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WITWATERSRAND,
JOHANNESBURG

Coal Combustion Products in Mine Backfilling

Prepared by

Cherante Pardesi

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Supervised by

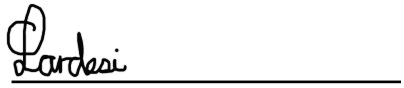
Craig Sheridan

Johannesburg

2021

Declaration

I, Cherante Leah Pardesi, hereby declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.



6th day of September 2021

Executive Summary

Fly ash and coarse ash are waste products that are generated in large quantities in South Africa from coal-based power stations. These ashes are often dumped in landfill sites, ash dams or lagoons and left to undergo chemical weathering. The growing presence of these disposal sites is creating numerous short and long-term environmental problems predominately due to the risk of element mobility, especially in the case of toxic metal release. In addition to the solid ash waste produced, a significant amount of wastewater is also produced. In an attempt to recover and reuse this water through various treatment methods, a stream containing predominately inorganic dissolved salts, known as brine, is formed. The disposal of this brine, as well as the ashes generated from coal-fired power stations, is a cause of concern due to the large quantities of waste produced which are not being utilized further in a sustainable manner. Furthermore, the disposal of brines creates an environmental risk due to the possible ingress of the inorganic salts and other trace elements into the surrounding environment.

The possibility that a potential solution exists to combat the disposal problems associated with both these wastes is worthwhile to explore. This potential solution exists through the use of mine backfilling, specifically cemented paste backfilling. Backfilling is defined as the process whereby mine tailings and other mine wastes are placed or reinserted into the void openings of underground mines in order to provide structural stability. Furthermore, the use of a cemented paste backfill is a viable option as it utilizes a mixture of different ash waste, hydraulic binders as well as brine. These constituents can be made into a thickened slurry or paste and pumped underground into the surrounding mine voids. This will reduce the current cost of disposal and simultaneously reduce the current adverse environmental impact associated with the disposal of these wastes. It is therefore important to investigate the environmental impact of both the current surface disposal methods and that of the cemented paste backfill in order to fully understand the leaching and mobility of the contaminant species and to determine the possibility of capturing salts from the brine solution into the cemented paste backfill. This study aimed to examine both these aspects through research methods which consist of a statistical analysis followed by a practical experimental verification.

Prior to examining the leachability of the cemented paste backfill, sixty-seven ash samples of different types (fly ash, coarse ash and mixed ash which consists of a mixture of the two ashes) in different states (fresh and weathered) were examined for statistically significant differences. A two-way analysis of variance (ANOVA) was conducted in order to determine if significant differences existed between the average values of the different ash states and types with regards to the total elemental concentration and leachability or leachable fraction. This analysis aimed to determine trends in the elemental release of these different ash types following long term chemical weathering. Furthermore, this analysis provided information on the relationship between the elemental release and the total concentration in the various ash in order to predict the long term environmental suitability of alternative disposal practices. It was found that fresh ashes have a higher SiO_2 content than weathered ashes particularly due to this phase being encapsulated in the glassy matrix of the ashes and are thus not easily released. Weathered ashes have a lower SiO_2 content as most of the SiO_2 has been leached out following repeated weathering cycles. Elemental release only occurs upon weathering when this glassy matrix has been broken down leading to the release of elements such as As, Sb, G, Rb, Ce, and Li. This is also seen in the case of Si, Fe, and K whereby a linear relationship was observed between the leachable fraction and the total elemental concentration where higher leachability was observed as the concentration increased in the weathered ashes. In some instances, the elemental release was independent of the state of the ash in specifically the case of Sn, Te, Ti, Pb, Bi, and Be. On the other hand, elements that were located on the more soluble internal fraction of the ashes such as B, Ga, and Sr and are more easily released in the fresh ashes. Generally, a relatively small difference is found regarding element mobility between fresh and weathered ashes suggesting that equilibrium has been reached between the ash particles and the surrounding water and once the readily available and easily leached elements are removed, the system remains stable with time and no further release occurs. Upon analysis of the elemental percentage leached out into solution, the percentages were found to be low indicating that the risk of metal leaching is not of concern. These results indicated favourable properties for further use in cemented paste backfill applications.

It was found that fly ash (FA) and coarse ash (CA) are useful in backfill applications due to their pozzolanic reactivity. This study examined the mineralogical and chemical constituents of the ashes that enhance this reaction, thus improving the long-term strength development of the cemented paste backfill (CPB). Favourable ash properties include class F ashes with

a high SiO_2 content ($SiO_2 \geq 50\%$), a low CaO content ($CaO \leq 10\%$), a low total equivalent alkalis content ($Na_2O_{eq} < 1.5\%$), a low MgO content ($MgO < 5\%$) and a low LOI ($LOI < 6\%$). If these properties are adhered to, the CPB shows favourable results in terms of both environmental and structural suitability. Environmental suitability refers to an instance whereby the CPB will not have a detrimental impact on the surrounding environment in terms of high concentrations of contaminants leached into the environment. Structural suitability refers to a case whereby significant strength development of the CPB is achieved such that the land above the CPB can be used for other purposes and will not be subjected to collapse.

