. 444-457).
- Simon, D., & Grabinsky, M. (2013). Apparent yield stress measurement in cemented paste backfill. *International Journal of Mining, Reclamation and Environment*, 27(4), 231-256.
<https://doi.org/10.1080/17480930.2012.680754>
- Slatter, P. T. (2005). Tailings transport—back to basics!. In *Paste 2005: Proceedings of the International Seminar on Paste and Thickened Tailings* (pp. 165-176). Australian Centre for Geomechanics.
- Taylor, H.F. (1997). *Cement chemistry* (2nd ed.). Thomas Telford.
- Van Weert, F., Van der Gun, J., & Reckman, J. (2009). Global overview of saline groundwater occurrence and genesis. *International Groundwater Resources Assessment Centre*.

- Wang, C., & Villaescusa, E. (2000). Backfill research at the western Australian school of mines. *MassMin 2000 Proceedings*, 1-15.
- World Gold Council. (2022). *Global mine production* [Data set].
<https://www.gold.org/goldhub/data/gold-production-by-country>
- Xiao, B., Fall, M., & Roshani, A. (2021). Towards understanding the rheological properties of Slag-Cemented paste backfill. *International Journal of Mining, Reclamation and Environment*, 35(4), 268-290. <https://doi.org/10.1080/17480930.2020.1807667>
- Xu, H., Apel, D., Wang, J., Wei, C., & Pourrahimian, Y. (2021). Investigation of backfilling step effects on stope stability. *Mining*, 1(2), 155-166. <https://doi.org/10.3390/mining1020010>
- Zhao, Y., Taheri, A., Karakus, M., Chen, Z., & Deng, A. (2020). Effects of water content, water type and temperature on the rheological behaviour of slag-cement and fly ash-cement paste backfill. *International Journal of Mining Science and Technology*, 30(3), 271-278.
<https://doi.org/10.1016/j.ijmst.2020.03.003>
- Zhou, X., Lin, X., Huo, M., & Zhang, Y. (1996). The hydration of saline oil-well cement. *Cement and Concrete Research*, 26(12), 1753-1759. [https://doi.org/10.1016/S0008-8846\(96\)00176-7](https://doi.org/10.1016/S0008-8846(96)00176-7)
- Zhou, Y., & Fall, M. (2022). Investigation on rheological properties of cemented pastefill with chloride-bearing antifreeze additives in sub-zero environments. *Cold Regions Science and Technology*, 196, 103506. <https://doi.org/10.1016/j.coldregions.2022.103506>

Chapter 3: Technical Paper 1 – Strength Development and Self-Desiccation of Saline Cemented Paste Backfill

(submitted)

3.1 Abstract

The effect of mixing water salinity and binder type on the strength development and self-desiccation (measured by suction and volumetric water content) of cement paste backfill (CPB) is explored. NaCl concentrations from 0 g/L to 300 g/L were used in CPB made with pure ground silica tailings and Portland Cement type I (PC). Concentrations of 10 g/L and 35 g/L were found to moderately increase UCS, while a concentration of 100 g/L had comparable UCS to non-saline CPB and a concentration of 300 g/L was found to significantly decrease UCS over all curing times. Water content and suction monitoring were conducted up to 28 days of curing time and found that suction only slightly contributed to UCS gain of the saline CPBs, and high salt contents (100 and 300 g/L) significantly inhibited the self-desiccation ability of CPB due to inhibition of cement hydration by the excessive amount of salt. The increase in strength of both saline and non-saline samples was attributed primarily to the increase in cement hydration products, while the increased strength of the samples with salinities of 10 g/L and 35 g/L was mainly attributed to the presence of Friedel's salt in the pores. The effect of PC replacement between 25% to 75% with slag on CPB with 35 g/L mixing water salinity was also studied. Slag replacement of 50% and higher resulted in significantly higher UCS over most curing times. Suction likely moderately contributed to UCS of the saline CPB with slag, in addition to the presence of Friedel's salt in the pores and the acceleration of cement and slag hydration by the presence of NaCl.

3.2 Introduction

The underground cavities created by mining activities must be backfilled to ensure worker safety, prevent subsidence at the ground surface, and provide stable surfaces for mining to continue (Abdul-Hussain, 2011; Ghada, 2019). Cemented paste backfill (CPB) is a relatively recent development in mine backfill that utilizes dehydrated mine tailings as the major component (Fall et al., 2008; Pokharel, 2008; Benzaazoua et al., 2004).

CPB is typically composed of approximately 70% - 85% dehydrated mine tailings, 2% - 9% binder, and water (Ghada, 2019; Pokharel, 2008; Fall and Benzaazoua, 2005). The optimal combination of tailings, binder type, and water is crucial to the economical and safe use of CPB (Pokharel, 2008; Belem et al., 2000). Therefore, much research has been conducted on various properties of CPB with different mixes and under different conditions (Benzaazoua et al., 2004).

Mines are located all around the world, including in regions without readily available freshwater (Van Weert et al., 2009; Hivon and Segó, 1993). Freshwater scarcity may mandate the use of saline groundwater or seawater for CPB mixing water, either for humanitarian, ethical, or practical reasons (Alberta Water, 2013). This can impact the engineering properties of the resulting CPB as mixing water salinity is known to impact the properties of cemented materials (Chen et al., 2020; Beya et al., 2015).

A crucial property of CPB is its mechanical stability, which describes the CPB's ability to maintain its structural integrity under stress and withstand physical disturbance after different curing periods (Belem et al., 2000). This is crucial in allowing the safe excavation of adjacent stopes as quickly as possible and with minimal ore dilution, which have significant impact on mining costs (Pokharel, 2008; Ghada, 2019). The most common representation of this property is the unconfined compressive strength (UCS) because it is cheap and easy to measure and is easily

incorporated into routine mine quality control (Wang et al, 2016; Fall and Benzaazoua, 2005; Jiang and Fall, 2017b; de la Vergne, 2000; Benzaazoua et al., 2004; Fall et al., 2010).

Another property of cemented materials is their self-desiccation ability. As cement particles hydrate, they react with the mixing water to create hydration products, which increase the strength of the material, decrease the amount of water present in the mix (i.e. decrease of pore water pressure) and increase the suction (Wang et al., 2016; Persson, 1997). It is known that a decrease in pore water pressure and/or an increase in suction can also contribute to the strength of porous materials (Fredlund and Rahardjo, 1993).

To date, limited research has been conducted on the effects of mixing water salinity on the strength of various cemented backfill mixes. Chen et al. (2020) studied the effects on gangue-cemented paste backfill. They found that salinities of 5 g/L – 20 g/L resulted in higher UCS at all curing times than non-saline mixing water, while salinities of 30 g/L and above resulted in lower UCS, and that a salinity of 5 g/L had the highest peak UCS. Jiang and Fall studied the relationship between mixing water salinity on frozen CPB (2017a) and slag CPB (2017b). They found that even low salinities of 5 g/L resulted in a lower UCS at all curing times when compared to non-saline CPB due to the salt's effect of increasing the quantity of unfrozen water in the CPB. Wang and Villaescusa (2000) studied the effects of highly saline (>50 g/L) mixing water on cemented tailings fill and found that the UCS was reduced at all curing times when compared to non-saline cemented tailings fill.

Studies have also been conducted on the self-desiccation of CPB under different curing conditions and/or with various compositions, including ordinary CPB (Helinski, et al., 2007; Ghirian and Fall, 2014), CPB with superplasticizer (Haruna and Fall, 2021), CPB with sulphate (Li and Fall, 2016), CPB with sodium silicate (gelfill) (Wang et al., 2016; Abdul-Hussain and

Fall, 2011), CPB with ground blast furnace slag (slag) (Tian and Fall, 2021), and slag-CPB with sulphate (Li and Fall, 2018).

Helinski et al. (2007) developed a model to predict the volume change in CPB due to self-desiccation. Ghirian and Fall (2014) concluded that the coupled thermo-hydro-mechanical processes that occur in CPB during its curing affect its suction development, and there is a strongly coupled behaviour between suction and UCS and UCS and saturated hydraulic conductivity. Haruna and Fall (2021) found that superplasticizers led to a lower electrical conductivity increase in the first day and higher matric suction after 20 days, which contributed to the delayed initial hydration and higher strength later. Li and Fall (2016) found that sulphate inhibited the evolution of self-desiccation in CPB at the early ages and the effect increased with sulphate concentration. Li and Fall (2018) found that low initial sulphate content had an initial negative effect on the strength and self-desiccation of slag CPB but a positive effect after 7 to 28 days of curing, and that high sulphate content had a negative effect at all curing times. Wang et al. (2016) found that an increase in initial temperature led to a more intense and rapid self-desiccation of CPB with sodium silicate, particularly at very early ages, due to the increase in rate of cement hydration and consumption of capillary water. Abdul-Hussain and Fall (2011) used the van Genuchten model to estimate the hydraulic conductivity of gelfill and proposed formulas to predict the model variables. He also found that the unsaturated hydraulic conductivity of gelfill decreases as suction, binder content, or degree of hydration increases. Tian and Fall (2021) found that non-isothermal curing conditions sped up and intensified the self-desiccation of both CPB and slag-CPB and that the effect was stronger in CPB.

Despite the progress made by previous studies in understanding the strength development of saline CPB, none of these studies examined the strength development of saline CPB that

contains slag. Moreover, none of the previous investigations on CPB addressed the self-desiccation of saline CPB. This paper will present the results of investigations into the impacts of mixing water salinity on self-desiccation and strength development of CPB with Portland Cement Type I (PC) and slag binders. Insight into this process could provide valuable information for backfill design and mine operations by allowing the efficient use of available saline groundwater or seawater, reducing the quantity of Portland cement required, and reducing the mining cycle, all of which reduce operational costs.

3.3 Materials and Methodology

3.3.1 Materials and CPB Sample Preparation

Samples were prepared using high purity ground silica from SIL-CO-SIL, general use Portland Cement Type I (PC), tap water, slag supplied by Lafarge Canada, and certified ACS crystalline sodium chloride (NaCl) from Fisher Chemical as required by the mix designs. The high purity ground silica (ST) was used to reduce data errors due to the chemical variations and sulphides in natural tailings, but some mixes were made using natural gold tailings (GT) for comparison. The dry tailings and binder materials were initially mixed separately from the water and salt, and then combined together for a minimum of seven minutes or until thoroughly mixed. A series of mixes was designed to explore the effects due to variations in mixing water salinity when all other components were held constant. Another series of mixes was designed to explore the effects due to variations in binder composition under constant mixing water salinity. The detailed mix design components are given in Table 3.1. The curing temperature for all mixes was about 20°C. The grain size distribution for the ST and GT are given in Figure 3.1. The chemical composition for the PC and slag is given in Table 3.2.

Table 3.1 Mix Design Parameters

Mix Name	Binder Content (%)	W/C Ratio	Tailings Type	% PC in Binder	% Slag in Binder	Mixing Water Salinity (g/L)
CPB-0	4.5	7.4	ST	100	0	0
CPB-10	4.5	7.4	ST	100	0	10
CPB-35	4.5	7.4	ST	100	0	35
CPB-100	4.5	7.4	ST	100	0	100
CPB-300	4.5	7.4	ST	100	0	300
CPB-75PC	4.5	7.4	ST	75	25	35
CPB-50PC	4.5	7.4	ST	50	50	35
CPB-25PC	4.5	7.4	ST	25	75	35
CPB-G-0	4.5	7.4	GT	100	0	0
CPB-G-35	4.5	7.4	GT	100	0	35

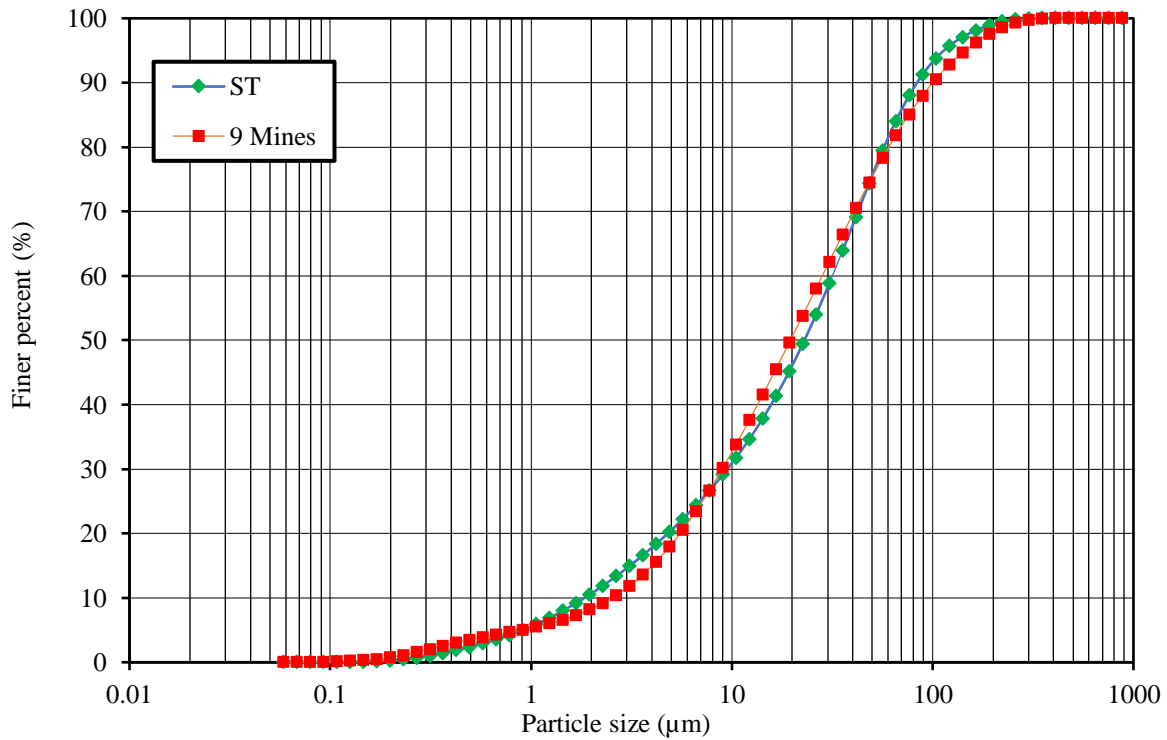


Figure 3.1 Grain size distribution for ST and GT

Table 3.2 Chemical Composition of PC and Slag

Element	PC (%)	Slag (%)
SO ₃	3.82	3.87
Fe ₂ O ₃	2.70	-
Al ₂ O ₃	4.53	9.54
SiO ₂	18.03	34.32
CaO	62.82	41.14
MgO	2.65	10.98
Relative Density	3.2	2.8

3.3.2 UCS Testing

The mechanical strength of each mix was determined using Uniaxial Compressive Strength (UCS) testing according to ASTM C 39. This test is the most commonly used in mine quality control operations as it is cheap and simple to perform (de la Vergne, 2003). Because there is no specific ASTM standard for strength testing of CPB, concrete standards are commonly applied. Cylindrical samples (50mm by 100mm) were cast of each mix and allowed to cure for 1, 3, 7, 28, and 60 days. After curing for the required amount of time, the samples were placed in a UCS testing machine (Digital Tritest 50) and loaded at a rate of 1 mm/min until failure occurred. Strain and load were recorded continuously to create a stress-strain curve and determine the peak or ultimate strength. A minimum of two samples of each mix and curing time were tested and averaged to reduce random errors.

3.3.3 Monitoring Program

A continuous monitoring program was conducted on samples of select mixes for a period of up to 28 days. Matric potential was measured using a TEROS 21 sensor by MeterGroup while volumetric water content (VWC) and electrical conductivity were measured using a TEROS 12 sensor. The TEROS 21 sensor can take measurements of suction from -9 kPa to -100,000 kPa and has an accuracy of $\pm 10\%$ of reading +2 kPa, over the range of -5 kPa to -100 kPa. The TEROS 12 sensor can measure water content in the range of 0-80%, with an accuracy of ± 0.01 from 1% to 40% and ± 0.15 from 40% to 80%. Both sensors were connected to a ZL6 Pro Data Logger, also by MeterGroup, to continuously collect sensor readings over the 28 days. Monitoring was conducted on the following mixes: CPB-0, CPB-35, CPB-100, and CPB-50PC (see Table 3.1).

3.3.4 SEM

Scanning electron microscopy (SEM) was performed on samples of the same mixes as for suction monitoring with a Hitachi S4800 FEG-SEM. Samples of each mix were prepared and allowed to cure for 28 days at room temperature. They were then removed from their molds and placed in an oven at 40°C for a minimum of 4 days to dry completely and stop the cement hydration process. Samples were then reduced in size to thin slivers, injected with an epoxy to control dust production, and fractured to reveal a natural internal surface. They were then coated with a conductive material and examined under SEM at the Electron Microprobe/SEM Laboratory of the University of Ottawa. Secondary and backscatter electron images were taken at a variety of magnifications and the same magnifications were compared between mix designs.

3.3.5 MIP

Mercury intrusion porosimetry (MIP) was performed on the same select mixes as for suction monitoring by using a Micromeritics Auto-Pore 9420 to evaluate the total porosity and pore size distribution of the CPB samples. Samples of each mix were prepared, cured, and dried in the same manner as for SEM. Samples were then reduced in size to cubic pieces approximately 0.5 to 1 cm in dimension.

3.3.6 TG/DTG

Thermogravimetry (TG) was performed on cement pastes of the same mixes as for suction monitoring by using a thermogravimetric analyzer SDT 2960. Samples were prepared and allowed to cure for 28 days at room temperature before being unmolded and dried in an oven at 40°C for at least 4 days to stop cement hydration. Samples were then ground into a fine powder and tested.

3.3.7 XRD

X-Ray Diffraction (XRD) analysis was performed on cement pastes of the same mixes as for suction monitoring using a Scintag XDS 2000 x-ray diffractometer. Samples were prepared and allowed to cure for 28 days at room temperature before being unmolded and dried in an oven at 40°C for at least 4 days to stop cement hydration. Samples were then ground into a fine powder and sent to the X-Ray Core Facility of the University of Ottawa for testing.

3.4 Results and Discussion

3.4.1 Effect of Salt Concentration on the Strength Development and Self-Desiccation of CPB with Portland Cement

The peak strengths for each mix were plotted to determine the trend in strength gain over time for PC-CPB. Figure 3.2 shows the UCS over different curing times for variations in mixing water salinity.

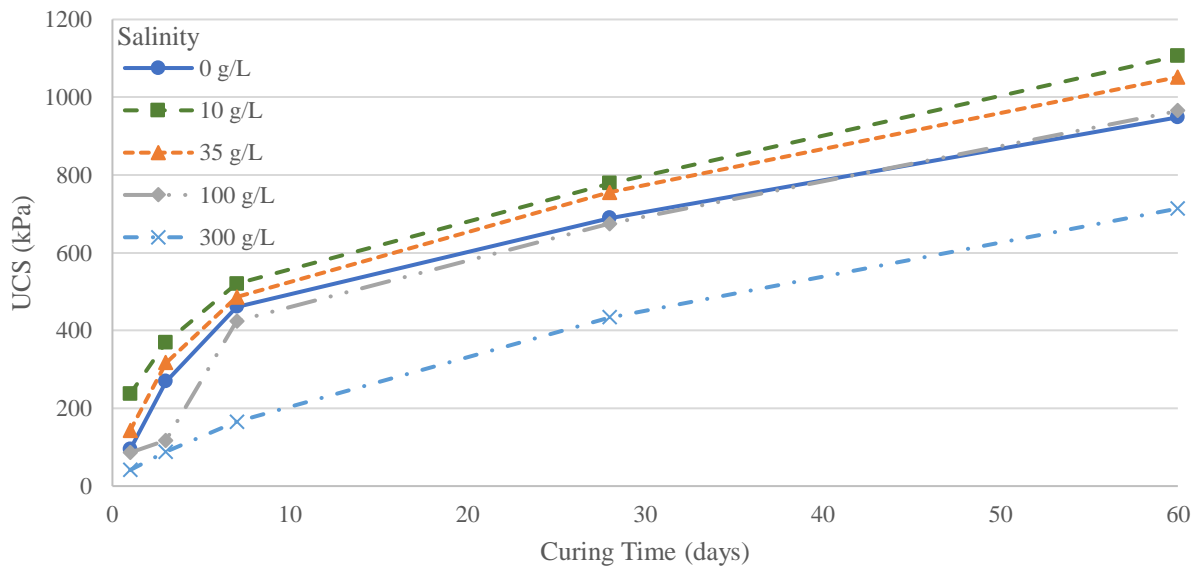


Figure 3.2 Impact of NaCl concentration on UCS of CPB with Portland cement

It is seen that at low mixing water salinities (10 g/L to 35 g/L), the UCS is higher at all curing times than for the control mix with non-saline mixing water. At moderate salinity (100

g/L), the strength is comparable to that of the control over long curing times (28 to 60 days), but weaker at very short curing times (up to approximately 7 days). At high mixing water salinity (300 g/L), the strength is significantly reduced over all curing times when compared against the control mix. The overall trend is $10 \text{ g/L} > 35 \text{ g/L} > 0 \text{ g/L} > 100 \text{ g/L} > 300 \text{ g/L}$.

MIP results are given in Figure 3.3 and Figure 3.4. They indicate that the 100 g/L sample has the highest total porosity, while the non-saline sample has the lowest total porosity. Generally, a lower total porosity would indicate a higher UCS of the porous medium (Poon, Wong, and Lam, 1997; Li and Aubertin, 2003; Neville, 2011; Roessler and Odler, 1985), but the 0 g/L and 100g/L samples have very similar UCS at 28 days. Meanwhile, the 35 g/L sample has a total porosity that is between the others and a higher UCS. This could be explained by several factors. It is possible that the pore structure may be impacted by the mercury intrusion process, as was proposed by Feldman and Beaudoin (1991) and Cook and Hover (1999). They proposed that the pressure from the mercury intrusion process could break the pore walls, making larger pores out of smaller pores and thereby increasing the threshold diameter. However, this is not always the case, as was shown by Ouellet et al. (2007) and Shi and Winslow (1985). Another possibility is the precipitation of secondary minerals in the pore structure, which could contribute to the UCS but be expelled during the MIP process and not appear in the results (Ouellet et al. 2007). A third possibility is that the results were impacted by any number of the MIP test inaccuracies, such as lost porosity or the “neck-bottle” effect, that are elaborated in Beaudoin and Marchland (2001, Ch 14). Finally, it is possible that another property of the CPB outweighs the negative effects of high total porosity or threshold diameters in terms of strength contribution.

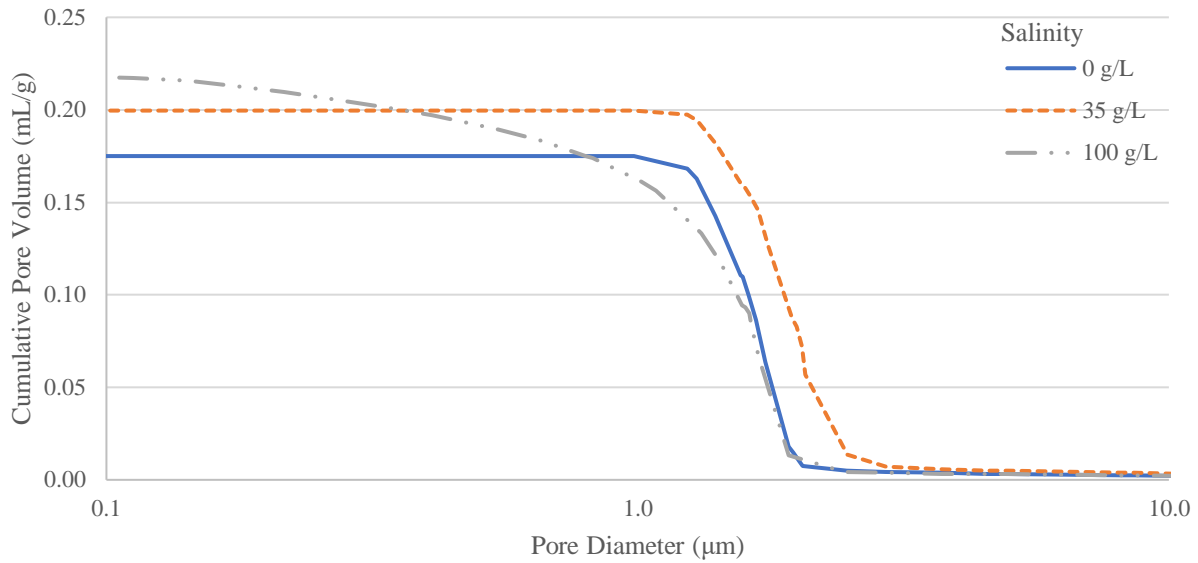


Figure 3.3 Impact of NaCl concentration on total pore volume after 28 days of curing

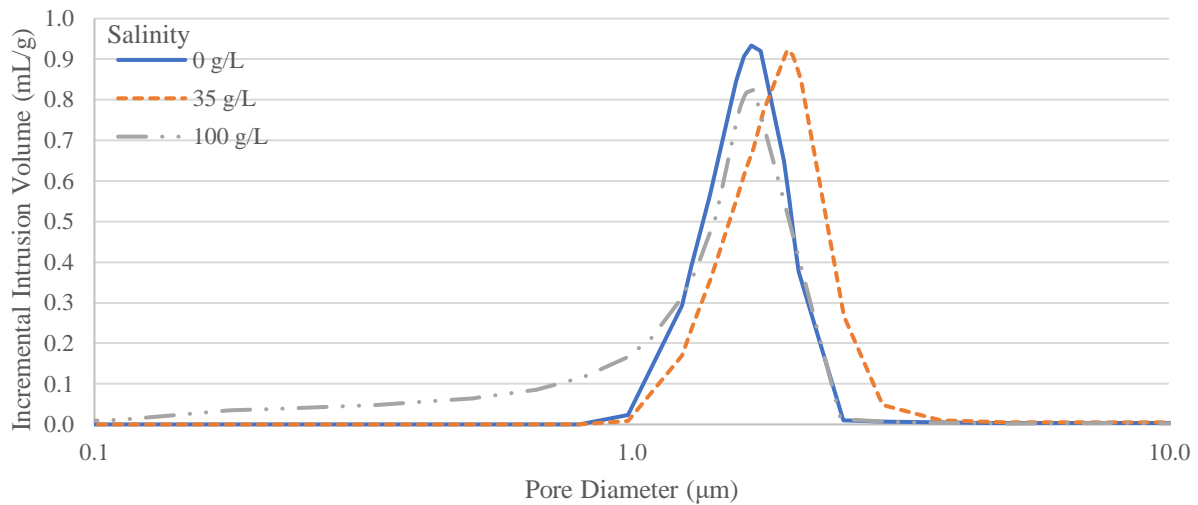


Figure 3.4 Impact of NaCl concentration on pore size distribution after 28 days of curing

It is well known that cement hydration reactions consume water (self-desiccation) and lead to a reduction in excess pore water pressure (Helinski et al., 2007; Persson, 2000) as well as an increase in strength (Bullard et al., 2011; Taylor, 1997). Therefore, the decrease in water content may be taken as an indication of the occurrence of hydration reactions (Simon,

Grabinsky, 2012). Previous studies have shown that salt impacts the rate of hydration reaction (Chen et al., 2020; Zhou et al., 1996).

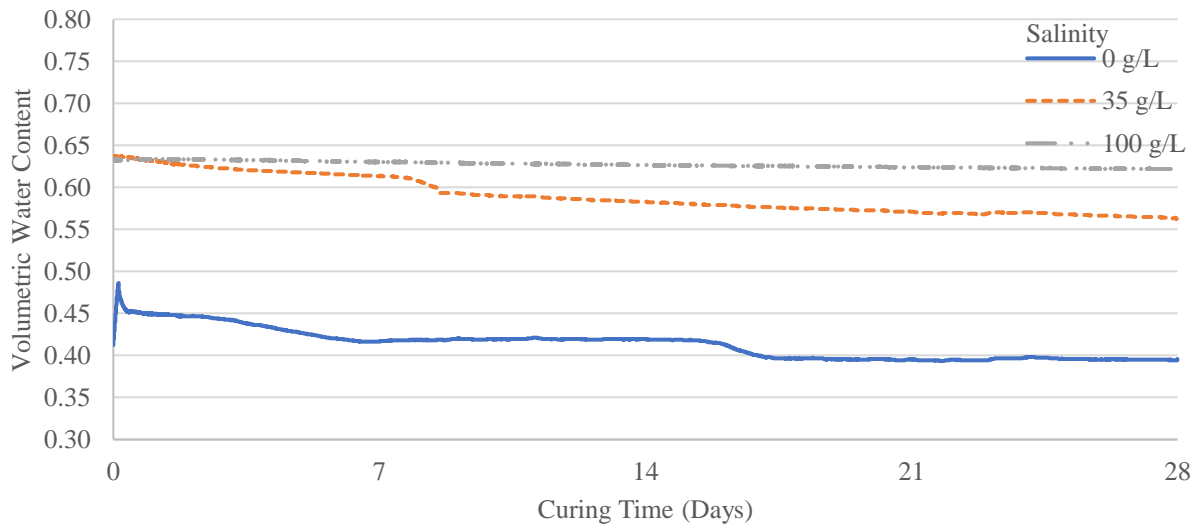


Figure 3.5 Impact of NaCl concentration on water content over first 28 days of curing

Water content monitoring results are presented in Figure 3.5. They indicate that the non-saline sample has the lowest water content throughout the curing process and that the two saline samples initially have similar contents but the 100 g/L sample decreases far less than either of the other two samples. The non-saline sample initially experiences a spike in water content and a delay before steadily decreasing, unlike the 35 g/L sample which immediately begins steadily decreasing.

Therefore, it can be seen from Figure 3.5 that a salt concentration of 100 g/L significantly suppresses and delays cement hydration (thus, it inhibits the self-desiccation), while a concentration of 35 g/L slightly accelerates it at the early stage.

Suction monitoring results, which also reflect the self-desiccation of the CPB samples, are presented in Figure 3.6.

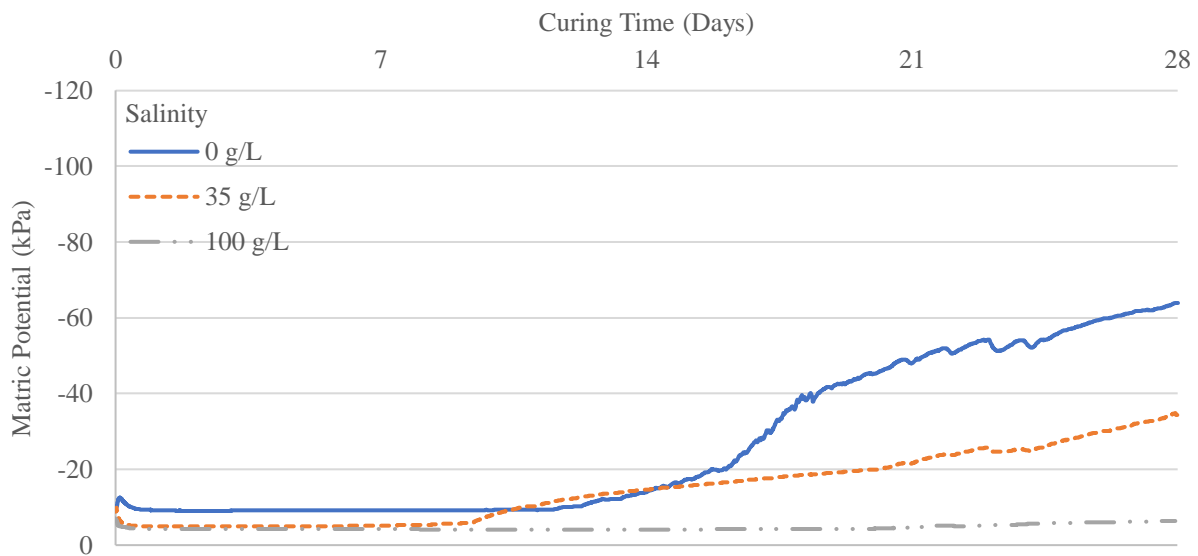


Figure 3.6 Impact of NaCl concentration on suction over first 28 days of curing

It can be seen that for all curing times, the 100 g/L sample has the lowest suction and it remains low and fairly constant throughout the 28-day monitoring period. In other words, this high salt concentration (100 g/L) significantly inhibits the self-desiccation capacity of the CPB. This finding is consistent with the results of the water content monitoring discussed above. For most curing times, the 35 g/L sample has the next highest suction and begins to increase after about 8 days of curing. The non-saline sample has the highest suction overall, but because it only begins to increase after about 11 days, it is briefly lower than the suction of the 35 g/L sample. The earlier increase in suction of the 35 g/L sample compared to the non-saline sample would suggest that this low salt concentration (35 g/L) slightly accelerates cement hydration in the early stage. However, the non-saline sample undergoes a much larger and faster increase in suction, so it quickly and significantly overtakes the 35 g/L sample.

Taken with the pore structure information provided by the MIP results, it can be surmised that the high suction experienced by the non-saline sample, as compared to the low salinity sample, is a result of its finer pore structure, lower overall porosity, and lower water content. The

100 g/L sample, though it had a similar pore size to the non-saline sample, experienced much less suction due to its higher water content or higher total porosity (Fredlund and Rahardjo, 1993).

It can then be concluded that matric suction is not primarily responsible for the higher UCS of the low salinity sample as compared to the non-saline sample.

XRD results are presented below in Figure 3.7 through Figure 3.9. They indicate that the non-saline sample had no Friedel’s salt, while the 35 g/L sample had a notable quantity and the 100 g/L sample had a significant quantity. Each sample has approximately similar quantities of CH over various peaks, but the 35 g/L sample has significantly more calcite than the other two samples.

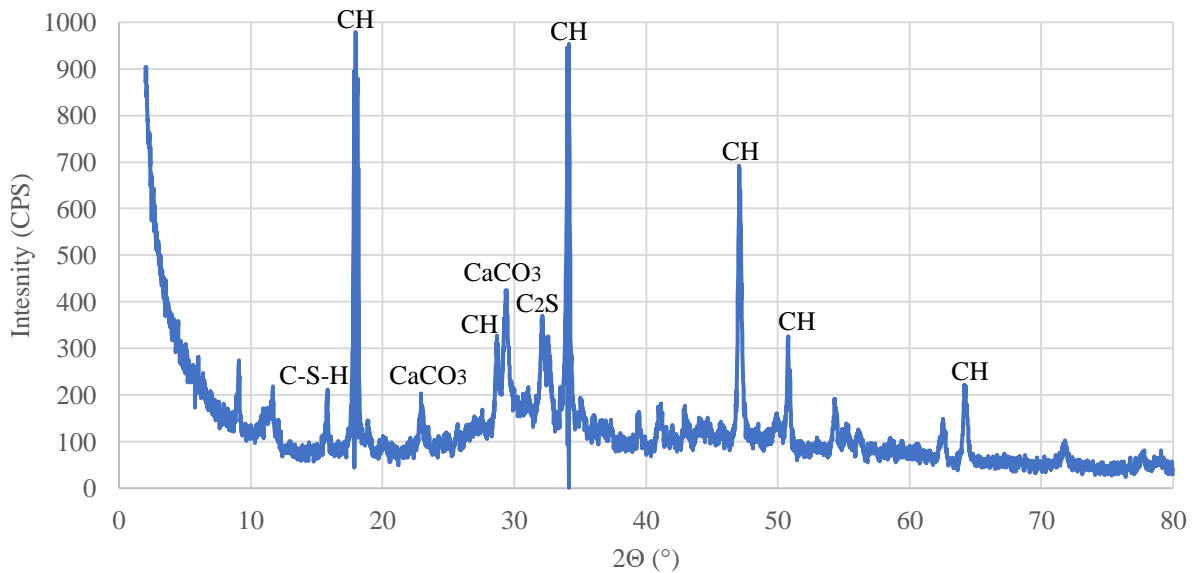


Figure 3.7 XRD results for non-saline CPB after 28 days of curing

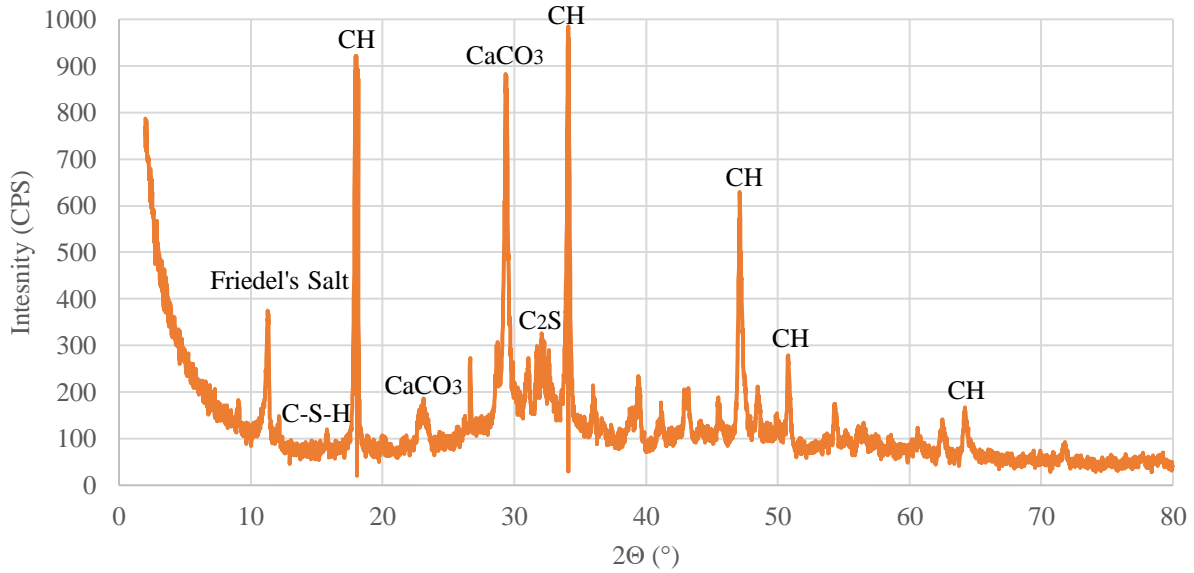


Figure 3.8 XRD results for CPB with 35 g/L NaCl after 28 days of curing

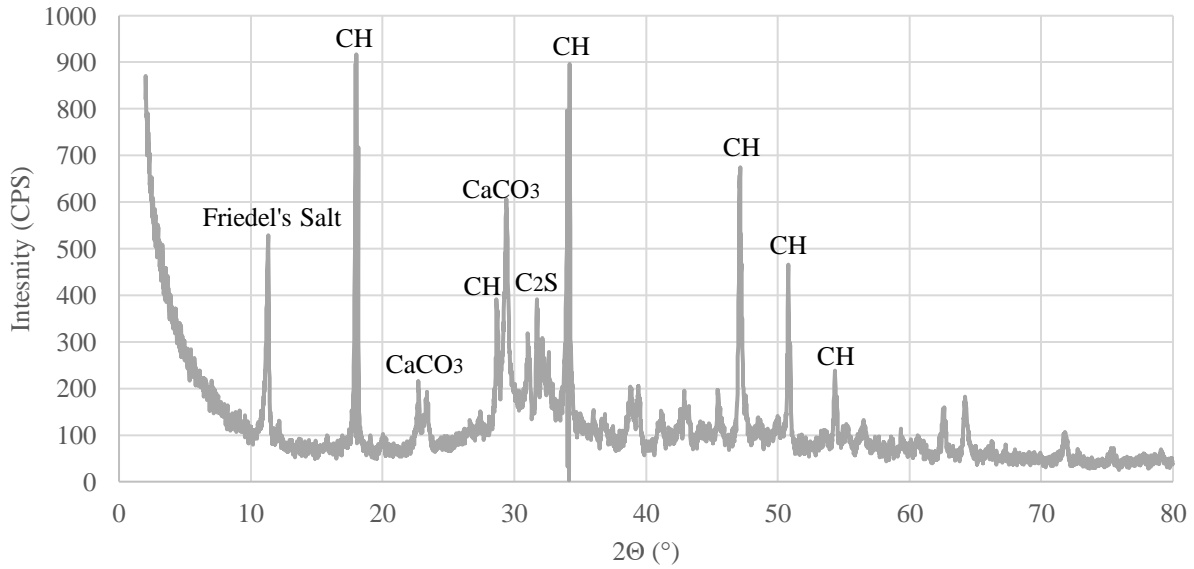
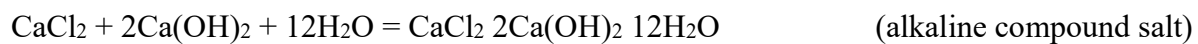
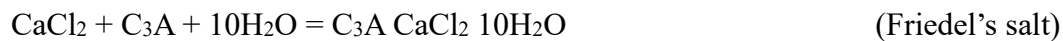


Figure 3.9 XRD results for CPB with 100 g/L NaCl after 28 days of curing

In the non-saline sample, ettringite is formed by the reaction of the C_3A with gypsum in a mechanism meant to prevent flash setting of the cement (Taylor, 1997). Ettringite can also be formed by the reaction of monosulphate and $CaCO_3$ when in the presence of CH (Taylor, 1997),

which explains why the non-saline sample had low amounts of CaCO₃. Ettringite also consumes more water than Friedel's salt, which explains the lower water content of the non-saline sample.

In the saline samples, the NaCl reacts with CH to form CaCl₂, which competes with the ettringite over C₃A to form Friedel's Salt and which also consumes CH to produce an alkaline compound salt (Chen et al., 2020). Thus, the presence of NaCl hinders the formation of ettringite, which accelerates hydration.



These processes leave a high concentration of Na⁺ in the pore water which can lead to weakening of the cement due to the high alkalinity (Shehata, Thomas, 2010; Wang et al., 2020). However, Na⁺ ions can displace some Ca²⁺ ions in the C-S-H and this is thought to cause a slight increase in UCS (Yaphary et al., 2020), though further research is still needed. Na⁺ can also react with calcite and cause a shift in the pore water ion concentration from Na⁺ to Ca²⁺ (Ishikawa and Ichikuni, 1984) which, by a mechanism described by Young et al. (1977), can slow the dissolution of C₂S. Eventually, the Ca²⁺ precipitates out of the solution in the two salts and the pore solution concentration changes again.

Clearly, there are many interconnected reactions and balances in this system, which are difficult to pinpoint with the tests performed in this study. Yet, it can be seen from the XRD results (Figure 3.7, Figure 3.8, and Figure 3.9) that the high salinity sample experienced a very high level of salt formation and an absence of ettringite. These factors explain the high water

content and low NaCl and CaCO₃ contents. Additionally, the excessive quantity of NaCl severely slowed the hydration of the 100 g/L sample (Chen et al., 2020; Wang et al., 2020). The high water content and slow hydration rate resulted in lower strength of the CPB. Minimal strength gains from Na⁺ absorption into the C-S-H were also mitigated by strength losses due to the high pore water alkalinity and consumption of CH by salt formation processes.

In the 35 g/L sample, the CaCO₃ remained mostly inert (Taylor, 1997) while the NaCl partially reacted to form Friedel's salt. It appears that the low salinity allowed for the benefits of accelerated hydration without causing excessive negative effects such as significant CH consumption and alkaline pore water. Additionally, Friedel's salt is less expansive than ettringite (Chen et al., 2020) and so is less likely to damage the microstructure of the hardening CPB. When it takes up pore space, it can contribute to the UCS of the porous material, though an excessive quantity could still damage the microstructure (Chen et al., 2020).

SEM results are presented in Figure 3.10 through Figure 3.12. They show that the high salinity (100 g/L) sample contained a large quantity of precipitated salts and less hydration products, while the low salinity (35 g/L) sample had a combination of hydration products and precipitated salts which resulted in less visible pore space, and the non-saline sample contained a more even distribution of hydration products and empty pores. These results validate the earlier consideration that a low amount of salt formation can provide structural benefits and an increase in UCS by filling pore spaces without excessively harming the hydration products. These results are consistent with the findings of Wang et al. (2020) that there exists an optimal salt concentration that results in the densest microstructure.

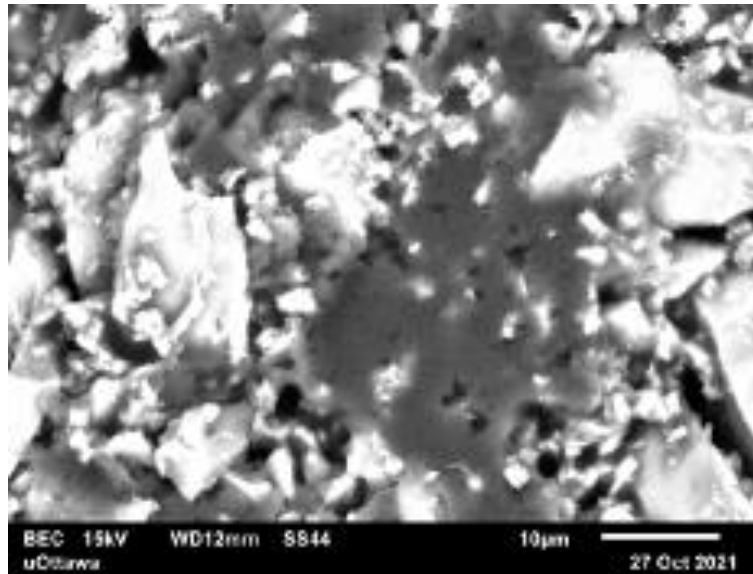


Figure 3.10 SEM image of CPB with 35 g/L NaCl after 28 days of curing

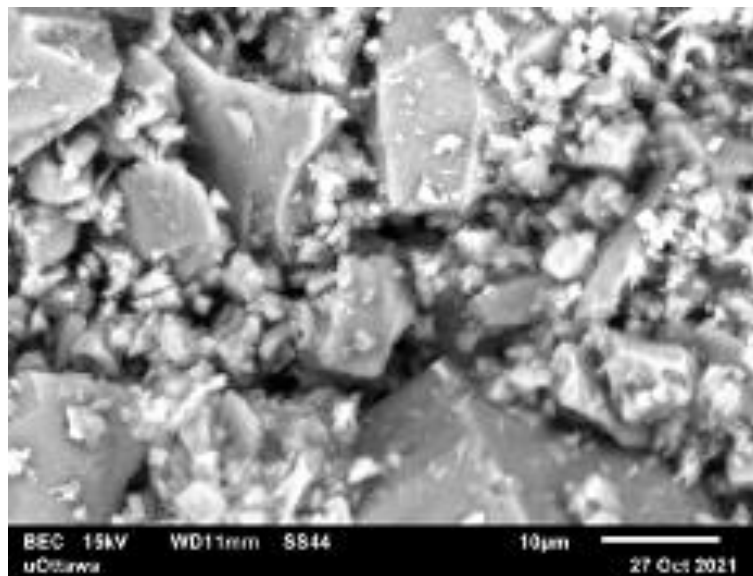


Figure 3.11 SEM image of CPB with 100 g/L NaCl after 28 days of curing

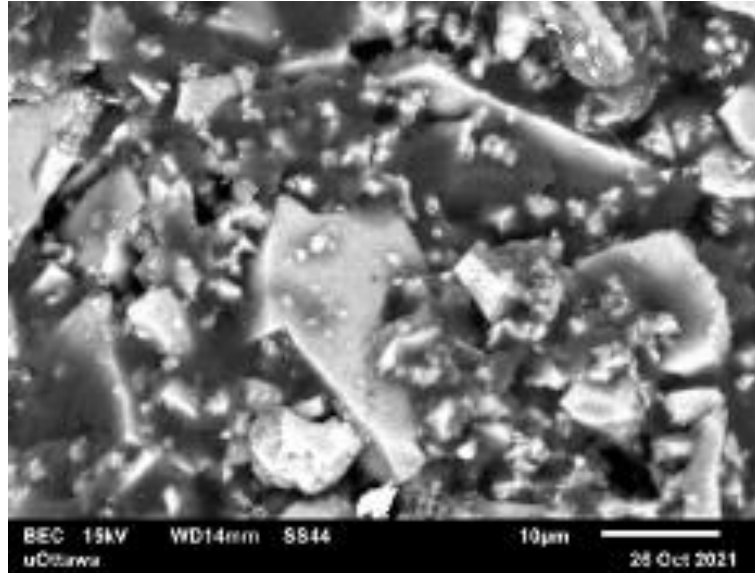


Figure 3.12 SEM image of non-saline CPB after 28 days of curing

UCS data in Figure 3.13 shows that CPB mixed with natural gold tailings exhibits similar behaviour to CPB mixed with manufactured silica tailings: low mixing water salinity (35 g/L) has higher UCS at most curing times than the control sample.

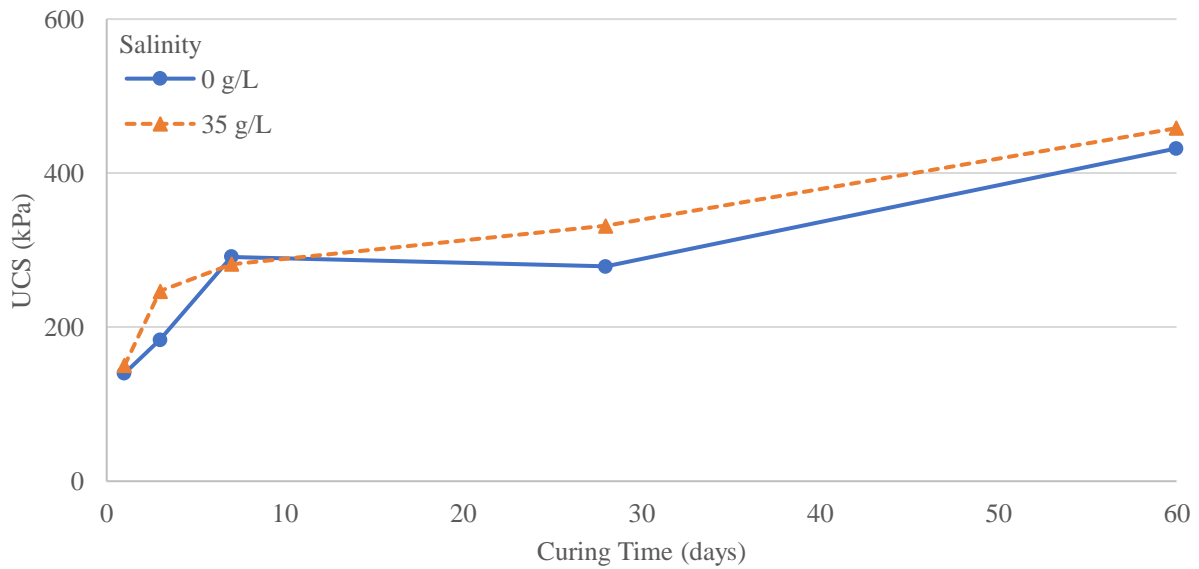


Figure 3.13 Impact of NaCl concentration on UCS of CPB made with GT

3.4.2 Effect of Binder Type on the Strength Development of Saline CPB

Separately, the peak strengths for the mixes with constant salinity and variations in slag content were also plotted over curing time to determine the effects of slag replacement on strength gain. The results are shown in Figure 3.14. Note that the control mix in this case is the 35 g/L salinity mix shown in Figure 3.2.

It can be seen that slag makes no significant difference in very early strength gain (up to 1 day). For short cure times (between 1 day and 1-2 weeks), a very high slag replacement of 75% yields the highest strength gain, with other mixes showing little strength differentiation. At longer cure times, a 50% replacement of PC with slag results in the greatest strength gain, followed by 75% replacement (75% slag and 25% PC), then 25% replacement (25% slag, 75% PC), then no replacement (100% PC).

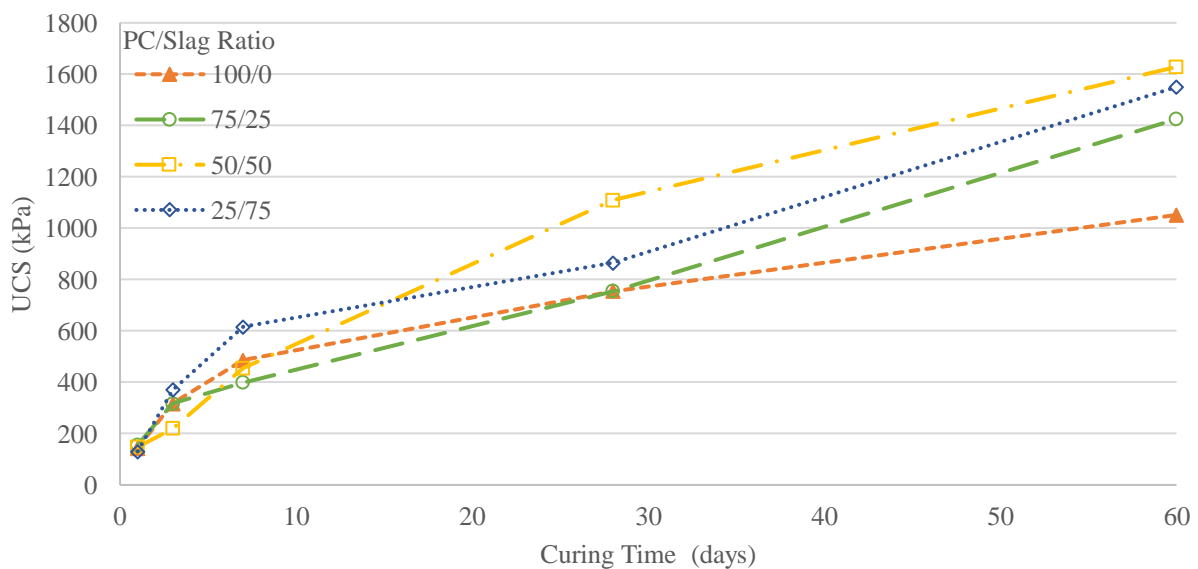


Figure 3.14 Impact of slag replacement on UCS of saline CPB (NaCl content: 35 g/L)

Taylor (1997) states that slag reacts more slowly than alite, and therefore that slag cements gain strength more slowly than pure PC cements, in proportion to their slag contents.