In order to further examine the environmental suitability of the use of FA, CA, MA and brine in the CPB, several leaching procedures such as the tank leach test (TLT), weathering cell test (WCT), and acid neutralization capacity (ANC) tests were employed. The structural suitability for backfilling was examined by measuring the unconfined compressive strength (UCS) at various predetermined intervals. The UCS showed that CPB mixtures containing greater proportions of FA which met the favourable characteristics stated above met the required strength limits. However, additional factors such as particle size and loss on ignition (LOI) determined the extent to which the reaction hydration products were produced and subsequent strength development. It was found that a smaller particle size drastically improved the pozzolanic reaction and strength development in comparison to samples containing ash characteristic of a larger particle size. The leaching behaviour of trace metals such as Pb, As, Cr and Ni, as well as other ionic species associated with soluble salts such as Ca, Na, Mg, K, Fe, Al, B, and Ba, were investigated to examine the potential environmental impact. Acid neutralization tests showed that leaching increased linearly as the pH of the leachant decreased for Ca, Mg and B. Leaching is found to be independent of solution pH with regards to the release of Na, K, and Ba. Cr and Pb exhibited amphoteric behaviour with higher solubility observed at the extreme ends of the pH range. Results from the TLT used to simulate flooding of the CPB showed that the leachable concentrations of soluble salts in the leachate were released in the order of Na > Ca > K > Mg. A large fraction of these soluble salts are available as they are deposited on the surface of the monoliths and thus a high release was observed initially upon contact with water. Results showed that the CPB posed a significantly lower environmental risk in comparison to surface ash disposal. The leachates contained a lower amount of soluble salts and metals in comparison to the WCT. This indicates that these elements are encapsulated within the CPB. Furthermore, the

total elemental percentage leached out of the ashes in the TLT was significantly smaller than the percentage release for the WCT and the surface ash disposal. Particle size and exposed surface area have the greatest effect on the leaching behaviour of the monoliths. The addition of small proportions of CA reduces leachability as a lower elemental release is seen for Na, Mg, K, and Ba in comparison to the backfill mixtures containing only fly ash. The presence of CA improves the interparticle friction which creates a denser CPB that exhibits lower leachability. By physically and chemically altering the FA, CA and brine interaction a more environmentally suitable option exists for the co-disposal of these wastes through the development of a CPB.

The overall findings suggest that the use of CPB technology is a potential solution for the sustainable co-disposal of ash and brines as a net environmental benefit is achieved whilst still ensuring the necessary structural and environmental properties are met.

Dedication

I would like to dedicate this work to God for his guidance and wisdom and my entire family for their perpetual support and understanding.

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Table of Contents

Declaration....i

Executive Summary....ii

Dedication....vi

Acknowledgments....vi

Table of Contents....vii

List of Figures....xi

List of Tables....xiv

List of Abbreviations....xvi

Definitions....xviii

1. Introduction....1

1.1. Background....1

1.2. Problem Statement....4

1.3. Research Questions....5

1.4. Aims and Objectives....6

1.5. Research Approach....7

1.5.1. Characterization of Ash and Brine....7

1.5.2. Statistical Analysis....7

1.5.3. Environmental and Structural Suitability of the CPB....8

1.5.4. Guidelines....8

1.6. Thesis Structure....9

2. Literature Review....11

2.1. Background....11

2.1.1. Mining and Ash Production....11

2.2. Backfilling....14

2.3. Coal Combustion Products....16

2.3.1 Fly Ash....16

2.3.2 Coarse Ash....17
2.3.3 Brine....19
2.4. Elemental Chemical Composition of Coal Combustion Products....20
2.4.1. Leaching of Trace Elements and Compounds....21
2.4.2. Sulphate....**Error! Bookmark not defined.**
2.4.3. Silica, Alkali Earth Metals and Calcium Oxide....25
2.4.4. Loss on Ignition....26
2.4.5. Class of Ash....27
2.4.6. Particle Size Distribution....29
2.5. Backfilling....30
2.5.1. Types of Backfilling Methods....30
2.5.2. Conventional Ash and Brine Management....32
2.5.3. Ash and Brine Backfilling System....34
2.5.4. Advantages of Backfilling....35
2.5.5. Disadvantages of Backfilling....38
2.5.6. Properties of the Backfill Material....39
2.6. Design of the Cemented Paste Backfill Applications....40
2.6.1. Composition....40
2.6.2. Workability....43
2.6.3. Permeability and Porosity....44
2.6.4. Leachability....45
2.6.5. Unconfined Compressive strength....51
2.6.6. Setting Time....55
2.7. Conclusion....55
3. Materials and Experimental Procedure....56
3.1. Introduction....56
3.2. Statistical Analysis....57

3.2.1. ANOVA 57
3.2.2. Two-Way ANOVA 59
3.2.3. Non-parametric tests 61
3.2.4. Post Hoc Tests 61
3.2.5. Plots 62
3.2.6. Relationship between Parameters 62
3.3. Experimental Methodology 65
3.3.1. Materials 65
3.3.2. Experimental Procedures 67
4. Results 73
4.1. Preliminary Analysis 73
4.2. Statistical Analysis Results 75
4.2.1. Oxides 77
4.2.2. Semi Metals 93
4.2.3. Basic Metals 97
4.2.4. Alkali Metals 100
4.2.5. Alkali Earth Metals 101
4.2.6. Transition Metals 103
4.2.7. Loss on Ignition (LOI) 109
4.2.8. pH 110
4.2.9. Total Dissolved Solids (TDS) 115
4.2.10. Electrical Conductivity 116
4.2.11. Discussion and Conclusion 117
4.3. Experimental Analysis Results 120
4.3.1. Abstract 120
4.3.2. Introduction 122
4.3.3. Materials and Methods 125