However, the UCS data shown clearly indicates that in the presence of NaCl, the opposite is true. The highest slag content mixes gained strength most quickly and remained strong.

MIP results for the slag-CPBs are presented in Figure 3.15 and Figure 3.16.

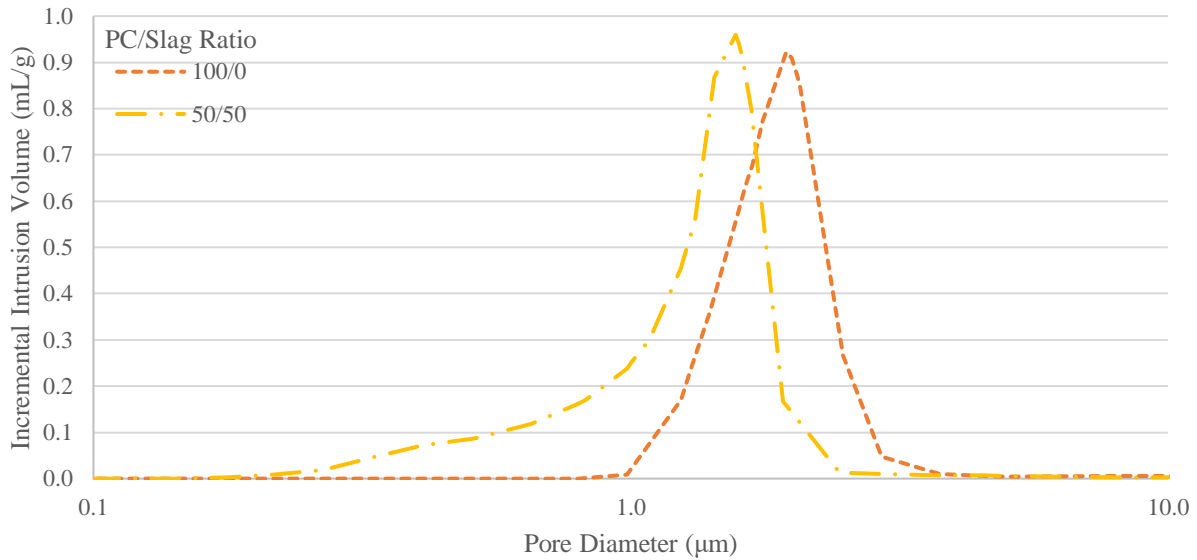


Figure 3.15 Impact of slag replacement on pore size distribution after 28 days of curing

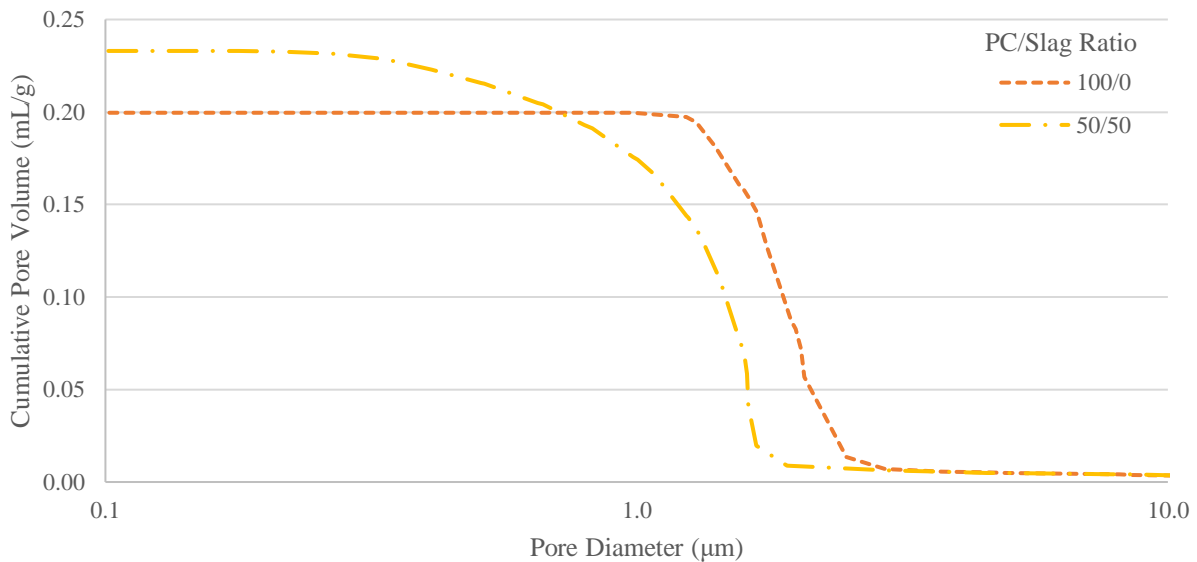


Figure 3.16 Impact of slag replacement on total pore volume after 28 days of curing

They indicate that the 50% slag replacement mix had a smaller threshold diameter, finer pore structure, and higher total porosity than the pure Portland cement mix. These results are

consistent with those in previous studies on seawater and alkali-activated slag paste (Kang and Kim, 2019). The fine pore structure could have contributed to the higher UCS observed in the slag mix as compared to the non-slag mix. Small pores may contribute to a higher total porosity, but not be detrimental to the UCS (O’Farrell et al., 2001).

Water content monitoring data is presented in Figure 3.17. It shows that the slag mix initially had a slightly higher water content than the PC mix, but that it quickly dropped after about 2 days of curing and remained lower throughout the monitoring period. This indicates more intense self-desiccation in the saline CPB with slag than in that with PC only. The PC mix took about 8 days before dropping noticeably. Otherwise, both mixes maintained similar water consumption rates and levels.

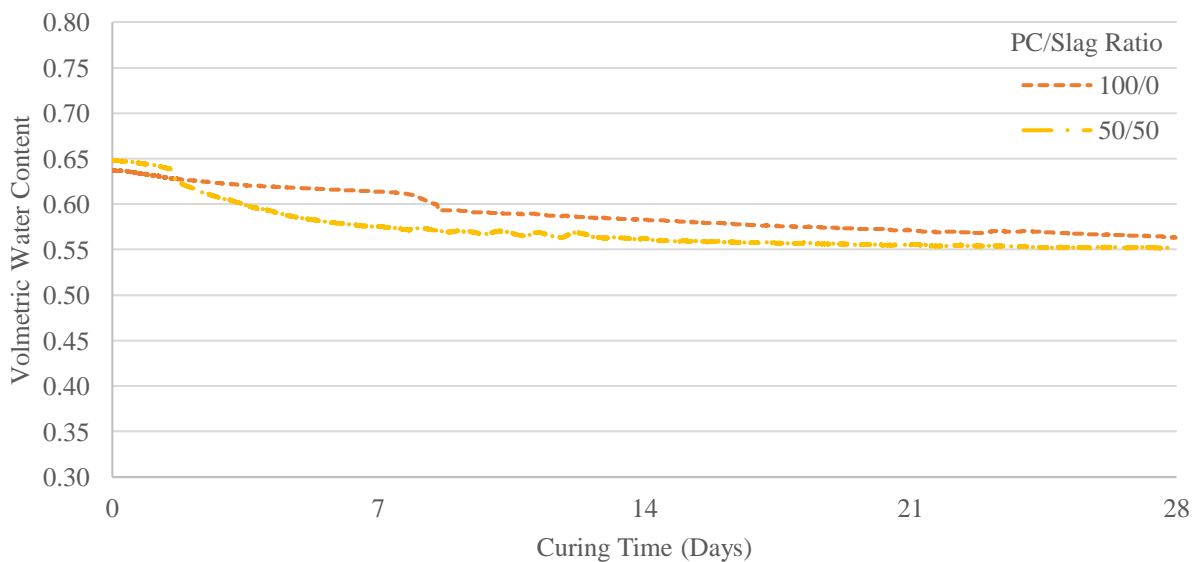


Figure 3.17 Impact of slag replacement on water content over first 28 days of curing

Suction monitoring data, shown in Figure 3.18, indicates that there is little difference in suction between PC mix and 50% slag mix up until about 4 days. After this point, the suction of the 50% slag mix begins to increase, while the PC mix remains constant. After about 10 days, suction in the slag mix begins to increase dramatically while the PC mix increases only slightly.

Simultaneous temperature monitoring indicates that the room temperature experienced significant fluctuations due to climate control issues during the monitoring of the slag mix. This is reflected in the suction data for the slag mix, and is consistent with Helinski et al. (2007) who indicated that pore pressure fluctuations are temperature sensitive. The trend resumed once external temperatures stabilized so the data is still considered reliable.

Given that water content levels were similar throughout the monitoring period, it can be concluded that the high suction levels experienced by the slag mix were primarily due to a finer pore structure (Fredlund and Rahardjo, 1993). Thus, it is likely that both the fine pore structure and the high suction contributed to the considerably higher UCS of the 50% slag mix over the PC mix.

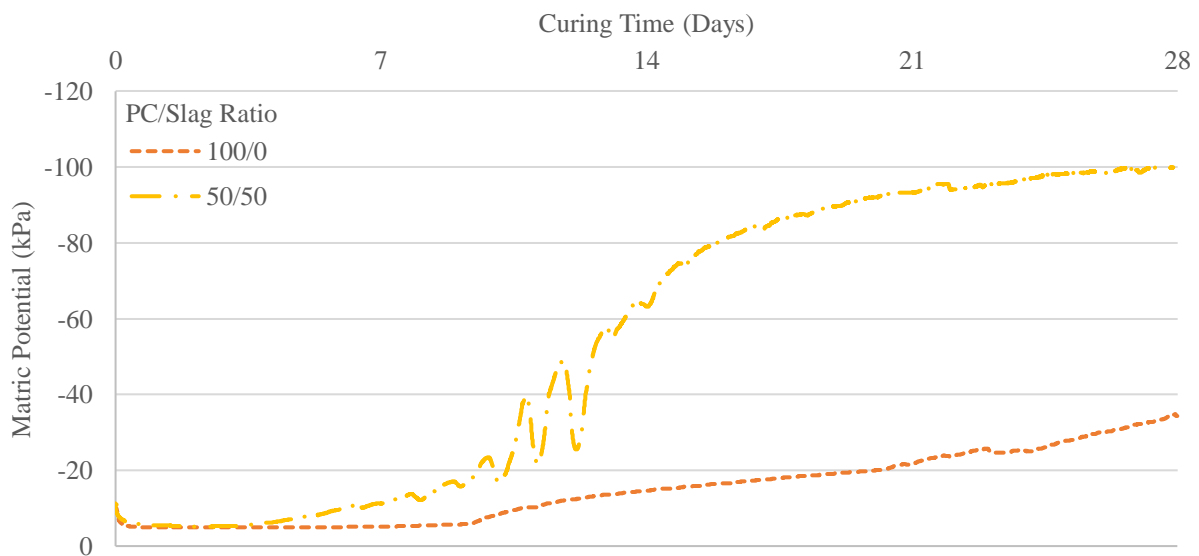


Figure 3.18 Impact of slag replacement on suction over first 28 days of curing

XRD results for the slag mix are presented in Figure 3.19. They indicate that the slag mix had considerably less CH than the non-slag mix (repeated in Figure 3.20). This is due to the CH reacting with the slag to form other hydrates (such as secondary C-S-H) and is well established in the literature (Taylor, 1997; Mehta and Monteiro, 2006). C-S-H is difficult to detect with the

testing methods used in this study, but it would have contributed significantly to the strength of the slag mixes, as it is the main binding phase in cemented materials. Additionally, slightly higher levels of Friedel's salt are observed in the slag mix when compared to the PC mix.

Finally, the slag mix contains less CaCO_3 than the PC mix.

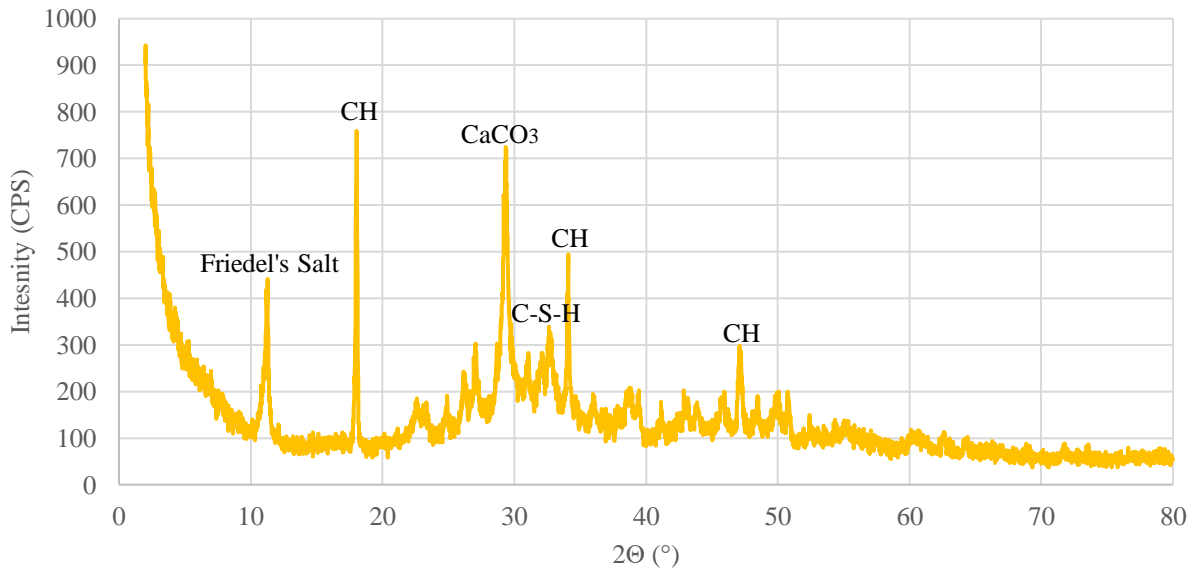


Figure 3.19 XRD results for saline CPB with 50% slag replacement after 28 days of curing

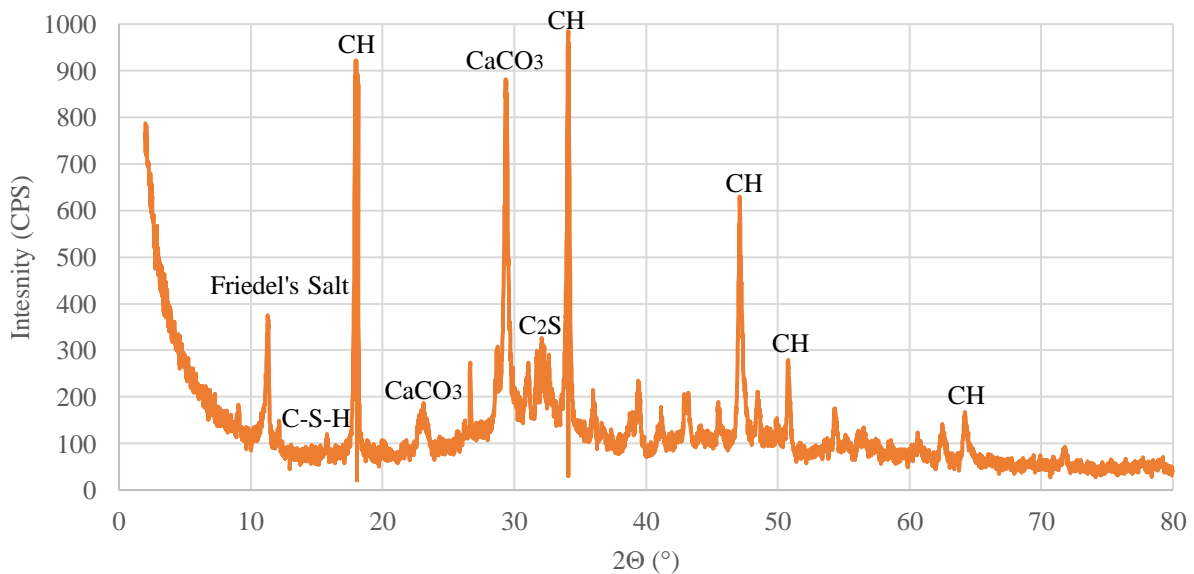


Figure 3.20 XRD results for saline CPB with 100% PC after 28 days of curing (Figure 3.8)

TG/DTG results are presented in Figure 3.21. They are consistent with the XRD results in that they show the slag mix has a lower quantity of CH and a higher quantity of Friedel’s salt than the PC mix. Additionally, they also show that the slag mix has no remaining NaCl.

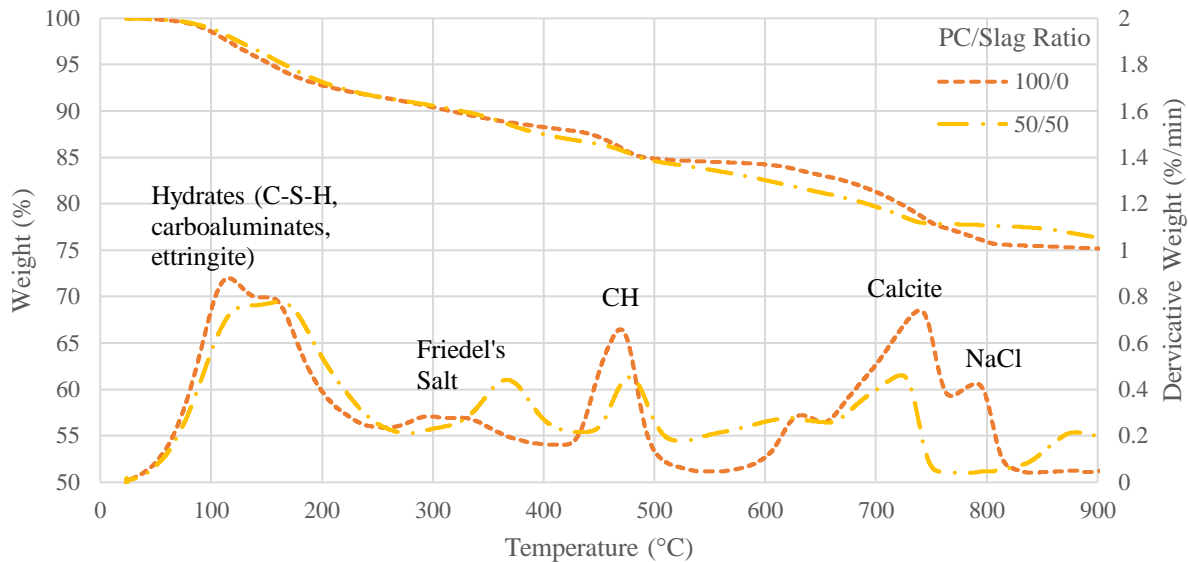


Figure 3.21 TG/DTG results for saline CPB with 100% PC and 50% slag replacement after 28 days of curing

Several factors contribute to the slag mix being stronger than the PC mix. At early ages (1 day to 2 weeks), the 75% slag mix had the highest strength, which may be attributed to the effects of slag’s generally finer particle size than PC. First, this allows the slag to fill spaces between PC and silica particles and increase the strength of the mix in spite of the low progression of hydration. Second, a finer particle size distribution also has a greater surface area which can increase the rate of hydration by providing additional sites for hydration products to nucleate, which is known as the filler effect (Oey et al., 2013). At later ages (after 2 weeks), the 50% slag mix has the highest strength, which is likely due to the reasons discussed above, as shown by the supplemental testing results. Additionally, it appears that NaCl has an accelerating effect on the hydration of slag for all curing times, and that the generally negative effects of NaCl are mitigated by the additional use of slag. Slag requires high alkalinity to activate (Taylor,

1997; Shehata and Thomas, 2010), which is initiated by the cement pore water. The presence of Na^+ ions increases the alkalinity of the pore water (Zhu et al., 2012), which accelerates the hydration of the slag as shown in the UCS and water content monitoring data. The consumption of Cl^- ions in precipitated salts and the absorption of Na^+ ions in C-S-H would also explain the lack of remaining NaCl in the TG/DTG results. A higher quantity of reacted NaCl would explain the higher quantity of Friedel's salt in the slag sample than in the PC sample, which would also explain the slightly lower water content in the slag mix. The precipitated Friedel's salt could have contributed to the UCS in the same manner that NaCl did for the PC sample. The greater content of the Friedel's salt is accommodated by the higher total porosity of the slag. It can be noted that the quantity of Friedel's salt in the slag mix is not as high as what was seen in the 100 g/L PC mix, and the slag mix has a higher total porosity, so it is possible that the quantities of Friedel's salt were not structurally problematic as they were for the 100 g/L sample. The lower levels of CaCO_3 are likely explained by magnesium from the slag reacting with the calcite to form a hydrotalcite-type phase (Taylor, 1997). Both this and the salts would have required the consumption of CH, reducing their levels in the slag samples as observed in the XRD and TG/DTG results. It appears that until 2 weeks of curing, the 75% slag mix was stronger than the 50% mix because the greater quantity of fine particles contributed to the strength more than the generally low hydration activity in both mixes. However, after 2 weeks, the mix with more PC experienced more hydration and this contributed more to the strength of the 50% mix than the fine particles did in the 75% mix.

SEM imaging (Figure 3.22) also indicate that the 50% slag replacement mix had more hydration product, smaller pores, and more Friedel's salt than the control. This supports the conclusions described in the previous paragraph.

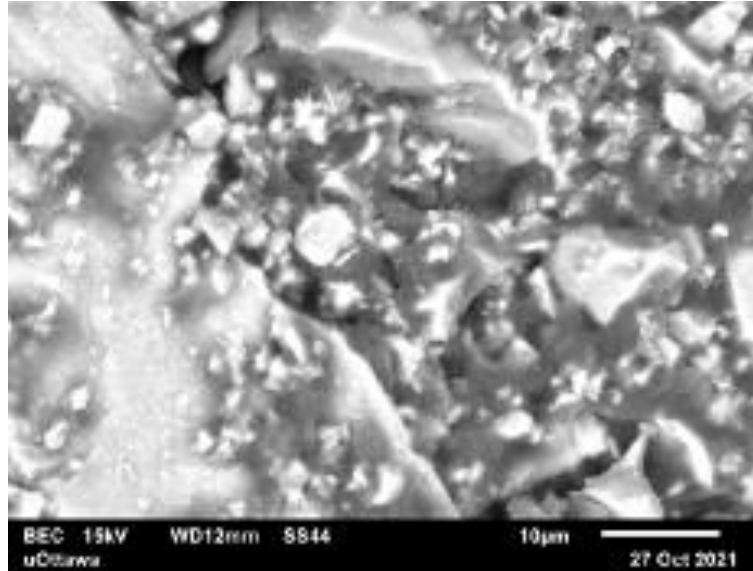


Figure 3.22 SEM image of saline CPB with 50% slag replacement after 28 days of curing

3.5 Summary and Conclusions

UCS testing, monitoring experiments (suction, volumetric water content), and microstructural analysis/testing were conducted on CPB with PC and a mixing water NaCl concentration from 0 g/L to 300 g/L in order to better gain an insight into the effect of mixing water salinity on the strength and self-desiccation of CPBs and the mechanisms responsible for the salinity-induced difference in behavior.

Results indicate that regardless of the type of binder and tailings used, 10 g/L and 35 g/L saline concentration lead to an increase in UCS over all curing times up to 60 days and a slight increase in the rate of self-desiccation at the early ages, when compared to the non-saline control mix. However, salinity of greater than 100 g/L leads to a reduction in UCS. Support testing indicates that suction may play a moderate role in the increase of UCS for low-salinity CPB, in addition to the presence of Friedel's salt in the pores. High mixing water salinity is detrimental to the speed of hydration and UCS.

UCS testing on CPB with 35 g/L NaCl concentration and slag replacement content of 25% to 75% indicates that high slag replacement in combination with low mixing water salinity leads to significant UCS gains over most curing times up to 60 days and accelerated hydration. High matric suction is developed and this likely moderately contributes to the increase in UCS, in addition to the contribution of precipitated Friedel's salt in the pores.

3.6 References

Abdul-Hussain, N. (2011). *Experimental study on the engineering properties of gelfill*. [MASC thesis, Ottawa, ON: University of Ottawa.] <http://dx.doi.org/10.20381/ruor-4482>

Abdul-Hussain, N. and Fall, M. (2011). Unsaturated hydraulic properties of cemented tailings backfill that contains sodium silicate. *Engineering geology*, 123(4), 288-301.
<https://doi.org/10.1016/j.enggeo.2011.07.011>

Beaudoin, J. J., and Marchand, J. (2001). Pore structure, in Ramachandran, V.S. and Beaudoin, J.J. (eds.) *Handbook of analytical techniques in concrete science and technology: Principles, techniques and applications*. William Andrew Inc.

Belem, T., Benzaazoua, M., and Bussiere, B. (2000). Mechanical behaviour of cemented paste backfill. In *Proc. of 53rd Canadian Geotechnical Conference, Montreal*, 373-380.

Benzaazoua, M., Fall, M., and Belem, T. (2004). A contribution to understanding the hardening process of cemented pastefill. *Min. Eng.*, 17 (2): 141-152.
<https://doi.org/10.1016/j.mineng.2003.10.022>

Beya, F. K., Mbonimpa, M., Belem, T., Benzaazoua, M., Kalonji, K. and Ouellet, S. (2015). Preliminary study of the influence of temperature and salinity on the thermal properties of hardening cemented paste backfill. In *Proceedings of the 68th Canadian Geotechnical Conference and 7th Canadian Permafrost Conference, Quebec, QC, Canada*. 20-23.

- Bullard, J.W., Jennings, H.M., Livingston, R.A., Nonat, A., Scherer, G.W., Schweitzer, J.S., Scrivener, K.L. and Thomas, J.J. (2011). Mechanisms of cement hydration. *Cement and concrete research*, 41(12), 1208-1223. <https://doi.org/10.1016/j.cemconres.2010.09.011>
- Chen, S., Du, Z., Zhang, Z., Zhang, H., Xia, Z. and Feng, F. (2020). Effects of chloride on the early mechanical properties and microstructure of gangue-cemented paste backfill. *Const. and Build. Mat.*, 235, p.117504. <https://doi.org/10.1016/j.conbuildmat.2019.117504>
- Cook, R.A. and Hover, K.C. (1999). Mercury porosimetry of hardened cement pastes. *Cement and Concrete research*, 29(6), 933-943. [https://doi.org/10.1016/S0008-8846\(99\)00083-6](https://doi.org/10.1016/S0008-8846(99)00083-6)
- de la Vergne, J. N. (2003). *Hard rock miner's handbook* (3rd ed.) McIntosh Engineering.
- Fall, M. and Benzaazoua, M. (2005). Modeling the effect of sulphate on strength development of paste backfill and binder mixture optimization. *Cem. and Conc. Res.* 35(2), 301-314. <https://doi.org/10.1016/j.cemconres.2004.05.020>
- Fall, M., Célestin, J.C., Pokharel, M. and Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, 114(3-4), 397-413. <https://doi.org/10.1016/j.enggeo.2010.05.016>
- Feldman, R.F. and Beaudoin, J.J. (1991). Pretreatment of hardened hydrated cement pastes for mercury intrusion measurements. *Cement and concrete research*, 21(2-3), 297-308. [https://doi.org/10.1016/0008-8846\(91\)90011-6](https://doi.org/10.1016/0008-8846(91)90011-6)
- Fredlund, D.G. and Rahardjo, H. (1993). *Soil mechanics for unsaturated soils*. John Wiley & Sons.

- Ghada, A. A. (2019). *Temperature dependency of the rheological properties and strength of cemented paste backfill that contains sodium silicate* [MAsc thesis, Ottawa, ON: University of Ottawa]. <http://dx.doi.org/10.20381/ruor-26207>
- Ghirian, A. and Fall, M. (2014). Coupled thermo-hydro-mechanical–chemical behaviour of cemented paste backfill in column experiments: Part II: Mechanical, chemical and microstructural processes and characteristics. *Engineering Geology.*, 170, 11-23. <https://doi.org/10.1016/j.enggeo.2013.12.004>
- Haruna, S. and Fall, M. (2021). Strength development of cemented tailings materials containing polycarboxylate ether-based superplasticizer: Experimental results on the effect of time and temperature.” *Canadian Journal of Civil Engineering*, 48(4), 429-442. <https://doi.org/10.1139/cjce-2019-0809>
- Helinski, M., Fourie, A., Fahey, M. and Ismail, M. (2007). Assessment of the self-desiccation process in cemented mine backfills. *Canadian Geotechnical Journal*, 44(10), 1148-1156. <https://doi.org/10.1139/T07-051>
- Hivon, E.G. and Sego, D.C. (1993). Distribution of saline permafrost in the Northwest Territories, Canada. *Canadian Geotechnical Journal*, 30(3), 506-514. <https://doi.org/10.1139/t93-043>
- Ishikawa, M. and Ichikuni, M. (1984). Uptake of sodium and potassium by calcite. *Chemical geology*, 42(1-4), 137-146. [https://doi.org/10.1016/0009-2541\(84\)90010-X](https://doi.org/10.1016/0009-2541(84)90010-X)
- Jiang, H. and Fall, M. (2017a). Yield stress and strength of saline cemented tailings in sub-zero environments: Portland cement paste backfill. *Int. Journ. of Min. Proc.* 160, 68-75. <https://doi.org/10.1016/j.minpro.2017.01.010>

- Jiang, H. and Fall, M. (2017b). Yield stress and strength of saline cemented tailings materials in sub-zero environments: Slag-paste backfill. *Journ. of Sust. Cement-Based Mat.* 6(5), 314-331. <https://doi.org/10.1080/21650373.2017.1280428>
- Kang, C. and Kim, T. (2020). Pore and strength characteristics of alkali-activated slag paste with seawater. *Magazine of Concrete Research*, 72(10), 499-508.
<https://doi.org/10.1680/jmacr.18.00390>
- Li, L. and Aubertin, M. (2003). A general relationship between porosity and uniaxial strength of engineering materials. *Canadian Journal of Civil Engineering*, 30(4), 644-658.
<https://doi.org/10.1139/103-012>
- Li, W. and Fall, M. (2016). Sulphate effect on the early age strength and self-desiccation of cemented paste backfill. *Construction and Building Materials*, 106, 296-304.
<https://doi.org/10.1016/j.conbuildmat.2015.12.124>
- Li, W. and Fall, M. (2018). Strength and self-desiccation of slag-cemented paste backfill at early ages: Link to initial sulphate concentration. *Cement and Concrete Composites*, 89,160-168. <https://doi.org/10.1016/j.cemconcomp.2017.09.019>
- Mehta, P. K., & Monteiro, P. J. (2006). *Concrete: microstructure, properties, and materials*, 3rd ed. McGraw-Hill Education.
- Zou, F., Zhang, M., Hu, C., Wang, F., & Hu, S. (2021). Novel CASH/PCE nanocomposites: Design, characterization and the effect on cement hydration. *Chemical Engineering Journal*, 412, 128569. <https://doi.org/10.1016/j.cej.2021.128569>
- Neville, A.M. (2011). Properties of Concrete, 4th. *London Pearson Education Limited*, 443(846).

- Oey, T., Kumar, A., Bullard, J. W., Neithalath, N., & Sant, G. (2013). The filler effect: the influence of filler content and surface area on cementitious reaction rates. *Journal of the American Ceramic Society*, 96(6), 1978-1990. <https://doi.org/10.1111/jace.12264>
- O'Farrell, M., Wild, S., and Sabir, B. (2001). Pore size distribution and compressive strength of waste clay brick mortar. *Cement and Concrete Composites*, 23(1), pp.81-91.
- Ouellet, S., Bussière, B., Aubertin, M. and Benzaazoua, M. (2007). Microstructural evolution of cemented paste backfill: Mercury intrusion porosimetry test results. *Cement and Concrete Research*, 37(12), 1654-1665. <https://doi.org/10.1016/j.cemconres.2007.08.016>
- Persson, B. (1997). Self-desiccation and its importance in concrete technology. *Mat. and Struct.*, 30(5), 293-305. <https://doi.org/10.1007/BF02486354>
- Persson, B. (2000). Consequence of cement constituents, mix composition and curing conditions for self-desiccation in concrete. *Materials and structures*, 33(6), 352-362. <https://doi.org/10.1007/BF02479644>
- Pokharel, M. (2008). *Geotechnical and environmental responses of paste tailings systems to coupled thermo-chemical loadings*. [MAsc thesis, Ottawa, ON: University of Ottawa.] <http://dx.doi.org/10.20381/ruor-18910>
- Poon, C.S., Wong, Y.L. and Lam, L. (1997). The influence of different curing conditions on the pore structure and related properties of fly-ash cement pastes and mortars. *Construction and Building Materials*, 11(7-8), 383-393. [https://doi.org/10.1016/S0950-0618\(97\)00061-5](https://doi.org/10.1016/S0950-0618(97)00061-5)
- Roessler, M. and Odler, I. (1985). Investigations on the relationship between porosity, structure and strength of hydrated Portland cement pastes. I. Effect of Porosity. *Cement and Concrete Research*, 15(2), 320-330. [https://doi.org/10.1016/0008-8846\(85\)90044-4](https://doi.org/10.1016/0008-8846(85)90044-4)

- Roessler, M. and Odler, I. (1985). Investigations on the relationship between porosity, structure and strength of hydrated Portland cement pastes. II. Effect of pore structure and of degree of hydration. *Cement and Concrete Research*, 15(3), 401-410.
[https://doi.org/10.1016/0008-8846\(85\)90113-9](https://doi.org/10.1016/0008-8846(85)90113-9)
- Shehata, M.H. and Thomas, M.D. (2010). The role of alkali content of Portland cement on the expansion of concrete prisms containing reactive aggregates and supplementary cementing materials. *Cement and Concrete Research*, 40(4), 569-574.
<https://doi.org/10.1016/j.cemconres.2009.08.009>
- Shi, D. and Winslow, D.N. (1985). Contact angle and damage during mercury intrusion into cement paste. *Cement and Concrete Research*, 15(4), 645-654.
[https://doi.org/10.1016/0008-8846\(85\)90064-X](https://doi.org/10.1016/0008-8846(85)90064-X)
- Simon, D. and Grabinsky, M.W. (2012). Electromagnetic wave-based measurement techniques to study the role of Portland cement hydration in cemented paste backfill materials. *International Journal of Mining, Reclamation and Environment*, 26(1), 3-28.
<https://doi.org/10.1080/17480930.2012.639193>
- Taylor, H.F. (1997). *Cement chemistry 2nd ed.* London, UK: Thomas Telford.
- Tian, X. and Fall, M. (2021). Non-isothermal evolution of mechanical properties, pore structure and self-desiccation of cemented paste backfill. *Construction and Building Materials*, 297, p.123657. <https://doi.org/10.1016/j.conbuildmat.2021.123657>
- Van Weert, F., Van der Gun, J., and Reckman, J. (2009). Global overview of saline groundwater occurrence and genesis. *International Groundwater Resources Assessment Centre*.
- Wang, C. and Villaescusa, E. (2000). Backfill research at the western Australian school of mines. *MassMin 2000 Proceedings*.

- Wang, J., Xie, J., Wang, Y., Liu, Y., and Ding, Y. (2020). Rheological properties, compressive strength, hydration products and microstructure of seawater-mixed cement pastes. *Cem. and Conc. Comp.* 114, 103770. <https://doi.org/10.1016/j.cemconcomp.2020.103770>
- Wang, Y., Fall, M. and Wu, A. (2016). Initial temperature-dependence of strength development and self-desiccation in cemented paste backfill that contains sodium silicate. *Cem. and Conc. Comp.* 67, 101-110. <https://doi.org/10.1016/j.cemconcomp.2016.01.005>
- Yaphary, Y.L., Lau, D., Sanchez, F. and Poon, C.S. (2020). Effects of sodium/calcium cation exchange on the mechanical properties of calcium silicate hydrate (CSH). *Construction and Building Materials*, 243, 118283. <https://doi.org/10.1016/j.conbuildmat.2020.118283>
- Young, J.F., Tong, H.S. and Berger, R.L. (1977). Compositions of solutions in contact with hydrating tricalcium silicate pastes. *Journal of the American Ceramic Society*, 60(5-6), 193-198. <https://doi.org/10.1111/j.1151-2916.1977.tb14104.x>
- Zhou, X., Lin, X., Huo, M., and Zhang, Y. (1996). The hydration of saline oil-well cement. *Cement and Concrete Research.*, 26(12), 1753-1759. [https://doi.org/10.1016/S0008-8846\(96\)00176-7](https://doi.org/10.1016/S0008-8846(96)00176-7)

Chapter 4: Technical Paper 2 – Rheology and Setting Time of Saline Cemented Paste**Backfill****(submitted)****4.1 Abstract**

The effect of mixing water salinity and binder type on the rheological properties and setting time of cement paste backfill (CPB) were explored. Viscosity, yield stress, and setting time testing were conducted on CPB made with PC and varying slag replacement quantities, silica tailings (ST), and mixing water with NaCl concentrations from 0 g/L to 300 g/L. Supplemental testing or analysis included pH determination, TG/DTG and XRD microstructure analyses, zeta potential measurements, and suction and electrical conductivity monitoring. Results indicate that low (10 g/L - 35 g/L) NaCl concentrations in PC-CPB increased the yield stress above the control while higher (100 g/L - 300 g/L) concentrations decreased it. An increase in NaCl concentration led to slower increases in viscosity over the first two hours of curing. Low (10 g/L - 35 g/L) NaCl concentrations reduced the time to initial and final setting while high (100 g/L - 300 g/L) concentrations increased it. In general, these results were due to the effects of the Na and Cl ions on the dissolution of the cement components, and on the changes in zeta potential due to chloride adsorption. Increases in slag replacement quantities on saline CPB had minimal effect on the yield stress during the first two hours after mixing, but decreased the viscosity. All tested slag contents increased the time to initial setting, though a replacement content of 75% did not increase the initial setting time as much as lower quantities. A slag replacement content of 25% increased the time to final set, though higher contents decreased it. This behaviour was due to the slower reaction rate of slag, combined with slag's consumption of NaCl and CH and

greater chloride binding capabilities. The results of this study will aid mines in designing more cost effective and efficient backfill programs.

4.2 Introduction

The removal of valuable mineral from underground mines creates large voids that pose a significant threat to safety for miners and surface features. To mitigate this and provide a platform for continuing operations, voids must be backfilled with cheap, stable material. Cemented paste backfill (CPB) is an established form of backfill that utilizes dehydrated mine tailings, binder, and water. This gives a significant added benefit in decreasing the volume of tailings that must be stored in tailings ponds at the surface, and reducing the associated environmental hazards and financial costs.

CPB typically consists of 2% - 9% binder, 70% - 85% tailings, and water (Belem and Benzaazoua, 2004; Abdul-Hussein, 2011; Bull, 2019). These ratios determine the CPB's performance by impacting properties such as strength gain and durability. The effects of small changes in these ratios, of additional additives, and curing conditions has been the subject of much study, in the effort to determine the most cost-effective combination for different applications.

Mines are located all over the world, including in areas without readily available fresh water for use in CPB (Meißner, 2021). These operations may consider using saline groundwater or seawater as a cheaper and more environmentally friendly alternative to fresh water (Jiang and Fall, 2017a and b; Xiao et al., 2021). Thus, it is important to understand the impacts of salinity on the properties of CPB.

One important property is its rheology, which describes complex flow behaviour of fluids (Banfill, 2003). CPB is usually mixed in plants on the ground surface and transported to the

stopes underground via pipes, either by pumping and/or gravity (Belem and Benzaazoua, 2004; de la Vergne, 2003). Significant costs and delays can be incurred if the CPB clogs the pipes or if it is not able to be pumped efficiently (Simon and Grabinsky, 2013; Wu et al., 2014). Therefore, the ability of CPB to be efficiently transported while maintaining the required strength properties, is of significant interest. The ability of CPB to be transported efficiently is a function of its rheological properties.

Rheology is a complex characteristic that cannot be described with a single measurement. However, both yield stress and viscosity are commonly used as there exist reasonably economic and simple means of measuring both. Yield stress describes the stress that must be applied to initiate flow while viscosity describes the internal resistance of a fluid to movement (Xiao et al., 2020).

Setting time is the time until CPB begins to gain mechanical strength and the ability to resist deformation. This property is crucial to the determination of when bulkheads can be removed from the entrance to the stope and mining operations can progress. Rapidly advancing mining operations improve the productivity of the mine, which is obviously associated with significant financial benefits. Early strength gain is also crucial to reduce the risk of liquefaction, which increases the safety of workers (Yin et al., 2012). Therefore, early strength gain, as demonstrated by a faster setting time, is a key objective in mine backfill design.

To date, studies have been conducted on the rheology of CPB made with ordinary Portland cement (e.g., Wu et al., 2014; Yang et al., 2022; Wu et al., 2013; Cheng et al., 2020a; Cheng et al., 2020b; Zhang et al., 2021; Cao et al., 2018; Niroshan et al., 2018; Liu and Fall, 2022; Hou et al., 2018; Deng et al., 2018; Li et al., 2020; Lang et al., 2015), with flocculants (e.g., Cao et al., 2021; Xu et al., 2021; Xu et al., 2020a), with pozzolanas (e.g., Jiang et al., 2020;

Yin et al., 2012; Xu et al., 2020b; Simon and Grabinsky, 2013; Zhao et al., 2020; Xiao et al., 2021), with superplasticizers (e.g., Liu et al., 2020; Ouattara et al., 2017; Haruna and Fall, 2020; Panchal et al., 2018; Klein and Simon, 2006), with nano-silica particles (e.g., Roshani and Fall, 2020a; Roshani and Fall, 2020b), with ultra-fine tailings (Xue et al., 2020), with superabsorbent polymers (e.g., El Mahboub et al., 2022), with alkali-activated slag (Kou et al., 2020), with sodium silicate (e.g., Cavusoglu et al., 2021; Ghada et al., 2020), with sulphates (Bian et al., 2021; Xiapeng et al., 2019), with activators (Xu et al., 2019), with coal mine fly ash (Wu et al., 2021), and in sub-zero environments (Zhou et al., 2022; Zhou and Fall, 2022; Jiang and Fall, 2017a; Jiang and Fall, 2017b).

Few studies have been conducted on the impacts of NaCl on CPB viscosity and yield stress at room temperature and only one study has briefly considered the impact of NaCl on setting time. Jiang and Fall studied the effects of NaCl on the yield stress of PC-CPB (2017a) and slag-CPB (2017b) in sub-zero environments. They found that NaCl significantly decreased the yield stress of CPB and slag-CPB by the adsorption of chloride ions onto the cement particles and hydration products. For slag-CPB, they also found there were competing factors which increased or decreased the yield stress and that the overall impact was determined by the NaCl content, slag content, and curing time. To the contrary, Zhao et al. (2020) found that an increase in salinity from mine process water led to an increase in yield stress regardless of binder type but that this effect was weaker when a commercial cement product containing slag was present. The presence of elements such as Ca and Mg may have enhanced the binder coagulation. Klein and Simon (2006) found that the addition of 3% (by mass of solids) NaCl led to a decrease in the setting time but had little effect on the pH of the paste. Zhou and Fall (2022) studied the effects of NaCl on CPB viscosity and yield stress in sub-zero environments and found that an increase

of NaCl decreased the yield stress due to the increased repulsive forces between particles and increased the viscosity due to the ability of chloride ions to accelerate cement hydration. The addition of slag was found to increase the yield stress. Viscosity decreased until the slag/PC ratio was 50/50 and then increased with continued increasing slag content. Xiao et al. (2021) found that slag-CPB had higher static yield stress and lower viscosity than PC-CPB, and that NaCl reduced both the yield stress and viscosity of slag-CPB. Simon and Grabinsky (2013) studied the effects of pore fluid ionic concentration and binder type on the apparent yield stress of CPB. They found that NaCl did not change the pH of the fluid significantly but that it did increase the zeta potential and thus would reduce the apparent yield stress, but that Na^+ is a potentially determining ion which could reduce the magnitude of the zeta potential.

Only one study has been conducted of the effects of NaCl on the setting times of PC-CPB (Klein and Simon, 2006). To date, no research has been conducted into the effects of slag content on the setting times of saline CPB.

There remains much to be understood about how mixing water salinity affects the rheology of CPB and slag-CPB. This paper will examine the setting time, viscosity, and yield stress effects of NaCl concentration on CPB and the effects of slag on saline CPB.

4.3 Materials and Methodology

4.3.1 Materials and Sample Preparation

Samples were prepared using high purity ground silica from SIL-CO-SIL, general use Portland Cement Type I, tap water, slag supplied by Lafarge Canada, and certified ACS crystalline sodium chloride (NaCl) from Fisher Chemical as required by the mix designs. The high purity ground silica (ST) was used to reduce data errors due to the chemical variations and sulphides in natural tailings, but some mixes were made using natural gold tailings (GT) for

comparison. The dry tailings and binder materials were initially mixed separately from the water and salt, and then combined together for a minimum of seven minutes or until thoroughly mixed. A series of mixes was designed to explore the effects due to variations in mixing water salinity when all other components were held constant. Another series of mixes was designed to explore the effects due to variations in binder composition under constant mixing water salinity. The detailed mix design components are given in Table 4.1. The curing temperature for all mixes was room temperature, or about 20°C. The grain size distribution for the ST and GT are given in Figure 4.1. The chemical composition for the PC and slag is given in Table 4.2.

Table 4.1 Mix Design Parameters

Mix Name	Binder Content (%)	W/C Ratio	Tailings Type	% PC in Binder	% Slag in Binder	Mixing Water Salinity (g/L)
CPB-0	4.5	7.4	ST	100	0	0
CPB-10	4.5	7.4	ST	100	0	10
CPB-35	4.5	7.4	ST	100	0	35
CPB-100	4.5	7.4	ST	100	0	100
CPB-300	4.5	7.4	ST	100	0	300
CPB-75PC	4.5	7.4	ST	75	25	35
CPB-50PC	4.5	7.4	ST	50	50	35
CPB-25PC	4.5	7.4	ST	25	75	35
CPB-G-0	4.5	7.4	GT	100	0	0
CPB-G-35	4.5	7.4	GT	100	0	35

Table 4.2 Chemical Composition of PC and Slag

Element	PC (%)	Slag (%)
SO ₃	3.82	3.87
Fe ₂ O ₃	2.70	-
Al ₂ O ₃	4.53	9.54
SiO ₂	18.03	34.32
CaO	62.82	41.14
MgO	2.65	10.98
Relative Density	3.2	2.8

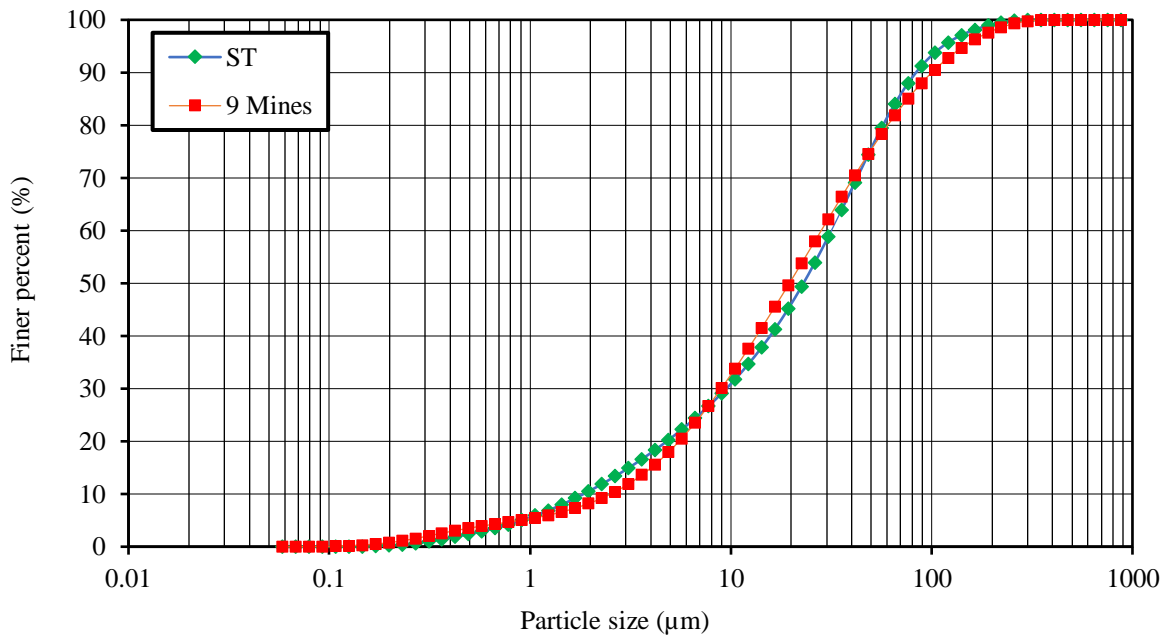


Figure 4.1 Grain size distribution for ST and GT

4.3.2 Yield Stress

Mixes were prepared as described above and placed into a cylindrical plastic mold with a diameter of about 10 cm, to a depth of approximately 15 cm. Testing was conducted with a Wykeham Farrance vane shear apparatus (Model 23500). Samples were tested immediately after mixing, and after 15 minutes, 1 hour, and 2 hours. Prior to each test, the sample was stirred with a spoon for 1 minute to simulate the shearing that would occur during transportation. Between tests, the samples were kept in a sealed plastic bag at room temperature. A minimum of two sets of tests were conducted for each mix with 2 different samples.

4.3.3 Viscosity

Mixes were prepared as described above and placed into a cylindrical plastic mold with a diameter of about 10 cm, to a depth of approximately 15 cm. Testing was conducted with a Brookfield DV-E Viscometer and spindle #5. Samples were tested immediately after mixing, and after 15 minutes, 1 hour, and 2 hours. Prior to each test, the sample was stirred with a spoon for 1

minute to simulate the shearing that would occur during transportation. Between tests, the samples were kept in a sealed plastic bag at room temperature. A minimum of two sets of tests were conducted for each mix with 2 different samples. Readings were recorded with video for 1 minute and later transcribed. Due to the impossibility of selecting a single RPM setting that could capture the entire range of readings for all samples, an RPM of 50 was used for all samples except the gold tailings samples. For the gold tailing samples, an RPM of 10 or 5 was used. The average of the readings from 30 seconds to 60 seconds after the start of testing were used.

It is understood that a viscometer is not able to fully measure the viscosity behaviour of a non-Newtonian fluid; nonetheless, it can provide a useful comparison of the effects caused by the variations in mix components, which is sufficient for the purposes of this study. A 5% error margin should be assumed.

4.3.4 Initial and Final Setting Time

Samples were prepared as described above and placed into molds appropriate for use with a Humbolt Vicat apparatus. Initial setting time was determined using ASTM C807. Current standards for determining the final setting time are not available for materials such as CPB. Therefore, a 5mm plunger attachment was used and the final setting time was taken as the elapsed time until the plunger's outer ring no longer made an indent in the surface of the CPB after 30 seconds. A minimum of 2 samples for each mix were tested and averaged.

Setting has been described as the transformation of a Portland cement paste from a fluid to a solid, but “does not yet have any significant strength” (Klein and Simon, 2005; Neville 1995). ASTM C125 (2021) defines setting as “the process, due to chemical reactions, occurring after the addition of mixing water, that results in a gradual development of rigidity of a cementitious mixture.” ASTM C125 further defines the time of initial setting as “the elapsed

time after initial contact of cement and water required ... to reach a penetration resistance of 500 psi” and the time of final setting as “the elapsed time ... to reach a penetration resistance of 4000 psi.” However, these values are somewhat arbitrary and are intended to reflect the beginning of solidification and the beginning of hardening respectively (Mehta and Monteiro, 2006).