4.3.4. Results and Discussion 130
4.3.5. Conclusions 157
5. Evaluation of Guidelines 160
5.1. Summary of Guidelines 160
5.2. Workability and Structural Suitability 161
5.3. Net Environmental Benefit 162
6. Discussion and Conclusion 166
6.1. Recommendations 169
References 171
Appendices 184
Appendix A: Statistical Analysis Raw Data of CCPs Major Oxides 184
Appendix B: Statistical Analysis Raw Data of CCPs Leachability 189
Appendix C: Statistical Analysis Raw Data of CCPs Concentration 198
Appendix D: Mass Percentage and Leachability For Major Oxides 206
Appendix E: Concentration and Leachability Data for Semi Metals 209
Appendix F: Concentration and Leachability for Basic Metals 210
Appendix G: Concentration and Leachability for Alkali Metals 211
Appendix H: Concentration and Leachability for Alkali Earth Metals 212
Appendix I: Mass Percentage, Concentration and Leachability for Transition Metals. 213
Appendix J: LOI, pH, TDS and EC 217
Appendix K: Correlation Coefficients 218
Appendix L: Code Used in R Studio 222
Appendix M:pH, TDS, EC and leachability of Tank Leach Test 233
Appendix N: pH, TDS, EC and leachability of Weathering Cell Test 235
Appendix O: Acid Neutralization Capacity 237
Appendix P: Unconfined Compressive Strength 240
Appendix Q: SEM EDS Spot Analysis 241

Appendix R: Leaching Test Comparison 242

List of Figures

Figure 2-1: Fly Ash Utilization In South Africa.....12
Figure 2-2: Fly Ash Utilization in the United States (American Coal Association, 2016) .13
Figure 2-3: Coarse Ash Utilization in the United States (American Coal Association, 2016) 13
Figure 2-4: Completed and Ongoing Backfilling Projects (Yumlu, 2010) 15
Figure 2-5: Elements in the Various Ash Types According to Relative Volatility.....21
Figure 2-6**:** Effect of LOI on Water Demand of Concretes at Equal Slump (Thomas,2007) 27
Figure 2-7: Conventional Ash and Brine Management System.....32
Figure 2-8: Backfilling Process Diagram 34
Figure 2-9: Internal and External Factors affecting the Leaching Behavior of the Cemented Paste Backfill.....46
Figure 3-1: ANOVA Methodology 64
Figure 3-2: UCS Sample Blocks 68
Figure 3-3: Monolith TLT Samples 70
Figure 4-1: Particle Size Distribution of Various Ashes 74
Figure 4-2: Waste Assessment Flow Diagram According to GN R. 635.....76
Figure 4-3: Interaction and Bar Plot of SiO_2 Variation Between the Different Ash States and Types 78
Figure 4-4: Humidity Cell Leachability of Silicon.....79
Figure 4-5: SiO_2 Decision Flowchart 81
Figure 4-6: Interaction and Bar Plot of CaO Variation Between the Different Ash States and Types 82
Figure 4-7: Relationship between Ca Leachability and CaO 83
Figure 4-8: Humidity Cell Leachability of Calcium 83
Figure 4-9: CaO Decision Flowchart 85
Figure 4-10**:** Interaction and Bar Plot of the Alkali Variation between the Different Ash States and Types.....86
Figure 4-11: Alkali Content Decision Flowchart 88

Figure 4-12: Interaction and Bar Plot of Al_2O_3 Variation Between the Different Ash States and Types....89
Figure 4-13: Relationship between Al Leachability and Al_2O_3 90
Figure 4-14: Relationship between Fe Leachability and Fe_2O_3 91
Figure 4-15: Relationship Between Total B and the Leachable Fraction....94
Figure 4-16: Relationship Between Total As and the Leachable Fraction....96
Figure 4-17: Leachability and Concentration Relationship of Ge, Sb and Te 96
Figure 4-18: Leachability of Basic Metals 98
Figure 4-19: Concentrations of Basic Metals....98
Figure 4-20: Interaction and Bar Plot of Ga Variation between the Different Ash States and Types 99
Figure 4-21: Relationship Between Total Pb and the Leachable Fraction....100
Figure 4-22: Interaction and Bar Plot of Li Variation Between the Different Ash States and Types 101
Figure 4-23: Leachability of Alkali Earth Metals 102
Figure 4-24: Relationship Between Total Ba and the Leachable Fraction....103
Figure 4-25: Change in the Total Leachable Concentration of Transition Metals (Cr, Cu, Ni, V, Zn, Zr)....107
Figure 4-26: Change in Concentration of Transition Metals....107
Figure 4-27: Interaction and Bar Plot of Nb and Ta Variation Between the Different Ash States and Types....108
Figure 4-28: Change in Concentration of Transition Metals....108
Figure 4-29: Interaction and Bar Plot of LOI Variation Between the Different Ash States and Types....110
Figure 4-30: Humidity Cell Change in pH 111
Figure 4-31: Interaction and Bar Plots showing pH Variation....111
Figure 4-32: pH Decision Flowchart....114
Figure 4-33: Interaction and Bar Plot of TDS 115
Figure 4-34: Total Dissolved Solids change following Weathering in Humidity Cell Test 115
Figure 4-35: Interaction and Bar Plot of EC....116
Figure 4-36: Electrical Conductivity change following Weathering in Humidity Cell Test 117
Figure 4-37: Fluoride change following Weathering in Humidity Cell Test 117