4.3.5 Monitoring Program

Monitoring was conducted on samples of select mixes for a period of up to 24 hours. Matric potential was measured using a TEROS 21 sensor by MeterGroup while volumetric water content (VWC) and electrical conductivity were measured using a TEROS 12 sensor. The TEROS 21 sensor can take measurements of suction from -9 kPa to -100,000 kPa and has an accuracy of $\pm 10\%$ of reading +2 kPa, over the range of -5 kPa to -100 kPa. The TEROS 12 sensor can measure water content in the range of 0-80%, with an accuracy of ± 0.01 from 1% to 40% and ± 0.15 from 40% to 80%. Both sensors were connected to a ZL6 Pro Data Logger, also by MeterGroup, to continuously collect sensor readings over the 24 hours. Monitoring was conducted on the following mixes: CPB-0, CPB-35, CPB-100, and CPB-50PC.

4.3.6 XRD

X-Ray Diffraction (XRD) analysis was performed on cement pastes of the same mixes as for suction monitoring using a Scintag XDS 2000 x-ray diffractometer. Samples were prepared and allowed to cure for 1 hour and 2 hours at room temperature before being dried in an oven at 40°C for at least 4 days to stop cement hydration. Samples were then ground into a fine powder and sent to the X-Ray Core Facility of the University of Ottawa for testing.

4.3.7 TG/DTG

Thermogravimetry (TG) was performed on cement pastes of the same mixes as for suction monitoring by using a thermogravimetric analyzer SDT 2960. Samples were prepared

and allowed to cure for 1 hour and 2 hours at room temperature before being dried in an oven at 40°C for at least 4 days to stop cement hydration. Samples were then ground into a fine powder and tested.

4.3.8 Zeta Potential

Samples were prepared of the same mixes as for suction monitoring and allowed to cure for 1 hour. They were then diluted with distilled water to a concentration of 0.1% and tested in a Zetasizer Nano. A minimum of 3 runs were taken on 2 different samples for each mix.

4.3.9 pH Testing

Mixes were prepared as described above and tested with an Oakton pH6+ meter. Samples were tested immediately after mixing, and after 15 minutes, 1 hour, and 2 hours. Prior to each test, the sample was stirred with a spoon for 1 minute to simulate the shearing that would occur during transportation. Between tests, the samples were kept in a sealed plastic bag at room temperature. Two sets of tests were conducted for each mix with 2 different samples.

4.4 Results and Discussion

4.4.1 Effect of Salt Concentration on the Rheology and Setting Time

4.4.1.1 Yield Stress

Figure 4.2 shows the influence of salt concentration on the yield stress of the CPB. The data shows that the initial yield stress decreases with increasing salinity, but also that low salinities (10 g/L and 35 g/L) show a faster and stronger rise in yield stress with time than high salinities and the control (0 g/L).

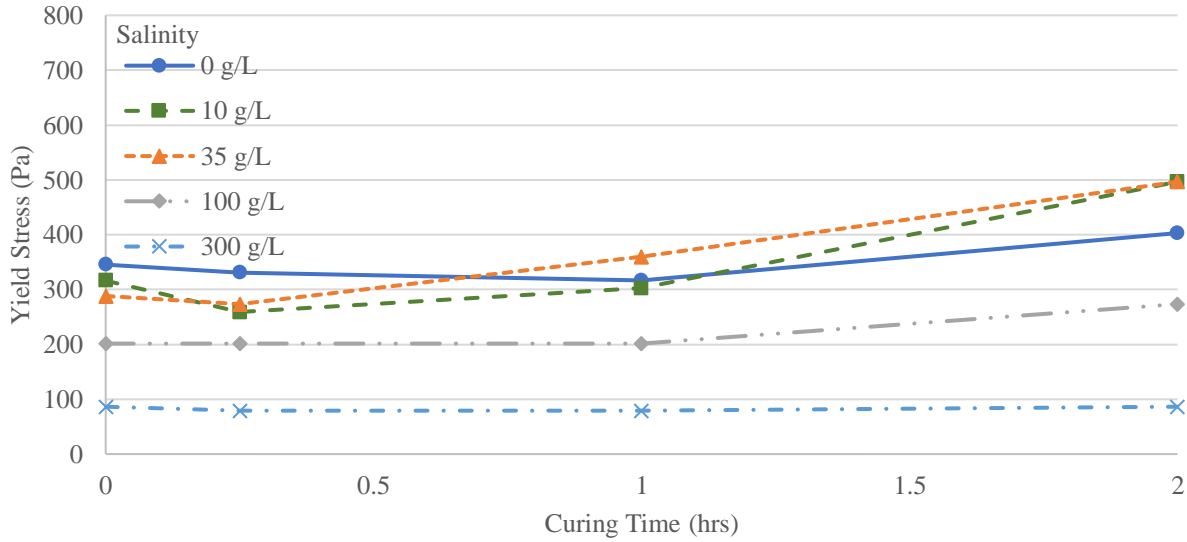


Figure 4.2 Impact of NaCl concentration on yield stress of CPB over first 2 hours of curing

The overall decrease in yield stress with increasing salinity is primarily due to the ability of NaCl to increase the magnitude of the zeta potential, as shown in Figure 4.3.

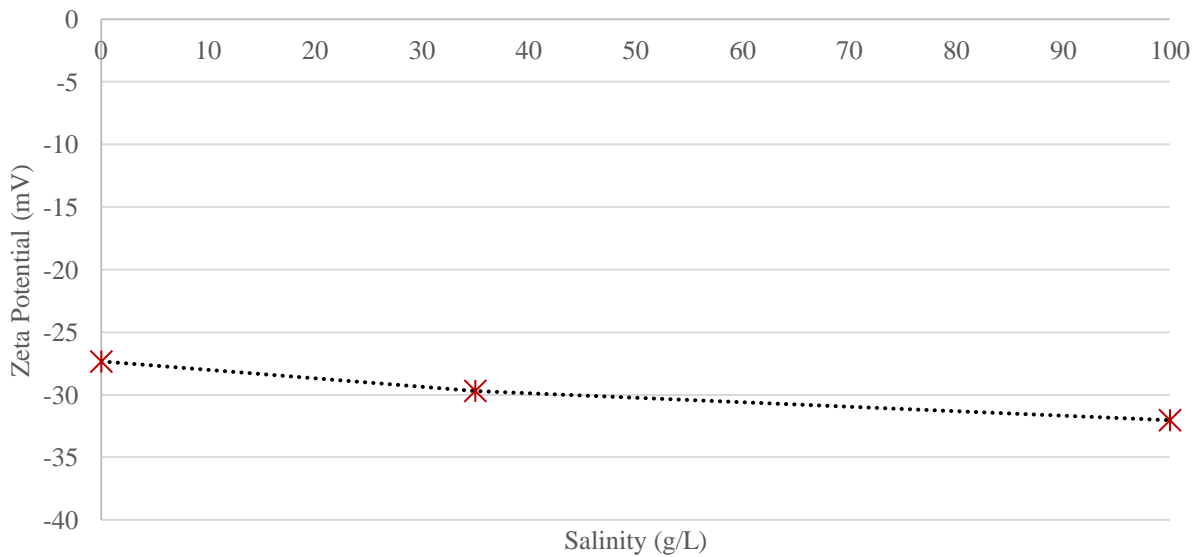


Figure 4.3 Impact of NaCl concentration on zeta potential after 1 hour of curing

Chloride ions from the NaCl are adsorbed onto the surfaces of the unhydrated cement particles and the cement hydration products which decreases the zeta potential (Beaudoin et al., 1990; Suryavanshi et al., 1996). An increase in zeta potential indicates greater electrostatic

repulsion between particles and therefore a greater distance between particles (Simon and Grabinsky, 2013; Taylor, 1997), which leads to less inter-particle friction and the observed reduction in yield stress. This is consistent with previous studies (Zhou and Fall, 2022; Elakneswaran et al., 2009; Li et al., 2020).

Further evidence for this cause is the association between NaCl, pH, and zeta potential. Though it has been found that NaCl does not directly have a significant impact on pH, it has been established that chloride ions impact the zeta potential and that zeta potential changes with a change in pH (Simon and Grabinsky, 2013; Klein and Simon, 2006; Elakneswaran et al., 2009). Figure 4.4 shows the change in pH with salinity over time, which confirms that the zeta potential changes as well.

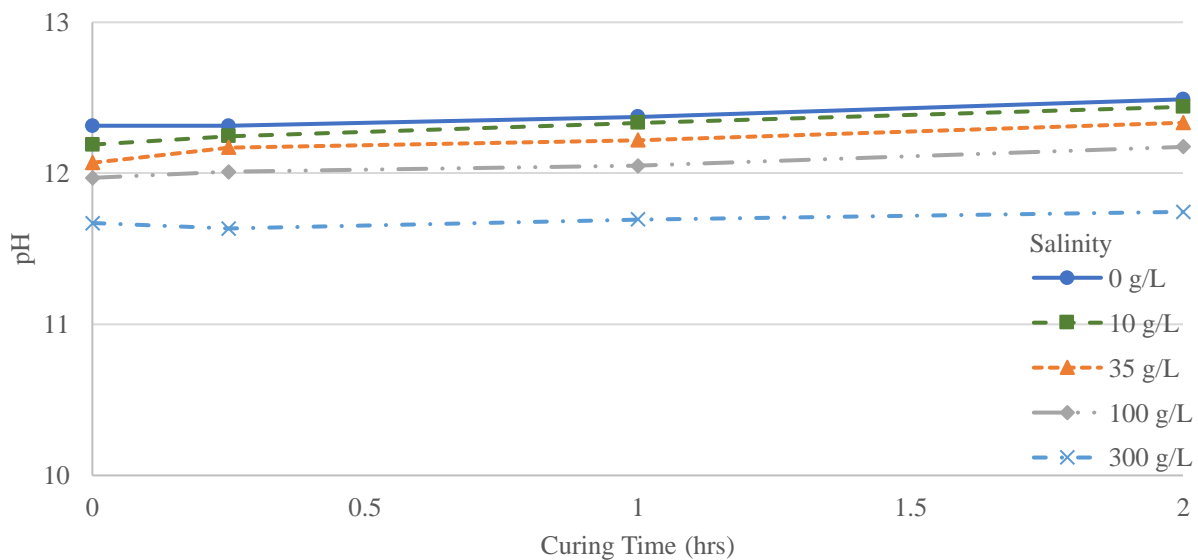


Figure 4.4 Impact of NaCl concentration on pH over first 2 hours of curing

Additionally, Figure 4.2 showed that the yield stress of CPB with low salinities began to increase sooner and more rapidly than those with high salinities or the control. This is because the hydration of cement is accelerated by small amounts of NaCl, leading to the production of more hydration products and the creation of flocculant structures, both of which increase

particle-particle contact and yield stress (Roshani and Fall, 2020; Zhao et al., 2020), while excessive quantities of salt retard cement hydration. The mechanisms for this were described by Mehta and Monteiro (2006) and will be explained in more detail in the section on setting time. The XRD results, shown in Figure 4.5 and Figure 4.6, indicate that the low-salinity sample (35 g/L) underwent more hydration than either the control (0 g/L) or the high-salinity sample (100 g/L), and that the high-salinity sample underwent the least. The differences in hydration products between samples and from 1 hour to 2 hours are small. This is because the CPB is still in the dormant phase of hydration and hydration products are slow to be formed until initial set occurs (Taylor, 1997; Mehta and Monteiro, 2006).

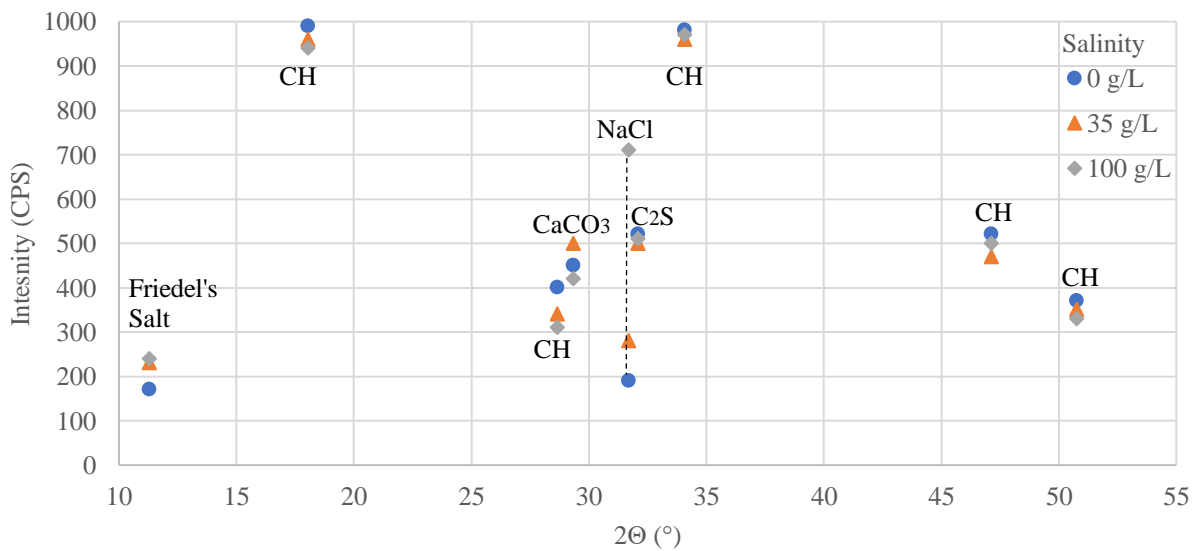


Figure 4.5 Comparison of XRD peaks for CPB with and without NaCl after 1 hour of curing

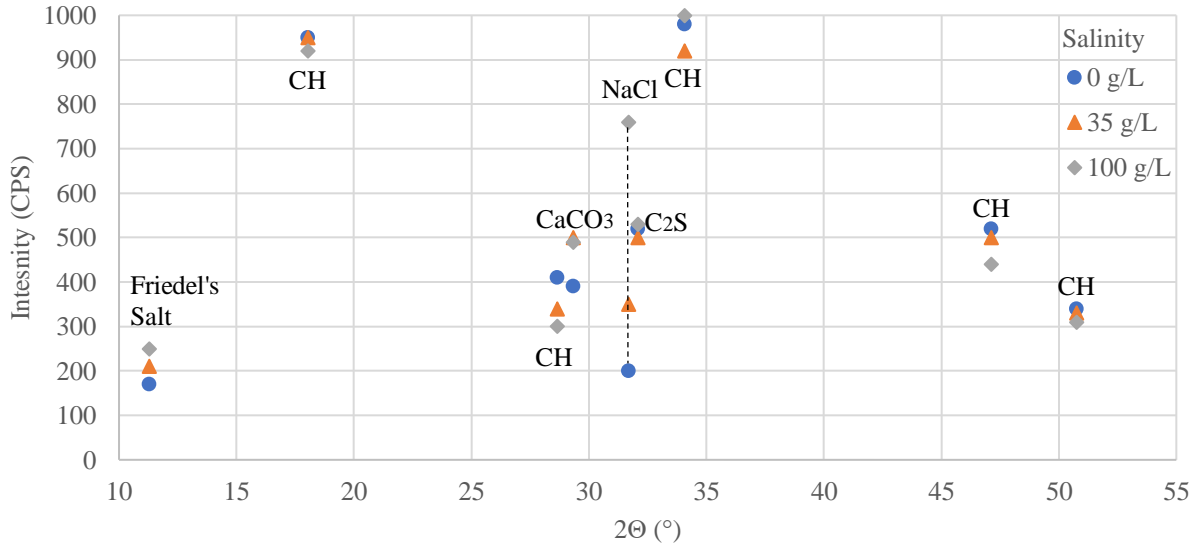


Figure 4.6 Comparison of XRD peaks for CPB with and without NaCl after 2 hours of curing

Electrical conductivity monitoring results, shown in Figure 4.7, provide further evidence of the impact of salinity on the early rate of hydration.

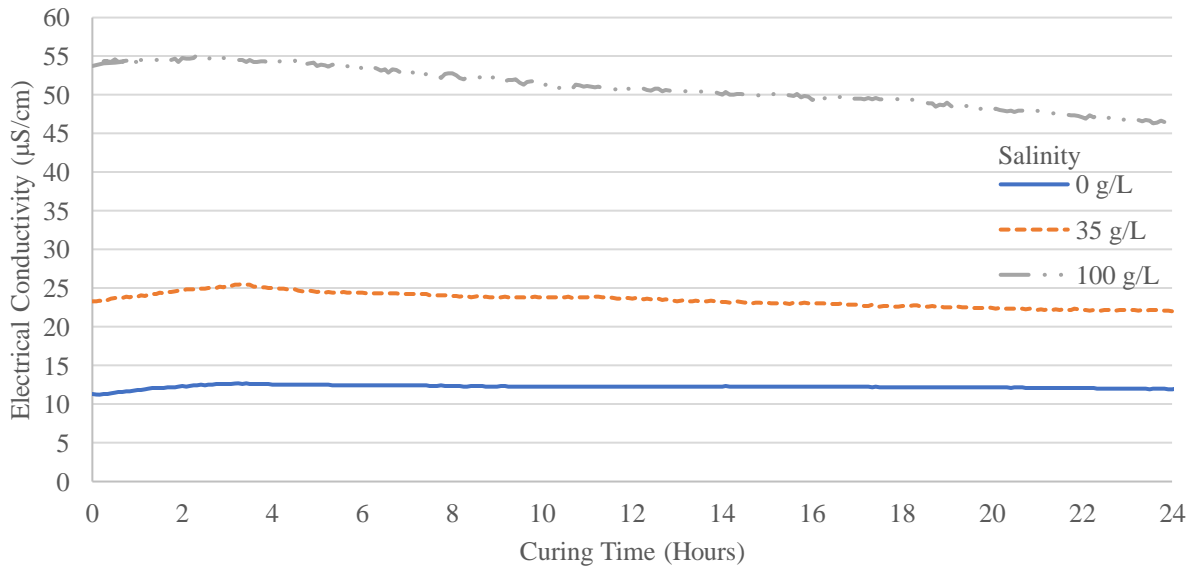


Figure 4.7 Impact of NaCl concentration on electrical conductivity over first 24 hours of curing

In the first three hours, the low-salinity sample shows the fastest rate of increase in electrical conductivity, followed by the non-saline sample and the high-salinity sample. It has

been established that electrical conductivity is a reliable indicator of the rate of hydration reactions (Simon and Grabinsky, 2012; Wei and Li, 2006; McCarter et al., 2002).

TG/DTG results (Figure 4.8 and Figure 4.9) generally corroborate the XRD results.

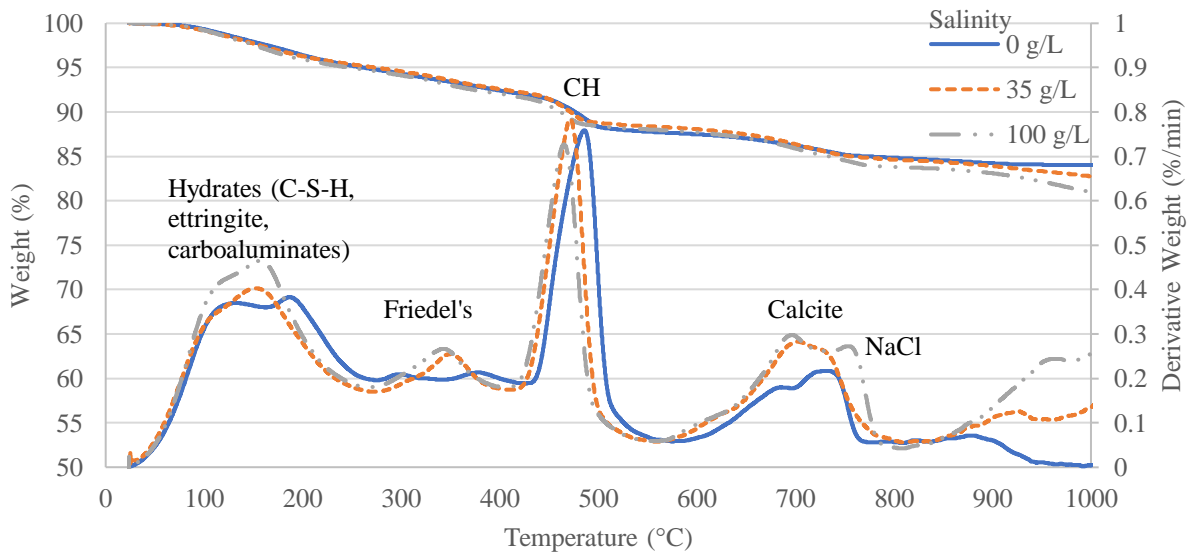


Figure 4.8 TG/DTG results for CPB with and without NaCl after 1 hour of curing

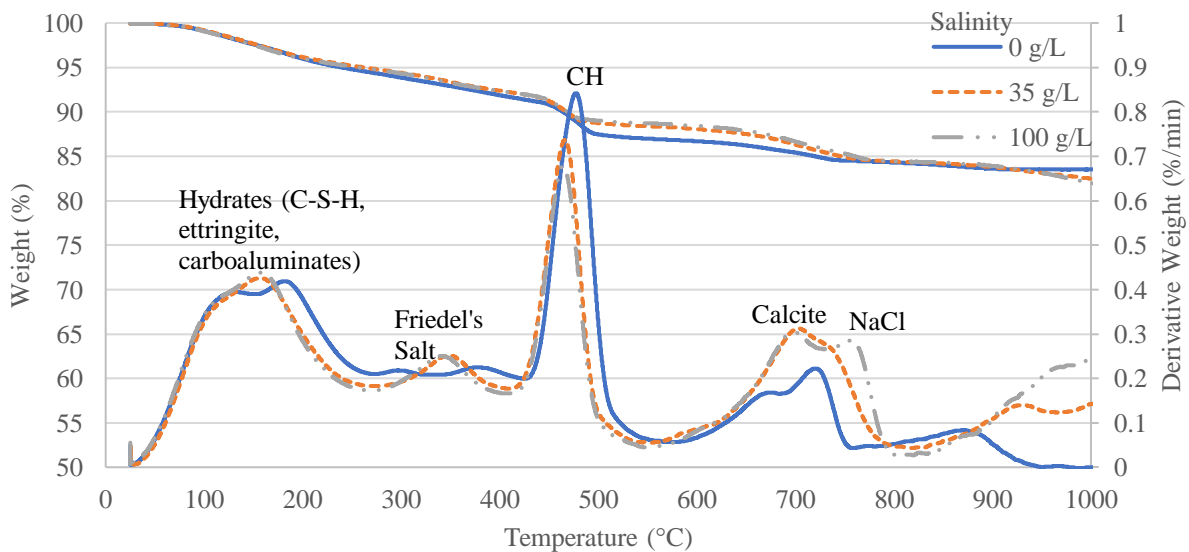


Figure 4.9 TG/DTG results for CPB with and without NaCl after 2 hours of curing

They indicate that between 1 and 2 hours of curing, the 100 g/L sample experienced a loss in hydrates and had the least amount of CH, and that the non-saline control sample

experienced an increase in CH, but that overall differences between the samples and curing times were small.

The yield stress results for the CPB mixes using natural gold tailings, shown in Figure 4.10, instead of pure silica tailings show a similar trend: small quantities of NaCl lead to a faster and stronger rise in yield stress than non-saline mixing water. This confirms that the principles discussed with respect to CPB made with silica tailings are valid for CPB made with natural gold tailings as well. pH testing data, shown in Figure 4.11, confirms that salinity has similar impacts on CPB made with natural gold tailings as with silica tailings and that adsorbed chloride ions are likely the cause of the change in both pH and zeta potential, which will have similar impacts to the yield stress as described for silica tailings.

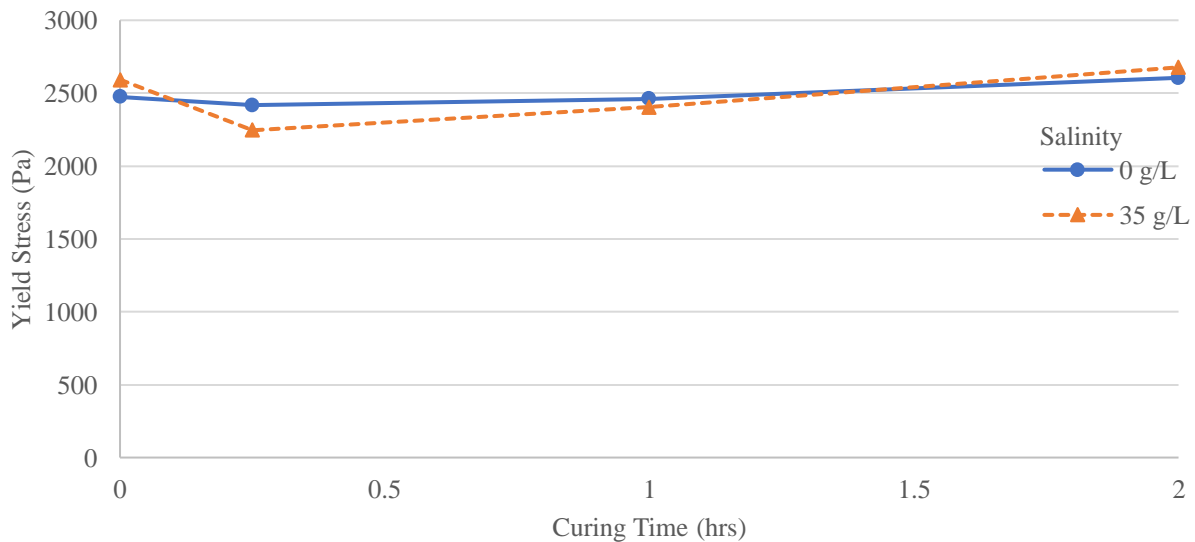


Figure 4.10 Impact of NaCl concentration on yield stress of CPB made with GT

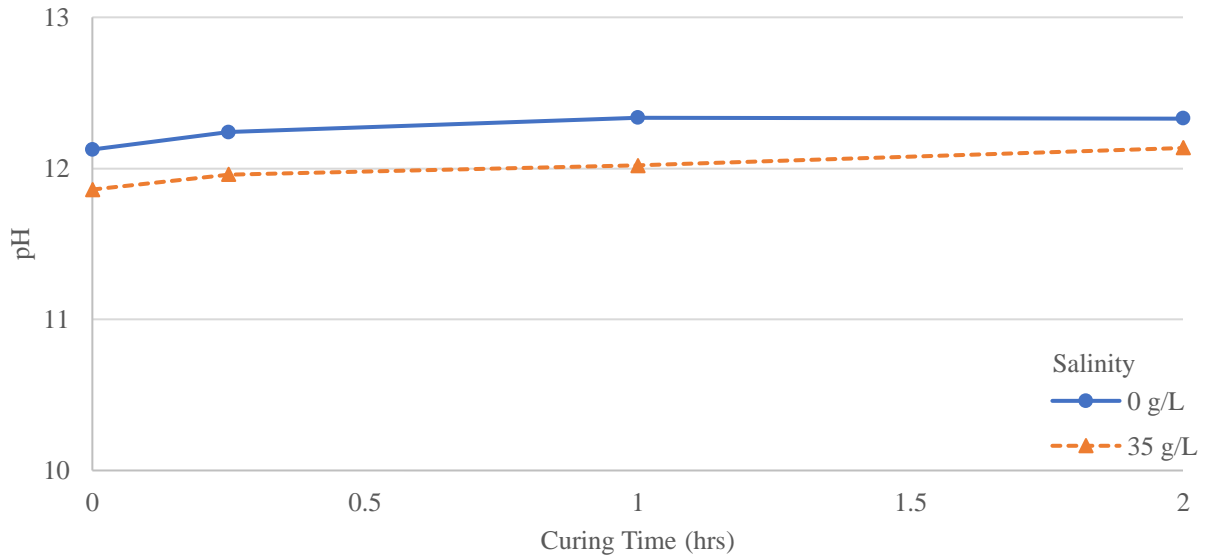


Figure 4.11 Impact of NaCl concentration on pH of CPB made with GT

4.4.1.2 Viscosity

Figure 4.12 shows the impacts of mixing water salinity on the viscosity of CPB made with silica tailings over time.

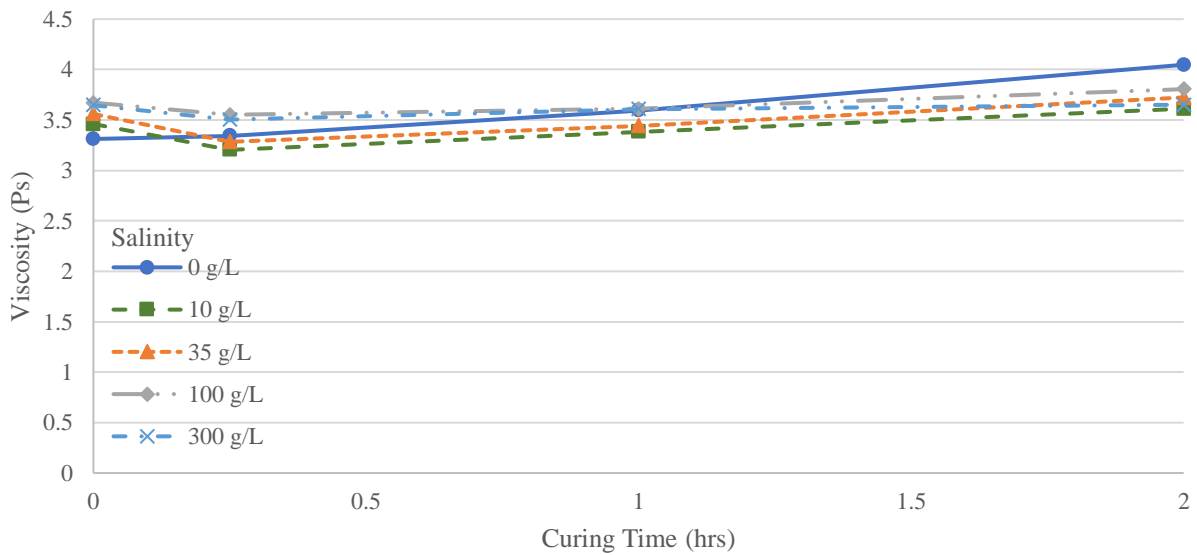


Figure 4.12 Impact of NaCl concentration on viscosity of CPB over first 2 hours of curing

The results show that an increase in salinity leads to an increase in the initial viscosity, but that this is not maintained over curing time. All the saline samples experience a slight

decrease in viscosity after 15 minutes of curing, after which they begin to increase again, while the non-saline CPB does not experience any decrease and simply increases. The non-saline CPB experienced the greatest increase in viscosity over the first 2 hours of curing while the CPB with the highest salinity experienced the least.

Numerous previous studies have found that viscosity is dependent on the solid volume fraction of cemented materials (Zhou and Fall, 2022; Xiao et al., 2021). Tailings, binder, NaCl, or hydration products can all contribute to the solid volume. It can be seen that the viscosity immediately after mixing increases with increasing salt content, and it can be surmised that the additional salt is the main cause for this. The decrease in viscosity from 0 to 15 min of curing in all the saline mixes is likely caused by the adsorption of NaCl crystals onto the surfaces of unhydrated cement particles and into the early hydration products which causes a reduction in the solid volume fraction. The non-saline mix experiences no initial decrease in viscosity because there is no NaCl to affect the solid volume fraction, either by its presence or binding capability. However, hydration reactions quickly start guiding the development of viscosity. The formation of hydration products consumes both solids and mixing water which has a net reduction in the water content and therefore an increase in the solid volume fraction and the viscosity (Cao et al., 2018; Niroshan et al., 2018; Li et al., 2020). At low concentrations, salt accelerates hydration, which can be seen in the rapid increase in viscosity from 15 minutes to 2 hours for the mixes with 10 g/L and 35 g/L salinity. The high salinity mixes (100 g/L and 300 g/L) experience much slower increases in viscosity after 15 minutes, as well as less of a decrease from 0 to 15 minutes. However, the non-saline mix experiences a steady increase in viscosity because the hydration reactions progress without the influence of NaCl. Suction monitoring results are shown in Figure 4.13 and give an indication of the change in solid volume fraction

(higher suction generally indicates greater solids concentration). It can be seen from the suction results that the 100 g/L sample underwent no suction increase (corresponding to little solids concentration increase and very little change in viscosity), while the 35 g/L sample underwent a strong but brief suction increase before beginning to decrease (corresponding to moderate increase in solids concentration and viscosity), and the non-saline sample underwent a steadier, but ultimately higher increase in suction over the first two hours of curing (corresponding to the steady and greatest increase in viscosity).

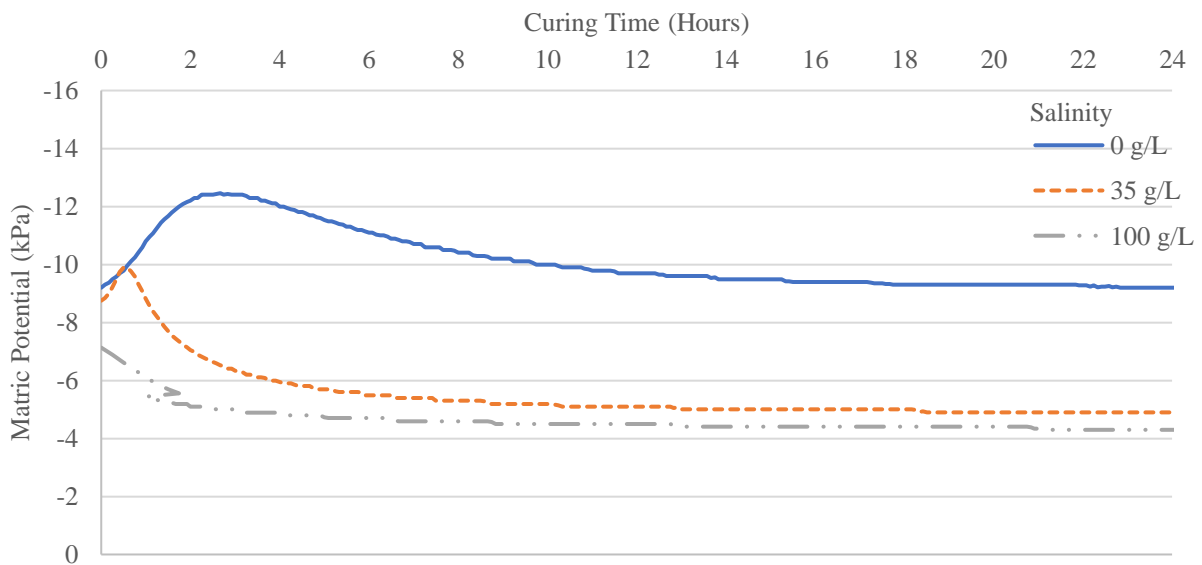


Figure 4.13 Impact of NaCl concentration on suction for first 24 hours of curing

Figure 4.14 shows the evolution of viscosity due to variations in salinity for CPB made with natural gold tailings. The trend is similar to that shown for silica tailings and confirms the conclusions made. The only difference is the drop in viscosity of the saline CPB after 2 hours of curing, which can be ascribed to the chemical variations of natural gold tailings (and the associated presence of sulphate ions).

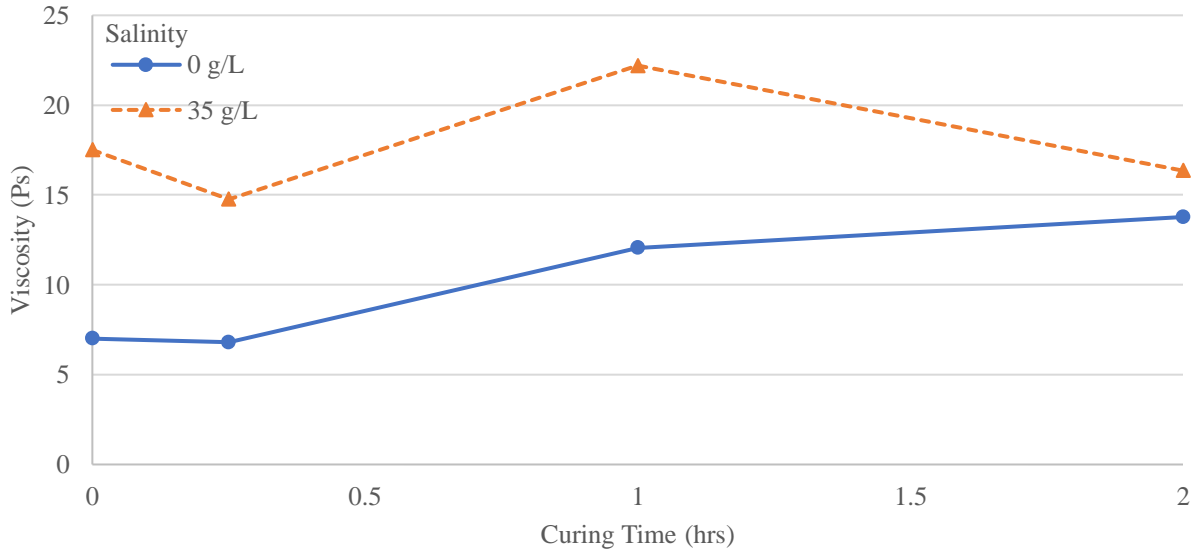


Figure 4.14 Impact of NaCl concentration of viscosity of CPB made with GT

4.4.1.3 Setting Time

The impacts of NaCl concentration on initial and final setting times are presented in Figure 4.15 and Figure 4.16 below.

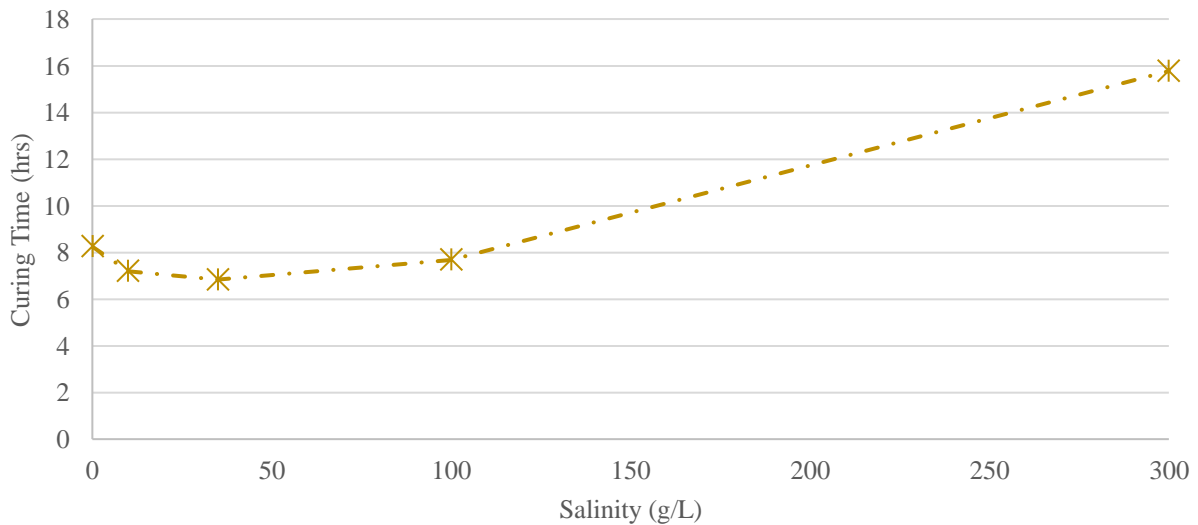


Figure 4.15 Impact of NaCl concentration on initial setting time of CPB

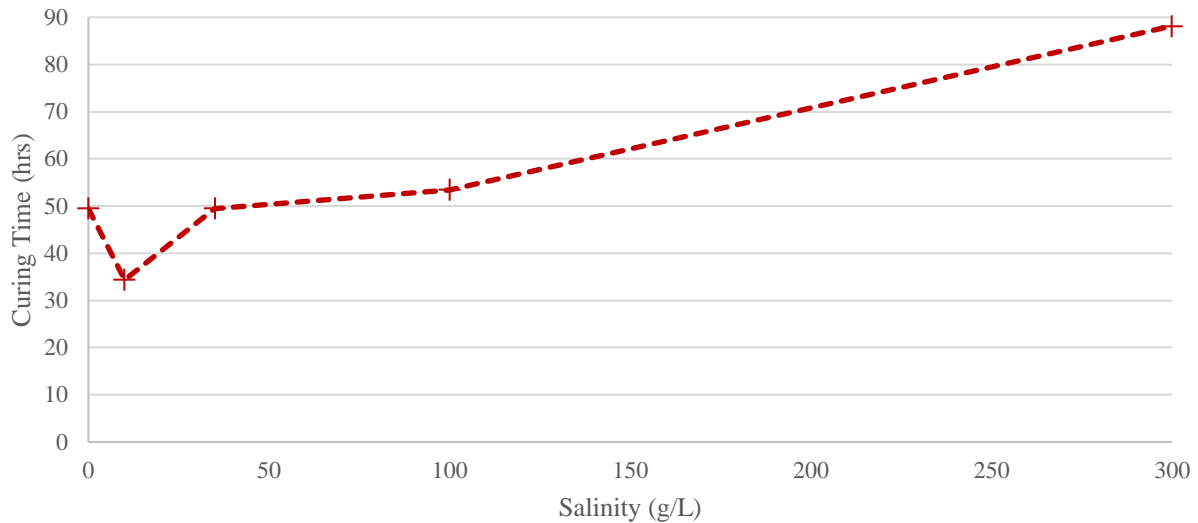


Figure 4.16 Impact of NaCl concentration on final setting time of CPB

Figure 4.15 clearly shows that low salinities (10 g/L to 35 g/L) have a shortening effect on the time to initial setting when compared to the non-saline mixing water, while high salinity (300 g/L) has the effect of lengthening the initial setting time. Figure 4.16 shows a similar relationship between mixing water salinity and final setting time, though with a stronger shortening effect by the 10 g/L concentration and a weaker effect of the 35 g/L concentration.

This is consistent with previous research in this relationship by Klein and Simon (2006). It is worth noting that Klein and Simon tested salt concentrations of 4 g/L and 77 g/L of NaCl, so the present results show a more complete picture of the relationship. Mehta and Monteiro (2006) explain that the setting of cement mixtures is guided by the dissolution rates of the anhydrous cement particles, which are in turn guided by the presence of cations and anions in the pore solution. In particular, the dissolution of the aluminate phases tends to control the setting behaviour of cement pastes. They state that monovalent cations (such as Na^+) reduce the solubility of the calcium phase and improve the solubility of the silicate and aluminate phases in the cement, while monovalent anions (such as Cl^-) have the opposite effect. At low ionic concentrations (<1% by weight of cement), the reductions in cement dissolution are more

prominent than the improvements which have the net effect of slowing the setting times; but at high concentrations (>1% by weight of cement), the improvements in dissolution rates are more prominent and the setting times are accelerated. All of the tested concentrations are considered to be “high” by Mehta and Monteiro, so it is consistent with the literature that even the low salinities tested in this study saw an acceleration in setting times. However, the present work has found that excessively high concentrations of NaCl (>100 g/L or 74% by weight of cement) have a significant retarding effect on the times of initial and final setting. This is likely due to the salt saturating the water and leaving little capacity available for the cement ions to dissolve. Indeed, salt residue was noticed in the beaker after adding 300 g/L saline mixing water to the solids.

Figure 4.17 shows that a similar relationship between NaCl concentration and initial and final setting times exist for CPB made with natural gold tailings as for CPB made with pure silica tailings.

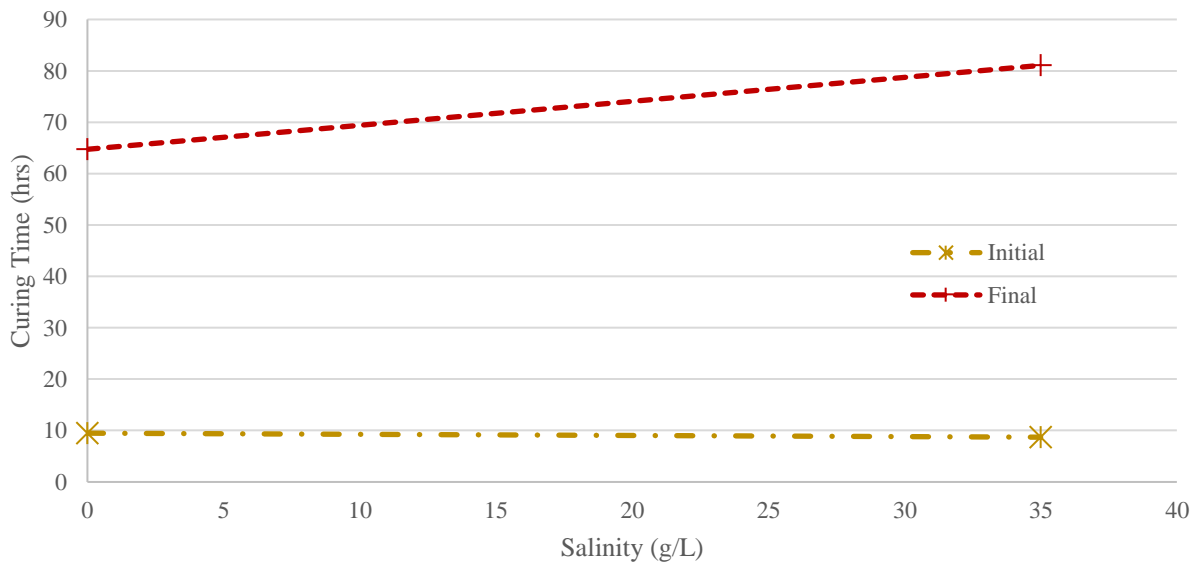


Figure 4.17 Impacts of NaCl concentration on the setting times of CPB made with GT

The main difference is that there is an increase in all setting times for all mixes and a significant increase in the time to final setting for CPB made with natural tailings and 35 g/L

NaCl. The presence of sulphates in the natural tailings (~7,000 ppm) increases the dissolution of gypsum, which in turn slows the dissolution of the C₃A and increases the times to setting.

4.4.2 Effect of Binder Type on the Rheology and Setting Time of Saline CPB

4.4.2.1 Yield Stress

Figure 4.18 shows the influence of slag replacement on the yield stress of saline (35 g/L) CPB. In general, slag content does not have as strong an impact on yield stress as mixing water salinity, but the presence of slag leads to a slight increase in yield stress. This is consistent with the results found in previous studies (Zhou and Fall, 2022; Jiang and Fall, 2016).

There are conflicting mechanisms that influence whether the yield stress of saline slag-CPB will increase or decrease relative to saline PC-CPB, each of which will be described in turn.

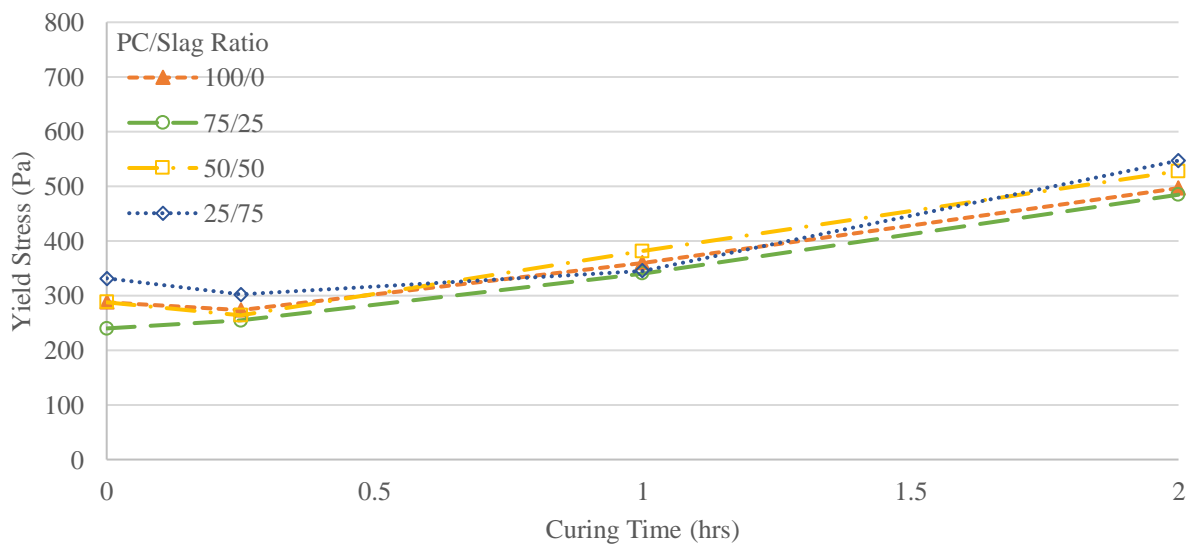


Figure 4.18 Impact of slag replacement on yield stress of saline CPB (NaCl content: 35 g/L) over first 2 hours of curing

The higher aluminate content of slag gives it a greater chloride binding capacity than PC (Xiao et al., 2021). This causes the slag mixes to have a more negative zeta potential, as seen in Figure 4.19, which indicates more electrostatic repulsion between particles. This leads to less inter-particle friction and a lower yield stress.

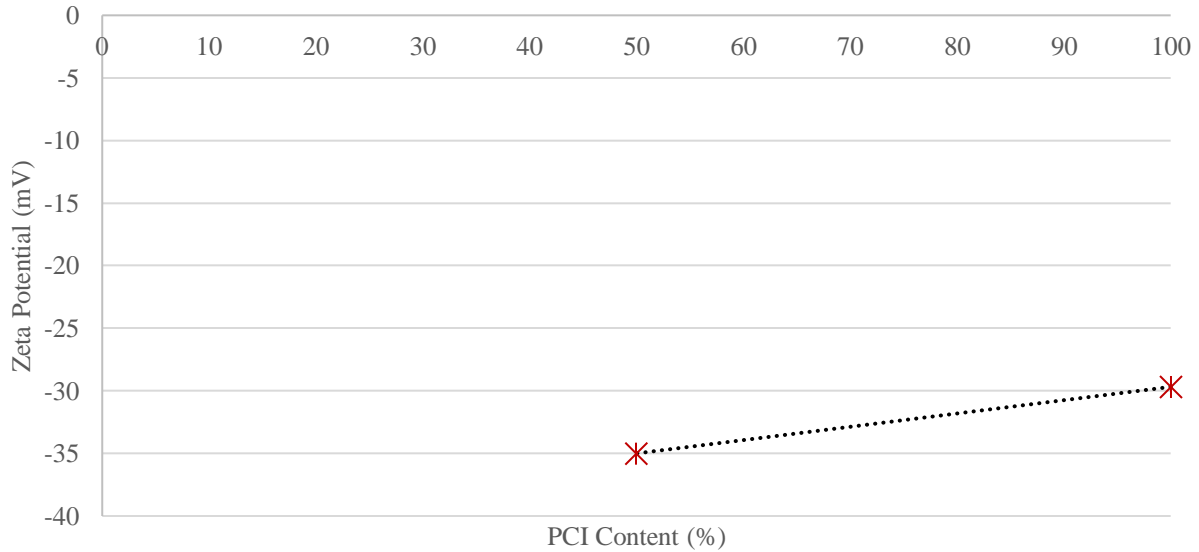


Figure 4.19 Impact of slag replacement on zeta potential after 1 hour of curing

The adsorption of chloride into the slag particles also reduces the amount of precipitated NaCl that could contribute to an increase in yield stress. The TG/DTG results shown in Figure 4.20 indicate that though both samples initially had the same amount of NaCl, the slag mix had none remaining, while the PC-only mix still had a notable amount of free NaCl.

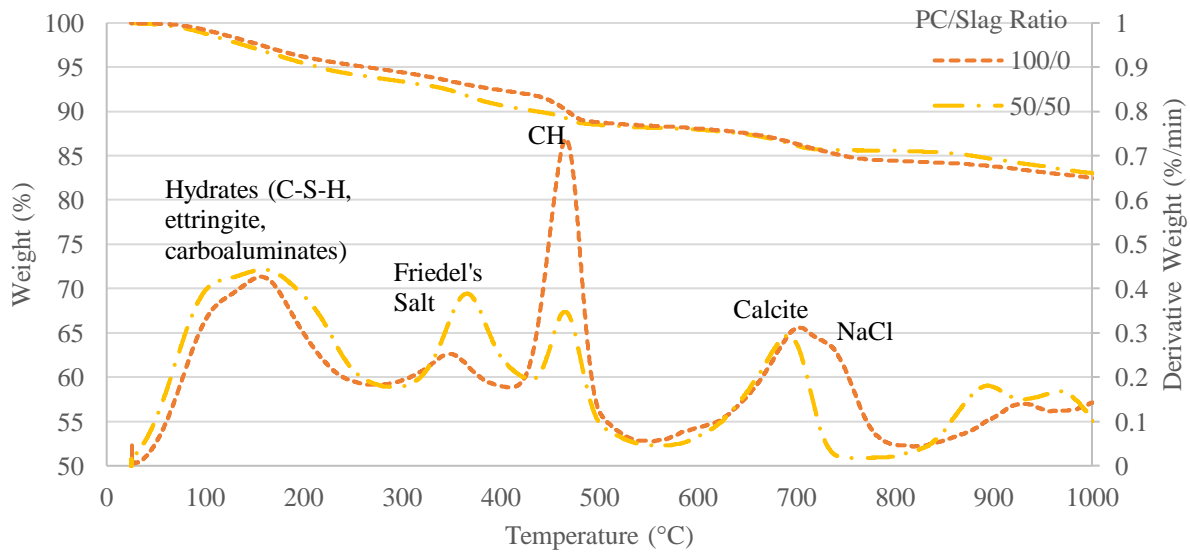


Figure 4.20 TG/DTG results for saline CPB with 100% PC and 50% slag after 2 hours of curing

Additionally, slag is less reactive than PC, so hydration progresses at a slower rate (as indicated by the electrical conductivity monitoring shown in Figure 4.21), which leaves unreacted water that lubricates the particles and further reduces the yield stress (Cao et al., 2018; Wu et al., 2014; Cheng et al., 2020; Zhou and Fall, 2022).