Figure 4-38: Graphical Abstract 121
Figure 4-39: Cumulative Particle Size Distribution of CCPs 132
Figure 4-40: SEM Micrograph of FA (A), CA (B), FA at 28 Days (C), MA1 at 28 Days (D) and MA3 at 28 Days (E) 133
Figure 4-41: UCS of CPB Samples at Various Curing Times 135
Figure 4-42: pH Evolution during the TLT 137
Figure 4-43: EC Evolution during the TLT 138
Figure 4-44: Ca Released during the TLT 138
Figure 4-45: Na Released during the TLT 139
Figure 4-46: Mg Released during the TLT 139
Figure 4-47: Al Released during the TLT 140
Figure 4-48: K Released during the TLT 140
Figure 4-49: Fe Released during the TLT 140
Figure 4-50: pH Evolution During the Weathering Cell Test 143
Figure 4-51: EC Evolution During the Weathering Cell Test 143
Figure 4-52: Cumulative Na Released for the Weathering Cell Test 144
Figure 4-53: Cumulative Ca Released for the Weathering Cell Test 144
Figure 4-54: Cumulative Al Released for the Weathering Cell Test 145
Figure 4-55: Cumulative Mg Released for the Weathering Cell Test 145
Figure 4-56: Cumulative K Released for the Weathering Cell Test 146
Figure 4-57: Cumulative Fe Released for the Weathering Cell Test 146
Figure 4-58: Cumulative Ba Released for the Weathering Cell Test 146
Figure 4-59: Cumulative Pb Released for the Weathering Cell Test 147
Figure 4-60: Cumulative Elemental Release for Different CPB following the Weathering Cell Test 147
Figure 4-61: Acid Neutralization Capacity of CPB Mixtures 151
Figure 4-62: Ca Release as a Function of pH 152
Figure 4-63: EC Release as a Function of pH 152
Figure 4-64: Elemental Release of Various Elements from the FA CPB Mixture as a Function of pH 153
Figure 4-65: Elemental Release of Various Elements from the MA1 CPB Mixture as a Function of pH 153
Figure 4-66: Elemental Release of Various Elements from the MA2 CPB Mixture as a Function of pH 154

Figure 4-67: Elemental Release of Various Elements from the MA3 CPB Mixture as a Function of pH.....154
Figure 4-68: Elemental Release of Various Elements from the CA CPB Mixture as a Function of pH.....155
Figure 5-1: CPB Mixtures Bleed Formation 162
Figure 5-2: Percentage Leached Out of Major Elements from Various Leaching Tests ..164
Figure 5-3: Percentage Leached Out of Minor Elements from Various Leaching Tests ..165

List of Tables

Table 2-1: Chemical Composition of Fly Ash Produced from Different Coal Types.....27
Table 2-2: Comparison between Class F and Class C Ashes 28
Table 2-3: Comparison of Advantages and Disadvantages of Various Backfill Methods..31
Table 2-4: Intrinsic and Extrinsic Factors for Backfilling.....40
Table 2-5: Mix Proportions for Concrete Mortars.....43
Table 2-6: Advantages and Disadvantages of Monolithic Leaching Tests 49
Table 2-7: Release of Elements following Backfilling 51
Table 2-8: 28 Day Compressive Strength Tests for CCPs implemented in Concrete Mortars 53
Table 2-9: UCS of Various CPB 54
Table 3-1: Different Ash Types and States Analyzed in Two Way ANOVA.....60
Table 3-2: Cemented Paste Backfill Mix Designs.....67
Table 3-3: Tank Leach Test Leachate Renewal 69
Table 4-1: Elemental Composition of Coal Combustion Products 73
Table 4-2: Chemical Composition of Brine 74
Table 4-3: Significance Level Annotations.....76
Table 4-4: Waste Type Classification 77
Table 4-5: Na_2O and K_2O Oxide and Leachability Percentage Changes Following Weathering.....86
Table 4-6: Percentage of Semi Metals Leached out from CCPs 94
Table 4-7: Percentage of Basic Metals Leached out from CCPs 97
Table 4-8: Percentage of Alkali Metals Leached out from CCPs 100
Table 4-9: Percentage of Alkali Earth Metals Leached out from CCPs.....102
Table 4-10: Metals Which Exceeded TCT Limits 104

Table 4-11: Metals Which Exceeded LCT Limits 105
Table 4-12: Percentage of Transition Metals Leached Out into Solution 106
Table 4-13: Element Concentration Ranges in CCPs 119
Table 4-14: Element Leachability Ranges in CCPs 119
Table 4-15: Paste Backfill Mix Design 126
Table 4-16: Brine Compositions 130
Table 4-17: Chemical Composition of CCPs 131
Table 4-18: UCS Comparison 136
Table 4-19: Comparison of the Cumulative Elemental Release (mg/kg) 149
Table 5-1: Percentage Leached Out of Various Elements in Varying Tests 163

List of Abbreviations

Symbol		Unit
A	Exposed surface area	m^2
AAS	Atomic Adsorption Spectroscopy	
AMD	Acid mine drainage	
ANC	Acid neutralization capacity	
ANOVA	Analysis of variance	
ASLP	Australian Standard Leach Procedure	
ASTM	American Society for Testing and Materials	
BFS	Blast furnace slag	
CA	Coarse ash	
CCP	Coal combustion products	
C_i	Elemental concentration during period *i*	mg/l
CPB	Cemented paste backfill	
DEA	Department Environmental Affairs	
DWLP	Deionized water leaching procedure	
EC	Electrical conductivity	mS/cm
EIA	Environmental impact assessment	
ESP	Electrostatic precipitators	
F	Fresh ash	
FA	Fly ash	
FCA	Fresh coarse ash	
FFA	Fresh fly ash	
FMA	Fresh mixed ash	
H_o	Homogeneity of variances	
HSD	Tukey's Honest Significant Difference	
ICP-MS	Inductively Coupled Plasma Mass Spectrometer	
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer	
LC	Leachable concentration	mg/l
LCT	Leachable concentration threshold	
LOI	Loss on ignition	%
MA	Mixed ash	
M_{ti}	Elemental mass released during the leaching period *i*	mg/m^2

NEB	Net environmental benefit	
NEM: WA	National environmental management: Waste Act	
OPC	Ordinary portland cement	
PSD	Particle size distribution	
r	Pearson correlation	
r_s	Spearman rank correlation	
S	Sample weight	kg
SANS	South African National Standards	
SD	Surface disposal	
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy	
SLP	Static leaching procedure	
SPLP	Synthetic precipitation leaching	
TC	Total concentration	mg/kg
TCLP	Toxicity Characteristic Leaching Procedure	
TCT	Total concentration threshold	
TDS	Total dissolved solids	g/L
TLT	Tank leach test	
UCS	Unconfined compressive strength	
V_i	Leachate volume	L
W	Weathered ash	
WCT	Weathering cell test	
WCA	Weathered coarse ash	
WFA	Weathered fly ash	
WMA	Weathered mixed ash	
XRD	X-ray diffraction	
XRF	X-ray fluorescence	
ZLD	Zero liquid discharge	

Definitions

Bleed: The volume of water that forms on top of the cemented paste when the solid material settles.