However, slag’s higher alumina content also leads to the formation of more Friedel’s salt (Xiao et al., 2021), as also shown by the TG/DTG results in Figure 4.20. This increases the solid volume of the mix and therefore the inter-particle friction and yield stress of the slag mix. Moreover, Friedel’s salt is bigger than NaCl, so the reduction in yield stress caused by the absence of NaCl is more than compensated for by the presence of Friedel’s salt, and the slag mix experiences a net increase in yield stress (Jiang and Fall, 2016; Xiao et al, 2021). Additionally, the formation of Friedel’s salt consumes water, which reduces the thickness of the water film around particles, thus reducing the lubrication between particles (Zhou and Fall, 2022) and further increasing the yield stress of the slag mixes.

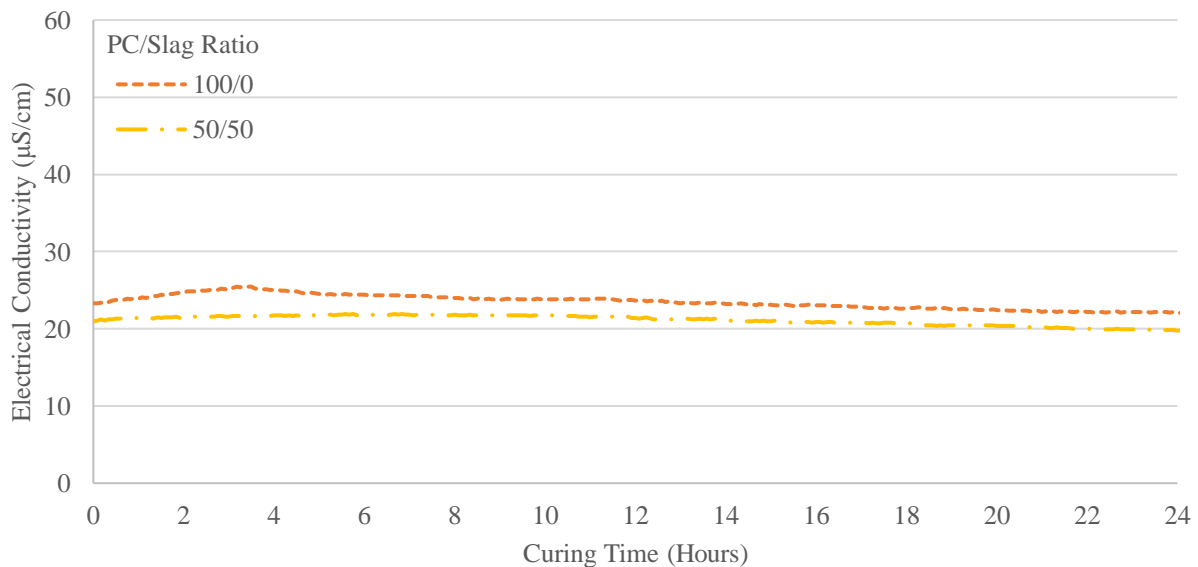


Figure 4.21 Impact of slag replacement on electrical conductivity over first 24 hours of curing

Finally, it can be seen from the pH testing results, shown in Figure 4.22, that the pH decreases at all curing times as the slag to PC ratio increases. This is due to the lower reactivity of slag compared to PC which causes a smaller amount of OH⁻ ions to be released. However, as curing time advances, more hydration occurs and the pH increases for all mixes. It has previously been found that the absolute value of the zeta potential increases with an increase in pH (Zhou and Fall, 2022), so it can be surmised that the increase in yield stress caused by the presence of Friedel’s salt is also compensating for the expected decrease in yield stress caused by the decrease in pH and zeta potential. This may also explain why the 50/50 PC/slag mix experienced the most increase in yield stress: this ratio experienced a greater increase in Friedel’s salt relative to the reduction in zeta potential and therefore a greater net increase in yield stress. Further research is required to explore this relationship.

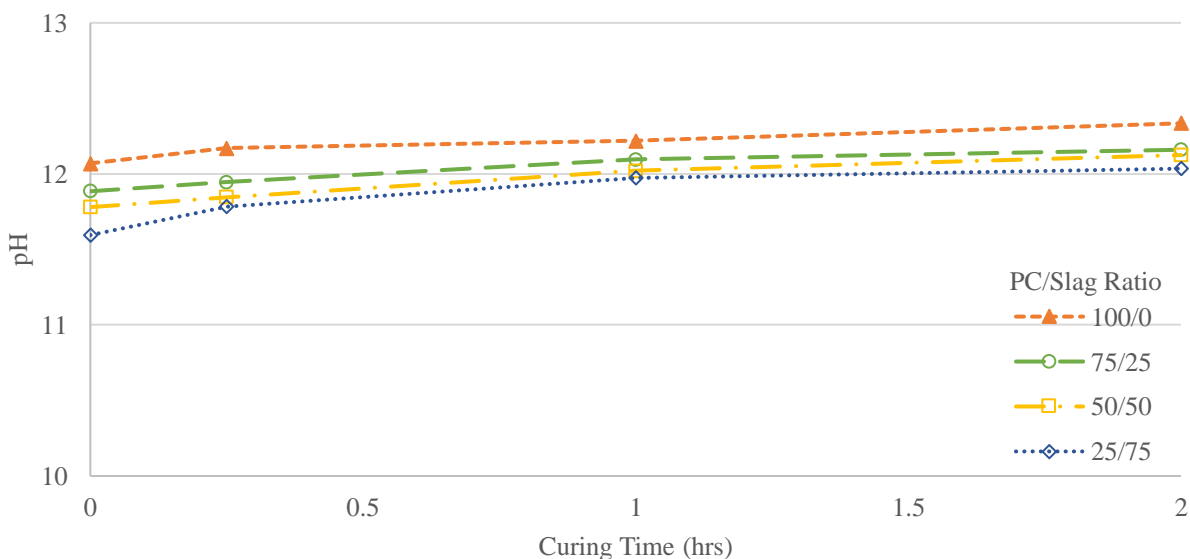


Figure 4.22 Impact of slag replacement on pH over first 2 hours of curing

4.4.2.2 Viscosity

The evolution of viscosity in saline CPB with varying slag content is shown below in Figure 4.23. It shows that an increase in slag content generally leads to a decrease in viscosity

and that slag causes the viscosity to decrease over the first two hours of curing, instead of increasing as CPB with only PC does. This effect is accentuated with increasing slag replacement.

Xiao et al. (2021) also found that CPB with slag had an overall lower viscosity than CPB with only PC; however, they tested non-saline samples and found that viscosity increased over curing time for the slag mix as well as the PC mix. It can therefore be assumed that the decrease in viscosity is due to the combined effect of slag and NaCl.

Slag’s slower reaction rate mentioned earlier may contribute to the results shown, but does not fully explain them.

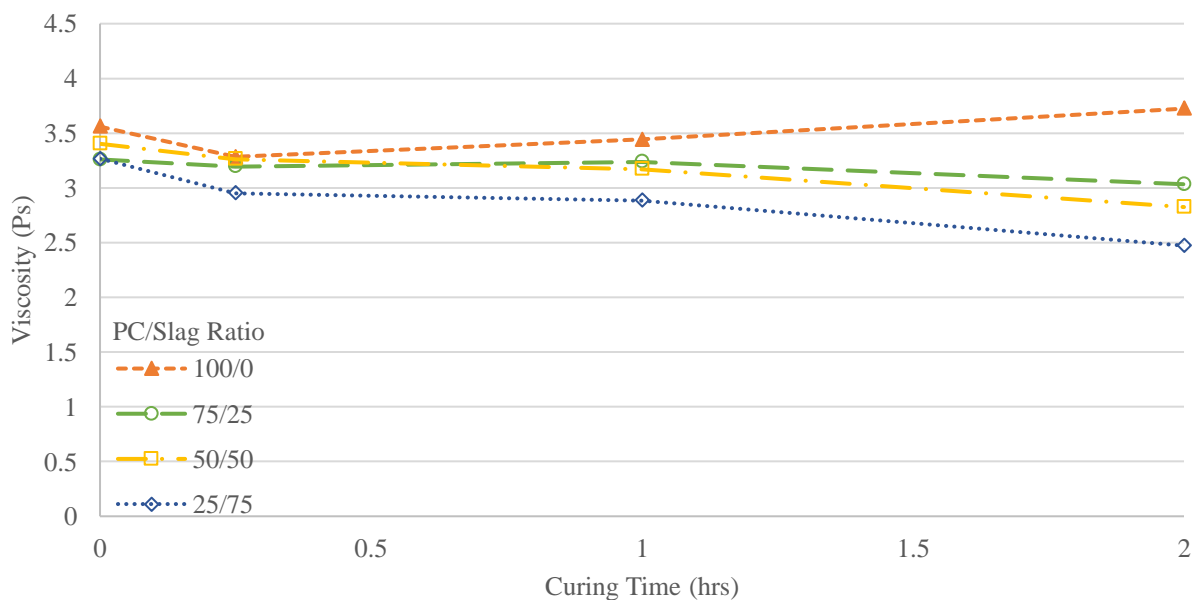


Figure 4.23 Impact of slag replacement on viscosity of saline CPB (NaCl content: 35 g/L) over first 2 hours of curing

A comparison of the peak values from the XRD results are presented in Figure 4.24 and Figure 4.25. They indicate that the PC-only mix saw a slight rise in NaCl between 1 and 2 hours of curing, and a slight decrease in CH and Friedel’s salt. Meanwhile, the slag mix saw a strong decrease in NaCl, CaCO₃, and CH and a small rise in Friedel’s salt. Overall quantities of CH were lower in the slag samples than in the PC samples.

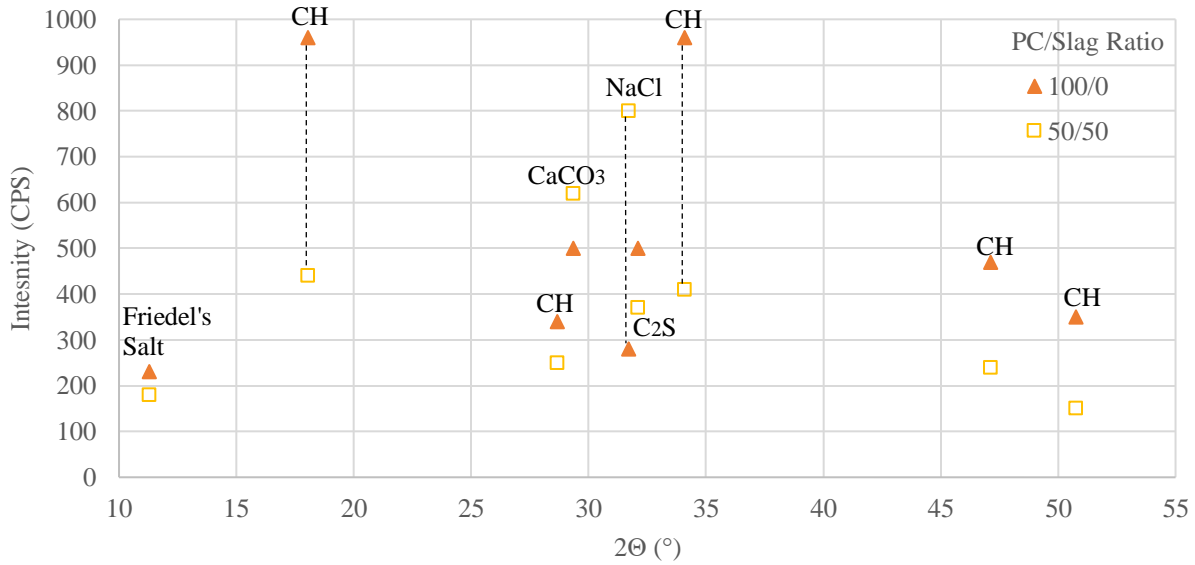


Figure 4.24 Comparison of XRD peaks for CPB with and without slag after 1 hour of curing

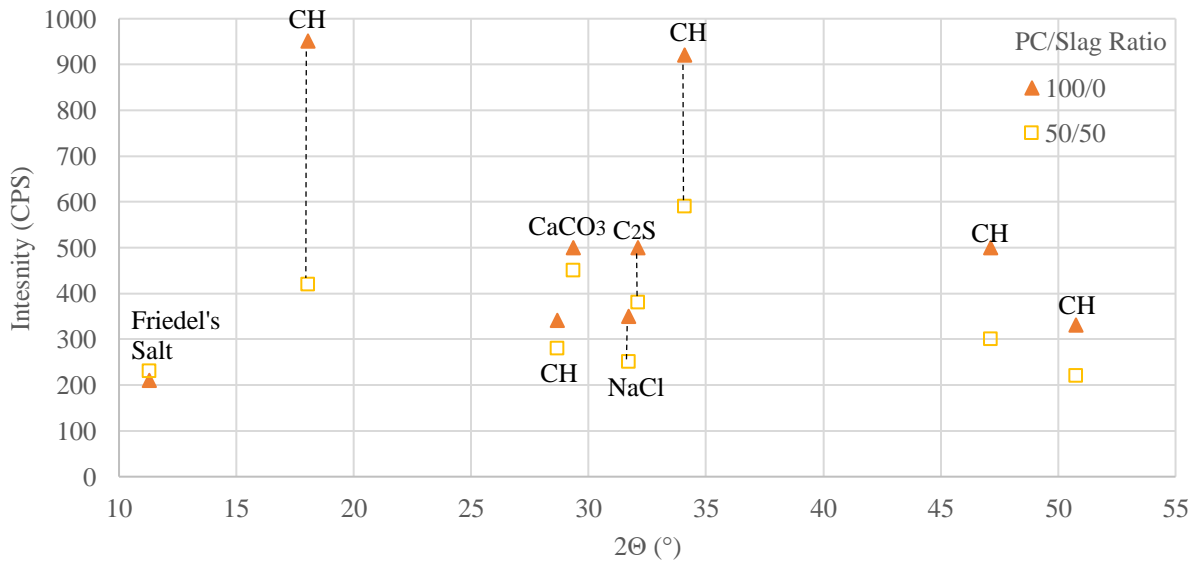


Figure 4.25 Comparison of XRD peaks for CPB with and without slag after 2 hours of curing

It is well known that slag consumes CH to form C-S-H, which is difficult to measure in either TG/DTG or XRD tests, due to its variable composition and gel structure. It can be concluded that the consumption of CH, NaCl, and CaCO₃ reduce the solid fraction of the slag-CPB which results in a lower viscosity over time. The production of C-S-H evidently does not compensate for the decrease in viscosity, possibly due to the increase in zeta potential from the

adsorbed chloride ions, which was shown previously in Figure 4.19. Furthermore, slag’s greater chloride binding potential than PC could also contribute to the reduction in viscosity due to increased zeta potential.

4.4.2.3 Setting Time

Figure 4.26 and Figure 4.27 below show the impacts of slag replacement on the times to initial and final set for saline CPB made with pure silica tailings and 35 g/L NaCl. The data shows that replacing any amount of PC with slag increases the time to initial set and that CPB made with 75% PC and 25% slag has an increase in time to final set, but further increase in slag replacement leads to a decrease in time to final set.

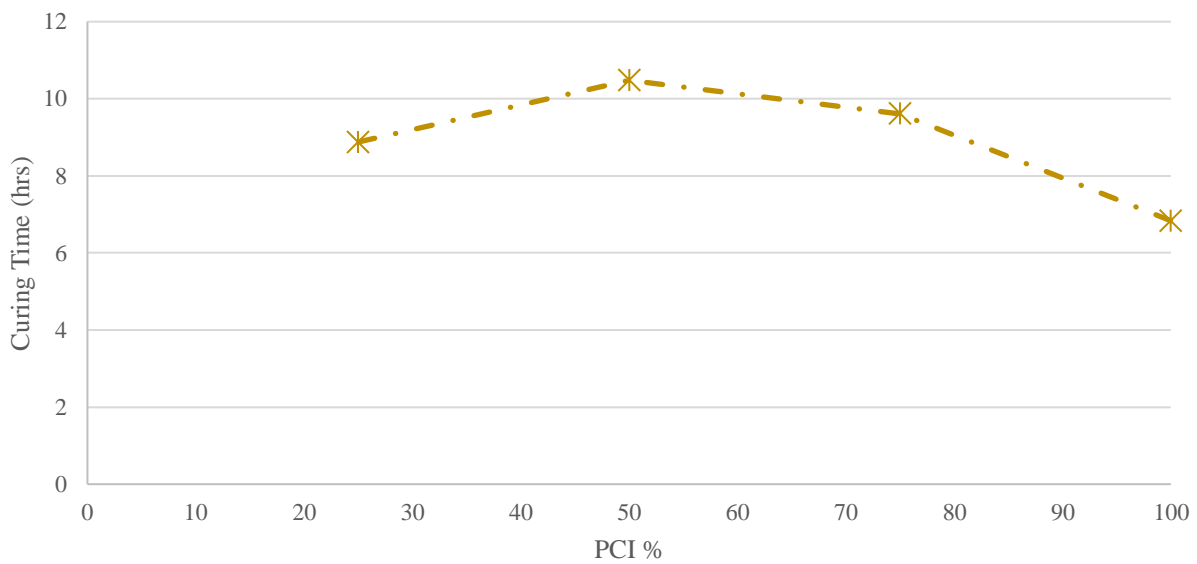


Figure 4.26 Impact of slag replacement on initial setting time of saline CPB (NaCl content: 35 g/L)

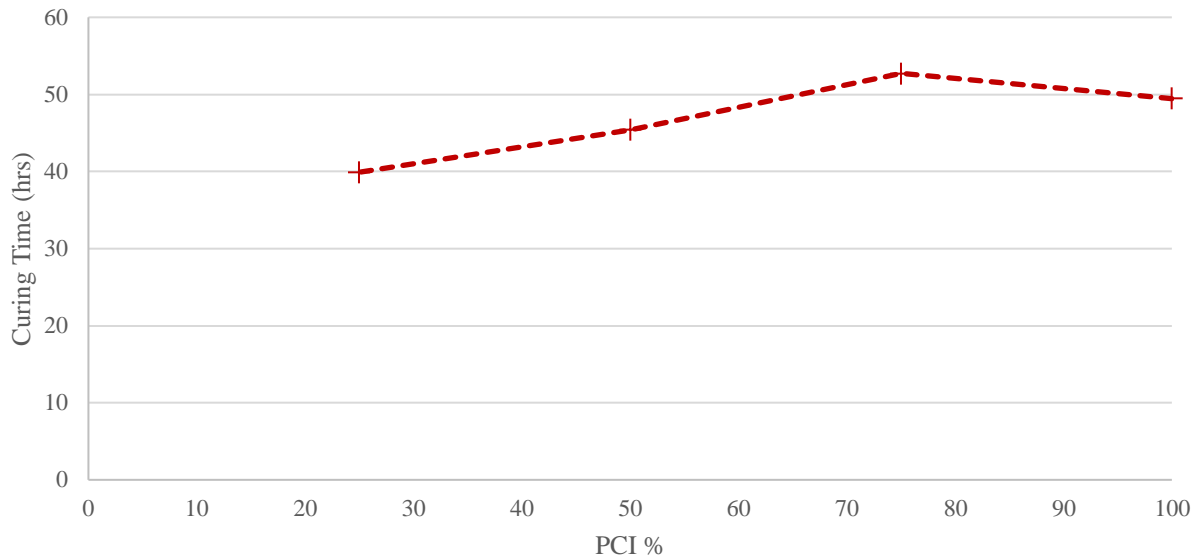


Figure 4.27 Impact of slag replacement on final setting time of saline CPB (NaCl content: 35 g/L)

It is well known that slag alone does not react with water and requires the formation of initial hydration products from the PC and water to begin the pozzolanic reactions, which are also slower than the cement reactions (Mehta and Monteiro, 2006). Therefore, replacement of PC with slag will result in an overall slower initial rate of reaction. This is why the time to initial set for all the slag mixes is higher than for the PC-only mix.

As was discussed earlier in the section on the setting time of saline PC-CPB, salinities above 35 g/L no longer promote the time to setting or can delay it. However, both the initial and final setting times begin to decrease after a certain slag replacement quantity. This is because the slag contains more alumina and significantly more silica than PC. Once there is sufficient CH in the paste to facilitate their reaction, they can contribute to accelerating the setting times, and the presence of Na^+ and Cl^- ions in the mixing water can facilitate their dissolution. It has been found that alumina controls the time to initial setting and silica contributes to final setting (Mehta and Monteiro, 2006), thus, the slightly increased quantity of alumina leads to a decrease in time to initial set at slag replacement quantities of greater than 50%, and the significantly increased

quantity of silica leads to a decrease in time to final set at slag replacement quantities of greater than 25%.

4.5 Summary and Conclusions

Viscosity, yield stress, and setting time testing were conducted on CPB with PC and a mixing water NaCl concentration from 0 g/L to 300 g/L. Results indicate that NaCl concentrations of 10 g/L and 35 g/L cause the yield stress to increase above the control within the first two hours after curing, while higher concentrations suppress the yield stress at all tested times. This is due to the role that NaCl plays in either accelerating or hindering cement hydration depending on concentration, and on the influence of the adsorbed chloride ions on the zeta potential of the paste. All tested NaCl concentrations led to a slight drop in viscosity 15 minutes after mixing, followed by an increase in viscosity, while the control experienced a steady increase for the first two hours after mixing. All concentrations of NaCl led to an overall lower viscosity after 2 hours compared to the control, though concentrations of 100 g/L and 300 g/L saw a significantly slower rate of increase compared to other concentrations and the control. This is due to the contribution of NaCl to the solid fraction of the paste and the influence of NaCl concentration on cement hydration. NaCl concentrations of 10 g/L and 35 g/L reduced the time to initial setting while a concentration of 300 g/L significantly increased it. A concentration of 10 g/L reduced the time to final set while concentrations greater than 35 g/L increased it. This is due to the varying net effects of the ionic concentrations on the dissolution rates of the different cement phases.

Viscosity, yield stress, and setting time testing were conducted on CPB with PC, 35 g/L NaCl, and varying slag replacement quantities. Slag content had little effect on the evolution of yield stress over the first two hours of curing due to a general balance in the effects of NaCl on

zeta potential, hydration acceleration, and slag's slower reaction time. An increase in slag content led to a decrease in viscosity over the first two hours of curing. Cement hydration and pozzolanic reactions consume NaCl, CaCO₃, and CH to form C-S-H and a small amount of Friedel's salt. This consumes water, but reduces the solid fraction of the paste, which have opposing effects on viscosity. Adsorption of chloride ions into the C-S-H combined with slag's greater chloride binding ability leads to increased zeta potential between paste components and a net loss in viscosity over the first two hours of curing. Increases in slag replacement of PC increase the time to initial set due to the overall slower reaction of slag, though this effect is eventually slightly mitigated at high replacement by the accelerating effects of NaCl on the dissolution of the additional alumina in the slag. A slag replacement of 25% increases the time to final set, while greater replacement quantities reduce it. This is due to the accelerating effects of the NaCl on the dissolution of the additional silica in the slag. This study will provide valuable information for designing efficient and cost-effective backfill mixes and systems, which will further allow mines to save on backfill, pumping, and surface tailings storage costs.

4.6 References

- ASTM Standard C125. (2021). *Standard Terminology Relating to Concrete and Concrete Aggregates*. ASTM International, West Conshohocken, PA, 1936, DOI: 10.1520/C0125-21A, www.astm.org
- ASTM Standard C807. (2021). *Standard Test Method for Time of Setting of Hydraulic Cement Mortar by Modified Vicat Needle*. ASTM International, West Conshohocken, PA, 1975, DOI: 10.1520/C0807-21, www.astm.org
- Banfill, P.F. (2003). The rheology of fresh cement and concrete-a review. *In Proceedings of the 11th international cement chemistry congress* (Vol. 1, pp. 50-62).
- Beaudoin, J.J., Ramachandran, V.S. and Feldman, R.F. (1990). Interaction of chloride and C-S-H. *Cement and Concrete Research*, 20(6), 875-883. [https://doi.org/10.1016/0008-8846\(90\)90049-4](https://doi.org/10.1016/0008-8846(90)90049-4)
- Bian, J., Fall, M. and Haruna, S. (2021). Sulfate-induced changes in rheological properties of fibre-reinforced cemented paste backfill. *Magazine of Concrete Research*, 73(11), 574-583. <https://doi.org/10.1680/jmacr.19.00311>
- Cao, S., Xue, G., Yilmaz, E. and Yin, Z. (2021). Assessment of rheological and sedimentation characteristics of fresh cemented tailings backfill slurry. *International Journal of Mining, Reclamation and Environment*, 35(5), 319-335. <https://doi.org/10.1080/17480930.2020.1826092>
- Cao, S., Yilmaz, E. and Song, W. (2018). Evaluation of viscosity, strength and microstructural properties of cemented tailings backfill. *Minerals*, 8(8), 352. <https://doi.org/10.3390/min8080352>

- Cavusoglu, I., Yilmaz, E. and Yilmaz, A.O. (2021). Sodium silicate effect on setting properties, strength behavior and microstructure of cemented coal fly ash backfill. *Powder Technology*, 384, 17-28. <https://doi.org/10.1016/j.powtec.2021.02.013>
- Cheng, H.Y., Wu, S.C., Zhang, X.Q. and Wu, A.X. (2020a). Effect of particle gradation characteristics on yield stress of cemented paste backfill. *International Journal of Minerals, Metallurgy and Materials*, 27(1), 10-17. <https://doi.org/10.1007/s12613-019-1865-y>
- Cheng, H., Wu, S., Li, H. and Zhang, X. (2020b). Influence of time and temperature on rheology and flow performance of cemented paste backfill. *Construction and Building Materials*, 231, 117117. <https://doi.org/10.1016/j.conbuildmat.2019.117117>
- Deng, X.J., Klein, B., Hallbom, D.J., de Wit, B. and Zhang, J.X. (2018). Influence of particle size on the basic and time-dependent rheological behaviors of cemented paste backfill. *Journal of Materials Engineering and Performance*, 27(7), 3478-3487. <https://doi.org/10.1007/s11665-018-3467-7>
- Elakneswaran, Y., Nawa, T. and Kurumisawa, K. (2009). Zeta potential study of paste blends with slag. *Cement and Concrete Composites*, 31(1), pp.72-76. <https://doi.org/10.1016/j.cemconcomp.2008.09.007>
- El Mahboub, K., Mbonimpa, M., Belem, T. and Maqsoud, A. (2022). Rheological characterization of cemented paste backfills containing superabsorbent polymers (SAPs). *Construction and Building Materials*, 317, p.125863. <https://doi.org/10.1016/j.conbuildmat.2021.125863>

- Ali, G., Fall, M. and Alainachi, I. (2021). Time-and Temperature-Dependence of Rheological Properties of Cemented Tailings Backfill with Sodium Silicate. *Journal of Materials in Civil Engineering*, 33(3), p.04020498. DOI: 10.1061/(ASCE)[MT.1943-5533.0003605
- Haruna, S. and Fall, M. (2020). Time-and temperature-dependent rheological properties of cemented paste backfill that contains superplasticizer. *Powder Technology*, 360, pp.731-740. <https://doi.org/10.1016/j.powtec.2019.09.025>
- Hou, C., Zhu, W., Yan, B., Guan, K. and Du, J. (2018). Influence of binder content on temperature and internal strain evolution of early age cemented tailings backfill. *Construction and Building Materials*, 189, pp.585-593. <https://doi.org/10.1016/j.conbuildmat.2018.09.032>
- Jiang, H. and Fall, M. (2017a). Yield stress and strength of saline cemented tailings in sub-zero environments: Portland cement paste backfill. *International Journal of Mineral Processing*, 160, pp.68-75. <https://doi.org/10.1016/j.minpro.2017.01.010>
- Jiang, H. and Fall, M. (2017b). Yield stress and strength of saline cemented tailings materials in sub-zero environments: Slag-paste backfill. *Journal of Sustainable Cement-Based Materials*, 6(5), pp.314-331. <https://doi.org/10.1080/21650373.2017.1280428>
- Jiang, H., Fall, M., Yilmaz, E., Li, Y. and Yang, L. (2020). Effect of mineral admixtures on flow properties of fresh cemented paste backfill: Assessment of time dependency and thixotropy. *Powder technology*, 372, pp.258-266. <https://doi.org/10.1016/j.powtec.2020.06.009>
- Klein, K. and Simon, D. (2006). Effect of specimen composition on the strength development in cemented paste backfill. *Canadian geotechnical journal*, 43(3), pp.310-324. <https://doi.org/10.1139/t06-005>

- Kou, Y., Jiang, H., Ren, L., Yilmaz, E. and Li, Y. (2020). Rheological properties of cemented paste backfill with alkali-activated slag. *Minerals*, 10(3), p.288.
<https://doi.org/10.3390/min10030288>
- Lang, L., Song, K.I., Lao, D. and Kwon, T.H. (2015). Rheological properties of cemented tailing backfill and the construction of a prediction model. *Materials*, 8(5), pp.2076-2092.
<https://doi.org/10.3390/ma8052076>
- Li, J., Yilmaz, E. and Cao, S. (2020). Influence of solid content, cement/tailings ratio, and curing time on rheology and strength of cemented tailings backfill. *Minerals*, 10(10), p.922.
<https://doi.org/10.3390/min10100922>
- Liu, S.G. and Fall, M. (2022). Fresh and hardened properties of cemented paste backfill: Links to mixing time. *Construction and Building Materials*, 324, p.126688.
<https://doi.org/10.1016/j.conbuildmat.2022.126688>
- Liu, Y., Li, H., Wang, K., Wu, H. and Cui, B. (2020). Effects of accelerator–water reducer admixture on performance of cemented paste backfill. *Construction and Building Materials*, 242, p.118187. <https://doi.org/10.1016/j.conbuildmat.2020.118187>
- McCarter, W.J., Chrisp, T.M., Starrs, G. and Blewett, J. (2003). Characterization and monitoring of cement-based systems using intrinsic electrical property measurements. *Cement and Concrete Research*, 33(2), pp.197-206. [https://doi.org/10.1016/S0008-8846\(02\)00824-4](https://doi.org/10.1016/S0008-8846(02)00824-4)
- Meißner, S. (2021). The Impact of Metal Mining on Global Water Stress and Regional Carrying Capacities—A GIS-Based Water Impact Assessment. *Resources*, 10(12), 120.
- Mehta, P.K. and Monteiro, P.J. (2014). *Concrete: microstructure, properties, and materials*. McGraw-Hill Education.
- Neville, A.M. (1995). *Properties of concrete* (Vol. 4, p. 1995). London: Longman.

- Niroshan, N., Sivakugan, N. and Veenstra, R.L. (2018). Flow characteristics of cemented paste backfill. *Geotechnical and Geological Engineering*, 36(4), pp.2261-2272.
<https://doi.org/10.1007/s10706-018-0460-8>
- Ouattara, D., Yahia, A., Mbonimpa, M. and Belem, T. (2017). Effects of superplasticizer on rheological properties of cemented paste backfills. *International Journal of Mineral Processing*, 161, pp.28-40. <https://doi.org/10.1016/j.minpro.2017.02.003>
- Panchal, S., Deb, D. and Sreenivas, T. (2018). Variability in rheology of cemented paste backfill with hydration age, binder and superplasticizer dosages. *Advanced Powder Technology*, 29(9), pp.2211-2220. <https://doi.org/10.1016/j.appt.2018.06.005>
- Roshani, A. and Fall, M. (2020). Flow ability of cemented pastefill material that contains nano-silica particles. *Powder technology*, 373, pp.289-300.
<https://doi.org/10.1016/j.powtec.2020.06.050>
- Roshani, A. and Fall, M. (2020). Rheological properties of cemented paste backfill with nano-silica: link to curing temperature. *Cement and Concrete Composites*, 114, p.103785.
<https://doi.org/10.1016/j.cemconcomp.2020.103785>
- Simon, D. and Grabinsky, M. (2013). Apparent yield stress measurement in cemented paste backfill. *International Journal of Mining, Reclamation and Environment*, 27(4), pp.231-256. <https://doi.org/10.1080/17480930.2012.680754>
- Simon, D. and Grabinsky, M.W. (2012). Electromagnetic wave-based measurement techniques to study the role of Portland cement hydration in cemented paste backfill materials. *International Journal of Mining, Reclamation and Environment*, 26(1), pp.3-28.
<https://doi.org/10.1080/17480930.2012.639193>

- Suryavanshi, A.K., Scantlebury, J.D. and Lyon, S.B. (1996). Mechanism of Friedel's salt formation in cements rich in tri-calcium aluminate. *Cement and concrete research*, 26(5), pp.717-727. [https://doi.org/10.1016/S0008-8846\(96\)85009-5](https://doi.org/10.1016/S0008-8846(96)85009-5)
- Taylor, H.F. (1997). *Cement chemistry* (Vol. 2, p. 459). London: Thomas Telford.
- Wei, X. and Li, Z. (2006). Early hydration process of Portland cement paste by electrical measurement. *Journal of materials in civil engineering*, 18(1), pp.99-105. [https://doi.org/10.1061/\(ASCE\)0899-1561\(2006\)18:1\(99\)](https://doi.org/10.1061/(ASCE)0899-1561(2006)18:1(99))
- Wu, D., Cai, S.J. and Huang, G. (2014). Coupled effect of cement hydration and temperature on rheological properties of fresh cemented tailings backfill slurry. *Transactions of Nonferrous Metals Society of China*, 24(9), pp.2954-2963. [https://doi.org/10.1016/S1003-6326\(14\)63431-2](https://doi.org/10.1016/S1003-6326(14)63431-2)
- Wu, D., Fall, M. and Cai, S.J. (2013). Coupling temperature, cement hydration and rheological behaviour of fresh cemented paste backfill. *Minerals Engineering*, 42, pp.76-87. <https://doi.org/10.1016/j.mineng.2012.11.011>
- Wu, H., Liu, Y., Wang, H., Wang, K. and Hu, W. (2021). Study on the effect of mixing water on coal mine filling cemented paste backfill performance under pH-T coupling conditions. *Arabian Journal of Geosciences*, 14(12), pp.1-10. <https://doi.org/10.1007/s12517-021-07301-1>
- Xiao, B., Fall, M. and Roshani, A. (2021). Towards understanding the rheological properties of Slag-Cemented paste backfill. *International Journal of Mining, Reclamation and Environment*, 35(4), pp.268-290. <https://doi.org/10.1080/17480930.2020.1807667>

- Xiapeng, P., Fall, M. and Haruna, S. (2019). Sulphate induced changes of rheological properties of cemented paste backfill. *Minerals Engineering*, 141, p.105849.
<https://doi.org/10.1016/j.mineng.2019.105849>
- Xu, W., Chen, W., Tian, M. and Guo, L. (2021). Effect of temperature on time-dependent rheological and compressive strength of fresh cemented paste backfill containing flocculants. *Construction and Building Materials*, 267, p.121038.
<https://doi.org/10.1016/j.conbuildmat.2020.121038>
- Xu, W., Li, Q. and Haruna, S. (2019). The effect of calcium formate, sodium sulfate, and cement clinker on engineering properties of fly ash-based cemented tailings backfill. *Advances in Materials Science and Engineering*, 2019. <https://doi.org/10.1155/2019/5370360>
- Xu, W., Tian, M. and Li, Q. (2020a). Time-dependent rheological properties and mechanical performance of fresh cemented tailings backfill containing flocculants. *Minerals Engineering*, 145, p.106064. <https://doi.org/10.1016/j.mineng.2019.106064>
- Xu, W., Zhang, Y., Zuo, X. and Hong, M. (2020b). Time-dependent rheological and mechanical properties of silica fume modified cemented tailings backfill in low temperature environment. *Cement and Concrete Composites*, 114, p.103804.
<https://doi.org/10.1016/j.cemconcomp.2020.103804>
- Xue, Z., Gan, D., Zhang, Y. and Liu, Z. (2020). Rheological behavior of ultrafine-tailings cemented paste backfill in high-temperature mining conditions. *Construction and Building Materials*, 253, p.119212. <https://doi.org/10.1016/j.conbuildmat.2020.119212>
- Yang, Y., Wu, D., He, L. and Wang, B. (2022). Coupled thermo-hydro-chemical effect on rheological behavior of fresh cemented tailings backfill. *Advanced Powder Technology*, 33(1), p.103393. <https://doi.org/10.1016/j.apt.2021.12.012>

Yin, S., Wu, A., Hu, K., Wang, Y. and Zhang, Y. (2012). The effect of solid components on the rheological and mechanical properties of cemented paste backfill. *Minerals Engineering*, 35, pp.61-66. <https://doi.org/10.1016/j.mineng.2012.04.008>

Zhang, Q.L., Li, Y.T., Chen, Q.S., Liu, Y.K., Feng, Y. and Wang, D.L. (2021). Effects of temperatures and pH values on rheological properties of cemented paste backfill. *Journal of Central South University*, 28(6), pp.1707-1723. <https://doi.org/10.1007/s11771-021-4728-4>

Zhao, Y., Taheri, A., Karakus, M., Chen, Z. and Deng, A. (2020). Effects of water content, water type and temperature on the rheological behaviour of slag-cement and fly ash-cement paste backfill. *International Journal of Mining Science and Technology*, 30(3), pp.271-278. <https://doi.org/10.1016/j.ijmst.2020.03.003>

Zhou, Y. and Fall, M. (2022). Investigation on rheological properties of cemented pastefill with chloride-bearing antifreeze additives in sub-zero environments. *Cold Regions Science and Technology*, 196, p.103506. <https://doi.org/10.1016/j.coldregions.2022.103506>

Zhou, Y., Fall, M. and Haruna, S. (2022). Flow ability of cemented paste backfill with chloride-free antifreeze additives in sub-zero environments. *Cement and Concrete Composites*, 126, p.104359. <https://doi.org/10.1016/j.cemconcomp.2021.104359>

Chapter 5: Synthesis of Results

5.1 Summary of Investigations

The factors investigated in both technical papers are summarized in Table 5.1.

Table 5.1 Parameters studied in this thesis

Chapter	Technical Paper	Curing Time									PC/Slag Ratio in Binder				NaCl concentration (g/L)				
		0 min	15 min	1 hr	2 hrs	1 day	3 days	7 days	28 days	60 days	100/0	75/25	50/50	25/75	0	10	35	100	300
3	1					X	X	X	X	X	X	X	X	X	X	X	X	X	X
4	2	X	X	X	X						X	X	X	X	X	X	X	X	X

The tests performed on the mixes in both technical papers are summarized in Table 5.2.

An “X” indicates that all curing times indicated in Table 5.2 were tested.

Table 5.2 Tests conducted in this thesis

Chapter	Technical Paper	Rheology			Microstructure						Monitoring			
		Yield Stress	Viscosity	Setting Time	UCS	TG/DTG	XRD	SEM	MIP	pH	Zeta Potential	Suction	VWC	EC
3	1				X	28 days	28 days	28 days	28 days			0-28 days	0-28 days	0-28 days
4	2	X	X	X		1, 2 hrs	1, 2 hrs			X	1 hr	0-24 hrs	0-24 hrs	0-24 hrs

Samples were prepared using pure ground silica, ordinary Portland Cement, tap water, NaCl, and ground granulated blast furnace slag when required by the mix design. Some samples were prepared with natural gold tailings instead of silica tailings and subjected to primary testing to ensure that conclusions drawn from the silica tailing samples were applicable to the materials

more likely to be used in industry. Finally, samples prepared for TG/DTG and XRD analyses were cement paste samples that were made without any tailings component at all.

5.2 Effect of NaCl Concentration

5.2.1 On Rheology

It was found that the yield stress of all mixes experienced an overall increase in yield stress after 2 hours of curing. Mixes with low concentrations of NaCl (10 g/L – 35 g/L) experienced a greater and more rapid increase than the non-saline control mix, while samples with high concentrations of NaCl (100 g/L – 300 g/L) experienced slower and less overall increase in yield stress than the control. The overall increase in yield stress was found to be due to the increase in hydration products over time as hydration reactions progress, leading to an increased flocculant structure and more particle-particle contacts. Low concentrations of NaCl were found to accelerate the hydration reactions when compared against the control, which led to a greater increase in yield stress, while high concentrations of NaCl retarded the hydration reactions and led to significantly lower increase in yield stress. It was also found that an increase in NaCl concentration led to a decrease in initial yield stress as compared to the non-saline control sample, and that the decrease increased with increasing NaCl concentration. The chloride ions were adsorbed onto the surfaces of the anhydrous cement and cement hydration products, which increased the absolute value of the zeta potential of the mixes and increased the inter-particle electrostatic repulsive forces, leading to less particle-particle contacts and lower yield stress.

It was found that an increase in NaCl concentration led to an increase in initial viscosity, but that the presence of NaCl also caused the viscosity to decrease in the first fifteen minutes after mixing, which then increased until two hours, while the non-saline control mix experienced

a continuous increase from initial mixing. The final viscosity of the non-saline mix was greater than the saline mixes after two hours due to not experiencing any decrease after 15 minutes. It was found that the increase in initial viscosity of the saline mixes was due to the increased solid volume fraction from the addition of the NaCl, and that the reduction in viscosity after 15 minutes was due to the adsorption of the NaCl onto the cement particles and hydration products. The ensuing increase in viscosity for all mixes was due to the formation of hydration products and consumption of water, which again increased the solid volume fraction, over the following two hours. Low salinity mixes experienced a greater viscosity increase than the control and the high salinity mixes experienced a lower viscosity increase. This was determined to be due to the hydration accelerating effects of low concentrations of NaCl and retarding effects of high concentrations. Suction monitoring confirmed the relative rates of hydration and changes in water content.

5.2.2 On Setting Time

It was found that concentrations of 10 g/L – 100 g/L of NaCl decreased the time to initial setting compared to the non-saline control, with 35 g/L leading to the shortest initial setting time. A concentration of 10 g/L of NaCl significantly decreased the time to final setting, but concentrations of 100 g/L – 300 g/L increased it. A concentration of 35 g/L NaCl had little difference in final setting time from the control mix.

Previous research indicates that the setting of cement is controlled by the dissolution rates of the cement components, which is guided by the presence of ions. Na⁺ ions reduce the solubility of the calcium phase and improve the solubility of the silicate and aluminate phases, while Cl⁻ ions have the opposite effect. At the NaCl concentrations tested, the net effect was an increase in dissolution rates and faster setting times. However, at high concentrations of NaCl,

the mixing water became saturated with NaCl which hindered the dissolution of the cement particles, as was evidenced by the NaCl residue left after mixing.

5.2.3 On Strength Gain

It was found that low concentrations of NaCl (10 g/L – 35 g/L) led to an increase in the UCS as compared to the control over all curing times tested, with a concentration of 10 g/L resulting in the highest UCS. High concentrations of NaCl (100 g/L – 300 g/L) led to a decrease in the UCS as compared to the control. A concentration of 100 g/L resulted in roughly comparable UCS to the control after 28 days of curing, while a concentration of 300 g/L resulted in significantly reduced UCS over all curing times tested.

This was determined to be due to a combination of factors. Factors considered include: acceleration, retardation, and suppression of hydration by NaCl, impact on fineness of pore structure, suction, precipitation of Friedel's Salt, NaCl, and ettringite into the pore spaces, and weakening or strengthening of hydration products by Na⁺ ion replacement and pH of pore solution. It was concluded that though low salinity mixes had higher porosity and greater pore sizes than the control and high salinity mixes, they also experienced a more moderate formation of Friedel's salt, ettringite, and precipitated NaCl. These products filled in the pore space and contributed to the UCS of the CPB. It was concluded that high salinity mixes produced an excess quantity of Friedel's salt which, while contributing to the UCS, also damaged the finer pore structure of the CPB and limited the formation of strength-contributing hydration products such as C-S-H. Suction was concluded to be an insignificant contributor of strength to UCS, though it provided useful information for the interpretation of results.

Low concentrations of NaCl were concluded to result in an optimal balance of pore structure, advantageous quantities of precipitated minerals, and hydration product formation for the highest UCS.

5.3 Effect of Binder Type

5.3.1 On Rheology

It was found that, in general, the quantity of PC replaced with slag in the binder had only a minor impact on the yield stress of saline CPB over the first two hours, with the presence of slag slightly increasing the yield stress. A number of factors contributed the yield stress in opposing directions and appeared to negate each other. Contributing to a decrease in yield stress, slag has a higher chloride binding capacity than PC, which allowed more of the Cl^- ions to be adsorbed and increase the zeta potential and inter-particle spacing of the mix, while also removing NaCl from the solution and reducing the quantity of particles. In addition, slag's slower reaction rate left more free water to lubricate particles. Contributing to an increase in yield stress, slag-CPB formed higher quantities of Friedel's salt, which is a large precipitate that consumes water and resulted in more inter-particle friction.

It was found that an increase in slag replacement led to a general decrease in viscosity of the saline CPB, though this effect was more noticeable from one hour of curing onwards. Contrary to PC-CPB which increases in viscosity from one hour to two hours, slag-CPB decreases. It was concluded that the combined effect of slag's slower reaction rate and consumption of CH, NaCl, and CaCO_3 resulted in a lower solid volume fraction than the PC mix and that the resulting C-S-H had not yet hardened enough to contribute to an increase in viscosity. In addition, slag's greater chloride binding capacity led to an increase in zeta potential and decrease in viscosity.

5.3.2 On Setting Time

It was found that the presence of slag increased the initial setting time of saline CPB, with a 50% replacement resulting in the longest time to initial set, and that a 25% replacement increased the time to final setting while greater replacement rates decreased it. It was determined that slag's overall slower hydration rates as compared to PC was the primary cause for the delayed initial set. The higher quantities of alumina and silica present in slag shifted the relative ratios of these minerals to NaCl and therefore the balance of ionic effects on delaying or accelerating setting. The slightly increased quantities of alumina contributed to a decrease in time to initial set at replacements above 50% and the significantly higher quantities of silica led to a decrease in time to final set at replacements above 25%.

5.3.3 On Strength Gain

It was found that the presence of slag in the binder led to little variation in UCS of saline CPB from 1 to 3 days, but then led to an increase in UCS from 7 to 60 days, with a 50% replacement resulting in the highest UCS at 28 and 60 days. It was determined that the slag mix had a finer pore structure than the PC mix after 28 days of curing which contributed to its higher UCS and significantly higher suction, which was also believed to contribute to the UCS. It was also determined that that the slag mix had a higher quantity of Friedel's Salt which also likely contributed to the UCS. It is important to note that the use of NaCl and slag in combination appeared to negate each other's negative effects. The increased alkalinity from the NaCl accelerated the usually slow hydration of slag, while the slag's higher alumina content led to the formation of more Friedel's Salt which was able to be accommodated in the slag mix's higher total porosity without damaging the microstructure. In addition, the hydration reactions involving slag consume CH to form secondary C-S-H which further contributes to the UCS.

5.4 Conclusions

It has been found that the addition of low concentrations (up to 35 g/L) of NaCl provide significant benefits to CPB in all tested parameters. These concentrations reduced initial yield stress and short-term viscosity (up to 2 hours), though they increased initial viscosity and short-term yield stress. This could still be considered advantageous as the yield stress roughly correlates with the stress needed to initiate flow while the viscosity is the stress needed to maintain flow. Therefore, both conditions are more favourable for the situation where freshly mixed CPB must be transported from a plant on the ground surface to the stope underground, reducing the energy required to both initiate and maintain flow. In addition, these concentrations reduce or do not affect the times to initial and final setting and have been shown to increase the UCS at all curing times up to 60 days. Reduced setting times and increased strength gain is very beneficial as it allows the barricades sealing in the stopes to be removed earlier, and mining to continue faster, improving mine productivity. In particular, a NaCl concentration of 10 g/L appears to provide the greatest benefit for short-term, mid-term, and long-term requirements. As mentioned in Section 2.1.1, the typical chloride content of seawater is 35 g/L, which was also demonstrated to offer numerous benefits such as increased strength gain over all curing times, lower initial yield stress, and shorter initial setting time. This encourages the application of seawater as an economical and environmentally friendly substitute or partial relief for freshwater in mine backfill. It should be noted that the presence of chlorides and other ions will accelerate the corrosion of the pipes used to transport the backfill, so corrosion-resistant pipes should be used.

Furthermore, it has been found that the use of slag also contributes benefits to saline CPB in most tested parameters as well. The replacement of some PC with slag had no significant

effect on the yield stress but did noticeably reduce the viscosity up to 2 hours of curing, which is neutral or favourable for pumping. The use of slag did negatively influence the time to initial setting but it also positively influenced the time to final setting, especially at higher replacement quantities of 50% to 75%. This indicates that judgement will be required from designers to prioritize the more critical parameters in each individual application, though it is likely that the final setting time will be more crucial in most applications. Additionally, the use of slag significantly improved the UCS at all tested curing times up to 60 days. In particular, high slag replacement contents of up to 50% and 75% provide the most benefit for short-term, some mid-term, and long-term requirements.

The results of this thesis provide highly encouraging and useful information for the design and implementation of CPB. It clearly demonstrates that the economical and practical approach of using slightly saline, non-potable, and locally available groundwater or seawater as mixing water and high slag replacement contents also provides significant engineering advantages for rheology, setting time, and strength gain. These engineering advantages further translate into cost savings for mines in the form of reduced pumping effort and costs, lower risk of pipeline clogging, reduced times to open stope barricades, faster time to opening secondary stopes, reduced risk of ore dilution, increased miner safety, and overall improvement of mine efficiency. Combined with the environmental benefits of using CPB to reduce surface storage of tailings and demand for third-party backfill material, it is hopeful that more mines in Canada and around the world will adopt this highly advantageous technology, which will lead to increased profits, better availability of crucial primary resources, and more sustainable operations.

Chapter 6: Conclusions and Recommendations

6.1 Conclusions

This study has demonstrated that:

- The initial yield stress of CPB decreases with increasing concentration of NaCl.
- The addition of 10 g/L – 35 g/L of NaCl leads to greater increase in yield stress with time compared to the non-saline control and the addition of 100 g/L – 300 g/L of NaCl leads to significantly lower increase in yield stress with time.
- The viscosity of non-saline CPB increases with curing time while the viscosity of saline-CPB decreases slightly 15 minutes after mixing and then increases with curing time.
- The initial viscosity of CPB increases with increasing concentration of NaCl, but non-saline-CPB has a higher viscosity after 2 hours of curing than saline-CPB.
- Initial and final setting times decrease with the addition of low (10 g/L – 35 g/L) concentrations of NaCl but increase with high (100 g/L – 300 g/L) concentrations.
- Slag replacement of PC in binder has little effect on yield stress of saline CPB.
- Viscosity of saline CPB decreases with increasing slag replacement and curing time.
- Initial setting time increases with slag replacement content until 50% and then begins to decrease slightly. Final setting time increases slightly with a slag replacement content of 25% but then decreases with increasing slag replacement.
- The UCS increases over all curing times with the addition of low (10 g/L – 35 g/L) concentrations of NaCl and decrease over most curing times with the addition of high (100 g/L – 300 g/L) concentrations. A concentration of 10 g/L provides the highest increase and 300 g/L results in significant reductions in UCS.

- The UCS of saline CPB increases at high slag replacement contents (50% – 75%) after 3 days of curing.

6.2 Recommendations

Though the results of this study were significant, the work undertaken was limited in time and facilities. Recommendations for future research include:

- Modelling of impacts of NaCl and slag content on rheology and UCS to predict optimal designs for both requirements.
- Examining the studied rheological properties at curing times of up to 4 to 6 hours, to understand the impacts facing future mines with deepening mineral reserves.
- Examining the studied UCS properties at curing times greater than 60 days, to understand the long-term impacts of NaCl on the durability of CPB, and the long-term impact of slag on saline-CPB. This would provide mines with flexibility in planning operations by allowing them to return to extract lower-grade ore at more economical times.
- A deeper examination into the mechanisms that guide the formation of ettringite, Friedel's Salt, and monosulphate throughout the hydration processes, so as to better understand the role of NaCl in this process and identify concentrations and additives to produce optimal properties.