Brine: A water or liquor with a salinity of over 2% containing a high concentration of predominately inorganic dissolved salts such as Na, Mg, Ca and Cl.

Cemented Paste: A material that is made from ash (fly ash or coarse ash) and water or brine with the addition of cement which will not segregate and will harden when disposed of.

Coarse Ash: Coal ash residue ash which darker grey in colour and porous, irregular and granular with a much larger particle size in comparison to fly ash.

Fines: The total amount of ash particles with a diameter < 20μm.

Flooded: Completely submerged in water.

Fly Ash: Fine grey powder that is spherical in shape, smooth and amorphous with ash particle size ranging from 1 – 100μm in diameter.

Fresh ash: Coal ash residue ash that has recently been combusted and not placed in ash dumps for a long period of time.

Leachability: The amount of salts removed or remobilized from the ash or monolith when exposed to water.

LOI: Measure of unburnt carbon content.

Monolith: A waste (In this case fly ash and coarse ash) that has been deliberately treated or modified to form a solidified material.

Net environmental benefit: This concept recognizes that there are risks and benefits associated with the multiple methods of waste disposal. In a conventional system whereby ash is surface disposed of, if the alternative option (Such as disposal through paste backfilling) poses a risk less than the sum of the conventional methods, then a net environmental benefit is realized.

Pozzolan: Pozzolans are siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

Slump: Indicator of workability whereby the consistency and ease at which concrete flows are measured.

State of ash: Refers to fresh ash or weathered ash

Type of ash: Refers to fly ash, coarse ash or mixed ash which consists of both fly ash and coarse ash

Weathered ash: Ash that has been surface disposed of for a long period of time and left exposed to the environment.

Workability: Easily transported, placed, moved and compacted without any particle segregation.

1. Introduction

This chapter deals with an introduction to the study. The background of the study, the problem statement, aims and objectives, research questions and the research approach are presented in this chapter.

1.1. Background

Large scale coal based power generation began in the early 1920s resulting in the global production of millions of tons of coal combustion products (CCPs) such as fly ash (FA) and coarse ash (CA) along with other by-products such as boiler slag and flue gas desulphurisation (Ahmaruzzaman, 2010). Worldwide coal FA production is estimated at 300 million tons per annum whereas, in South Africa alone, 25 million tons of FA is produced annually. Present day FA utilization is currently between 3 – 57% of the total supply with a global average of only 6% being productively used in the cement industry (Joshi and Lohita, 1997). The large majority is often placed temporarily in stockpiles or dumped in landfill sites, ash dams or lagoons and left to undergo chemical weathering. This creates vast amounts of fresh and weathered ash dams which cause numerous short and long term environmental problems. Most often FA and CA are dumped together in varying proportions of each ash type which is termed mixed ash (MA). As a result, there is currently a lot of interest in finding suitable and environmentally sustainable ways of utilizing these various ash types in order to prevent an increase in the number of existing ash dams as well as minimizing the growing environmental concern associated with these wastes.

Coal has been extensively mined in South Africa since the late 19th century. Most mining operations are viable for approximately 30 years however this is very site specific and will vary according to the operation. Following that, these mines are sometimes left abandoned without rehabilitation. There are approximately 6000 abandoned mines in South Africa (of which vary between coal, gold and other mining activities) ("Abandoned Mines in South Africa," 2015), the majority of which pose a series of environmental concerns such as:

- The risk of groundwater contamination through metal leaching;
- Underground fires through the spontaneous combustion of the remaining coal;
- Surface subsidence resulting in land instability; and
- Loss of biodiversity in the affected area.

Mining operations also produce other wastes such as brine. Brine is water or liquor with over 2% salinity containing predominately inorganic dissolved salts. Brine is formed from coal utilizing technologies such as gasification and combustion processes which creates large amounts of wastewater that requires further treatment. Brines are generated in inland energy and industrial complexes where it is not possible, nor desirable, to discharge effluents to the environment or nearby river courses. For coal processing, the preparation of boiler feed water is required in order to generate steam. During this process, a saline stream concentrated with the salts removed from the water is generated. This process could occur via a range of different treatment technologies such as ion exchange or membrane-based technologies such as reverse osmosis. Since these saline streams cannot be discharged, a zero liquid effluent discharge philosophy is applied and these saline brine streams are stored on-site in effluent storage dams. To manage these streams further desalination processes are introduced, to recycle water, further generating a brine stream requiring disposal. Cooling processes also generate saline blow-down streams further compounding the salt problem. Another source of saline water is contaminated mine water which can also be recovered using a desalination process also producing brines.

In an attempt to treat, recover and reuse this water, wastewater treatment methods produce excessive quantities of brine. Brine production or saline waste production is estimated at 5 000 000 tonnes/year according to the data provided in the Water Research Commission Report (Van der Merwe et al., 2009). It is estimated that the saline waste production for 2014 was 4 968 745 tonnes/year 4000 tonnes per day in South Africa. The need for brine usage is also becoming increasingly necessary as the minimization of industrial wastewater, through its treatment, reuse, or safe re-entry into the surrounding environment, is a critical part of water management and integral in tackling water scarcity issues. Furthermore, this is critical specifically in the case of inland regions. Brines generated at the coastal areas can be disposed of in the ocean however there are limited options for sinking salts inland.

The growing environmental concerns associated with mining operations and the production of CCPs and other wastes has promoted research into finding new and innovative ways to utilize CCPs, rehabilitate abandoned mines and reduce the current and long term environmental impact of these waste products. Mine backfilling has been found to be one such method to combat these problems listed above. Backfilling is defined as the process

whereby mine tailings and other mine wastes are placed or reinserted into the void openings of underground mines. There are numerous ways in which backfilling can be performed with the most common method being the cemented paste backfill (CPB). The CPB is comprised of a mixture of mine tailings or coal gangue, hydraulic binders such as FA or ordinary Portland cement (OPC) and water, which may consist of mine processed water or brine. These constituents are made into a thickened slurry or paste and pumped underground into the surrounding mine voids (Rong et al., 2017).

Mine backfilling is advantageous in industry as the mine voids filled with the thickened paste provide surface stability in areas where land subsidence is occurring as a result of crumbling support pillars. This provides a safe working environment for miners and increases mineral recovery by reducing ore dilution (Cui and Fall, 2016). It is found to also improve mine ventilation, reduce the risk of rockburst as the pressure is distributed more evenly and has the potential to reduce the environmental impact of the existing mine sites (Ke et al., 2015). This is done by minimizing water leaching into the mine voids thus preventing further generation of acid mine drainage (AMD) (Murarka and Erickson, 2006). Furthermore, it is an effective way to process and dispose of mining waste such as tailings, CCPs, and brine. This reduces the cost of disposal and further treatment making backfilling an economically viable process.

Given the advantages of backfilling, it is becoming an attractive approach to utilize CCPs and rehabilitate mines. The paste backfilling operation is further justified if a net environmental benefit (NEB) is achieved. The NEB is defined as the difference between the environmental risks of the current utilization of the CCPs and mine disposal processes in comparison to the environmental risks of the CCPs when implemented in a backfilling operation. Hence, the total environmental risk of the backfilling operation needs to be less than that of a surface ash disposal facility in order for a NEB to be achieved. The concept of a NEB will be further investigated in this thesis to prove the benefits of backfilling in comparison to the current ash surface disposal methods.

When examining if a NEB is achieved, the environmental specifications and risks need to be critically determined. Environmental specifications include the chemistry and reactivity of the CCPs with the CPB as well as the effect on the surrounding surface water, groundwater, air and soils upon interaction with the paste. One such environmental

specification is the potential release of harmful elements through leaching into the surrounding environment. The leaching of the CPB needs to be minimal and monitored to ensure that the CPB does not act as a source of contamination to the receiving environment. Another specification is the chemical composition of the CCPs. The presence of alkali earth metal oxides such as sodium oxide (Na_2O) and calcium oxide (CaO) need to be limited as they play a significant role in the alkali-silica reaction (ASR) (Shehata and Thomas, 2000). The ASR is undesirable as it causes concrete cracking which weakens the CPB. The CPB also requires various structural specifications to be met to ensure surrounding stability and strength. The unconfined compressive strength (UCS) is an important parameter used to determine the structural suitability. Typically, a 28 day UCS in the range of 0.5 – 2 Mpa is required in order to ensure slope stability when designing a CPB (Brackebusch, 1995).

In order to ensure the above specifications are met and a NEB is gained, detailed characterization of the CCPs prior to use is necessary. This characterization was done through a statistical analysis that was conducted on sixty-seven ashes from various power stations throughout South Africa. This analysis was used to determine trends and guidelines of the mineralogical characteristic of the different ashes which provided information on the reactivity of the ash upon use in a CPB. Mineralogical properties of the ashes which aim to minimise the ASR, promote the pozzolanic reaction, minimize metal leaching and ensure a CPB with high strength is achieved. Such characterization allows the required personnel to design a CPB to meet their desired environmental and structural objectives for each site-specific case. Chemical testing should be carried out on both the inputs and outputs of the CPB process as the chemical nature of the paste changes during the process and ultimately determines the extent of the environmental impact. Leach tests on the CCPs prior to implementation as well as on the constructed CPB was important to ensure leaching is not a concern and a NEB is achieved. Limited research exists when both conditions prior to and following implementation are investigated as well as the use of varying CCPs such as FA and CA coupled with brine.

1.2. Problem Statement

The vast amounts of FA, CA and brine waste produced are cause for environmental concern. The need for waste minimization and water conservation is growing and it is of utmost importance to dispose of both the solid and liquid wastes from the mining industry in a sustainable manner in order to keep the environment safe and in accordance with the

environmental laws. However, the constraints imposed by these laws often pose difficulties especially in ensuring the concentration of leachable species in the ash and brine are below the required limits. In the current surface ash disposal methods, the brine and ash are co-disposed of together as the brine is often used in conjunction with the ash to make a slurry or used to moisten the ash particles for dust suppression prior to disposal in the ash dams. Both these wastes contain toxic elements and trace metals which may migrate into the surrounding environment through leaching upon contact with water. This process is enhanced as a result of chemical weathering of the ashes which may lead to the mobilization of major and minor elements such as Si, Ca, Al, Mg, Fe, Na, and K, as well as various trace elements such as Co, Cd, As, Se, Zn, Mo, Mn, Pb, B, Cu, and Ni. Thus, the current surface ash disposal methods of these wastes are not sustainable as a long term solution for disposal.

Brine and ash surface disposal is problematic as it can cause serious long term health, environmental and further land-use problems. This had promoted research into finding alternative waste disposal methods that have a lower environmental impact. This study aims to reduce the current environmental concerns associated with these wastes through the development of the CPB whilst ensuring the environmental and structural properties are met. Since there is currently no well-defined technical evaluation or permitting process which outlines the conditions or suitability for which the use of CCPs in backfilling is feasible; this dissertation aims to provide guidelines based on a statistical analysis of the chemical composition of various ash types and analytical techniques that relates the chemical and physical characteristics of the CCPs to the environmental or structural performance of the CPB. Such guidelines will give an indication to the user of whether a specific ash with definite characteristics is indeed suitable for backfilling as well as guidelines of the expected outcomes upon implementation of the CPB.

1.3. Research Questions

The study aims to address the following research questions –

- What are the chemical or mineralogical factors of the ashes that influence and enhance the pozzolanic reaction?
- What is the relationship between leachability and the total elemental concentration of the various elements and compounds found in the CCPs?

- What mineral phases form or dissociate through water ingress of the CPB and do the newly formed secondary mineral phases dissociate over time to release contaminants?
- How does the co-disposal of CCPs and brine affect the leachability of major and trace elements from the ash-brine interaction in the CPB?
- What mix design of FA, CA and brine have the most favourable characteristics for the further use of the CPB in terms of structural and environmental suitability?
- Is the co-disposal of brine, FA and CA through the construction of a CPB environmentally and structurally suitable and sustainable?

1.4. Aims and Objectives

The aim of this study is to –

1. Find a sustainable solution for the disposal of brines and CCPs through the development of a CPB.
2. To determine the relationship between leachability and concentration or elemental mass composition of the various CCPs.
3. To provide guidelines that relate the chemical and physical characteristics of the ashes (FA and CA) to the environmental and structural suitability in the CPB.
4. To provide a detailed insight into the leaching and removal of major and trace elements from the CPB ash-brine interaction systems.
5. To determine the most optimal mix design to develop a CPB with the required structural and environmental properties.

The following research objectives will be met throughout this study –

- Gather the detailed characterization and classification data on the CCPs such as FA, CA and MA. This data will include information such as elemental chemical composition, state of ash (fresh or weathered), leachability and concentration data;
- Statistically analyse the data through the construction of an ANOVA to determine the significant differences between the average values of the different states and types which will then be used to determine the relationship or trends between the CCPs;
- Provide guidelines/limits which relates the chemical composition of the CCPs to the leachability and thus suitability in the CPB;

- Determine the relationship between the elemental release due to leachability and the total elemental concentration in the CCPs;
- Use these guidelines to construct CPB monoliths and examine the environmental and structural properties of these monoliths. This will allow an in-depth understanding of the interaction chemistry between the ash and brine systems as well as the expected leaching behaviour;
- Identify the mineral phases that form or dissociate as a result of the ash brine interactions. Furthermore, this will provide an understanding of the pozzolanic reactivity of the ashes; and
- Compare the environmental impact of the current surface ash disposal to that of the CPB to determine if a NEB is achieved.

1.5. Research Approach

The research approach used in this study in order to achieve the aims and objectives is highlighted below.

1.5.1. Characterization of Ash and Brine

Several analytical techniques were used in this study such as x-ray fluorescence (XRF), scanning electron microscopy-energy dispersion spectroscopy (SEM-EDS), inductively coupled plasma-mass spectroscopy (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and atomic adsorption spectroscopy (AAS) which was used to characterize the ashes, brine, and the leachate. This analysis was carried out on the fresh FA and CA samples as well as the brine in order to determine the chemical and mineralogical compositions. SEM analysis was conducted on each of the constructed monoliths to examine changes in particle morphology and reaction products.

1.5.2. Statistical Analysis

Sixty-seven ashes including fresh and weathered FA, CA and MA samples from various coal-fired power stations across South Africa were analysed. A detailed compositional, leachability and concentration analysis of these ashes following weathering was performed. In cases whereby leachability is mentioned, this refers to the total leachable concentration. An ANOVA was conducted in order to determine if a significant difference exists between the leachability or concentration means of the different ash groups i.e FA, CA or MA or between the different ash states i.e fresh or weathered. This significant difference indicates

that these ashes would behave differently from one another and hence will have a significantly different effect when implemented in the CPB. Thus, guidelines and flowcharts were constructed for each of the elements or compounds which had a significant difference between the means. These decision making flowcharts were developed to allow the user to screen any type of ash based on a specific compound or property for its potential use in the CPB. Furthermore, the relationship between leachability and the total elemental composition or the total concentration was analysed to examine trends between the two parameters and to predict the environmental impact of the ashes.

1.5.3. Environmental and Structural Suitability of the CPB

From the guidelines determined through the statistical analysis, CPB monoliths were constructed with varying proportions of ash and brine. Each of these CPB mixtures were analysed in terms of environmental and structural performance. The environmental suitability was determined through conducting TLTs that were used to simulate flooded CPB applications as well as WCTs which aimed to simulate the accelerated chemical weathering of the CPB mixtures. This allowed the concept of a net environmental benefit (NEB) was analysed in order to determine if the CPB application had a lower negative environmental impact in comparison to that of the surface ash disposal methods. A lower environmental impact would be one whereby the CPB had a lower elemental release occurs. Thereafter, the structural performance was determined through the UCS testing at pre-determined days. Various CPB mixtures that contained different amounts of FA and CA were analysed to determine the best mix design which provided both favourable properties in terms of leaching and structural strength.

1.5.4. Guidelines

Following the statistical and experimental analysis, various guidelines/limits were formulated which stated whether the composition of that particular element or compound was suitable and could be implemented in the CPB. This was based on the environmental suitability i.e whether a particular element has a concentration and leachability within the required limits, as well as the structural suitability i.e what mix design met the required minimum strength and what were the limits of ash replacement? These guidelines are formulated to ensure that when a CPB is designed, it would meet the required environmental

and structural specifications. These guidelines were formulated purely to assist the user/reader on the expected outcome when

1.6. Thesis Structure

This thesis has been divided into six more additional chapters which are outlined below –

Chapter 2: Literature Review

The chapter deals with a review of the available literature. It provides a detailed review of the various CCPs in terms of morphology, mineralogy, leachability, and chemical composition. Furthermore, this chapter reviews the literature on cemented paste backfilling in terms of the usage of brine as well as important factors to consider when designing a CPB.

Chapter 3: Materials and Experimental Procedure

This chapter explains all the materials used in this study as well as the experimental methodology used for the characterization of the ashes and brine. Furthermore, the experimental methodology carried out both in terms of the statistical analysis and practical experimentation is presented.

Chapter 4: Results

This chapter presents and discusses the preliminary results of the ash and brine characterization, the results of the ANOVA which stated the statistical differences between the different ash types (FA, CA or MA) as well as the different states (fresh or weathered). The statistical analysis results are presented on all major oxides by XRF and on all trace elements determined through acid digestion. The chapter also discusses the compositional change of the ashes upon chemical weathering, the potential relationship between the elemental release (leachability) and the total concentration of the various elements in the ashes as well as the percentage of each element leached out into solution following the leachability tests. Furthermore, this chapter presents and discusses the experimental results of the different CPB mixtures composed of FA, CA, and brine in terms of the environmental and structural suitability. The results of the TLT, WCT and ANC tests carried out to determine the mobility of species in the CPB monoliths under different pH conditions are presented and discussed in this chapter.

Chapter 5: Evaluation of Guidelines

Chapter 5 presents a summary of the proposed guidelines for use in the CPB applications. A critical comparison between the proposed guidelines for the use of CCPs in CPB applications against the practical implementation in the CPB is also presented in this chapter.

Chapter 6: Discussion and Conclusion

Chapter 6 presents a discussion providing a summary and the conclusions of the study showing the overall effect of the use of FA, CA and brine through the co-disposal in CPB applications as well as the potential elemental release of species. The recommendations for future work are also presented in this chapter.

2. Literature Review

2.1. Background

2.1.1. Mining and Ash Production

Mining is a major component of the extractive industries. It involves surface techniques such as strip mining or quarrying in open pits and underground extraction involving drilling holes, tunnels, and shafts to obtain valuable ore and a range of minerals and metals. Mining has been the backbone of the South African economy for the past 150 years and is ranked the fifth largest mining industry in the world (Baxter, 2015). The mining sector has drastically improved the country's infrastructure, which has resulted in an increase in the gross domestic profit of 7.3% per year. This sector has provided numerous employment opportunities of approximately half a million people (Ledwaba and Mutemeri, 2018). As a result, mining is a vital and necessary sector in the South African economy. One of the main mining products aside from gold and diamonds is coal. Coal is the third largest mineral exported from South Africa with an estimated 3.4 billion tons of mineable coal remaining (Zieleniewski and Brent, 2008).

Despite coal mining being such a large and important sector, the economy faces numerous challenges with wide-scale mining operations. Some of these problems outlined by London and Kisting (2016) include:

- Water pollution as multiple water bodies in and around the Witwatersrand area have been contaminated through the generation and discharge of AMD (Durand, 2012);
- Loss of biodiversity and soil erosion;
- Surface subsidence which causes land instability;
- Creation of numerous open pits and deep underground void openings; and
- Occupational injuries and health problems.

Coal mining and utilization in South Africa is extensive due to the numerous coal-fired power stations. Approximately 77% of the electricity production in South Africa is dependent on these coal-fired power stations. Coal based power generation is widely used owing to its relatively cheap cost and abundance in comparison to other energy sources. However, this is changing whereby coal would soon not be the cheapest form of electricity when considering all the externalities.

In 2015, 119.2 million tons of coal were combusted resulting in the production of approximately 35 million tons of ash (Reynolds-Clausen and Singh, 2017). Due to this quantity of ash, many power stations are running out of disposal storage space. Furthermore, the cost of ash disposal is increasing with increasingly stringent liner requirements required by the regulators. This means South Africa has a vast amount of CCPs which are readily available for further use. Currently, the cement and concrete making industries are the only large-scale consumers of FA. Figure 2-1 shows FA utilization in South Africa which only amounts to 2.5 million tons per year. As a result, 90% of the FA is still unused and requires further disposal (Kruger, 2015). The FA utilization in the United States is estimated at 14.4 million tons per annum (60%) according to the American Coal Ash Association (ACAA) (American Coal Association, 2016) as shown in Figure 2-2. The remaining 40% is land disposed of as a slurry in waste dam sites and left to undergo chemical weathering.

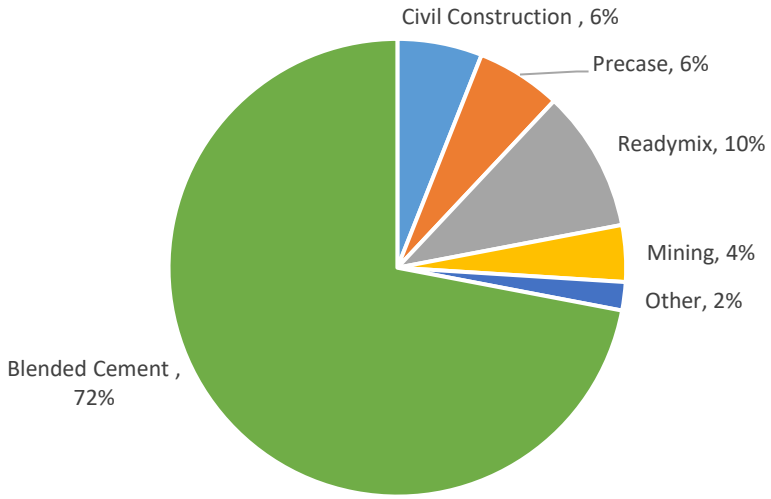

Figure 2-1: Fly Ash Utilization In South Africa

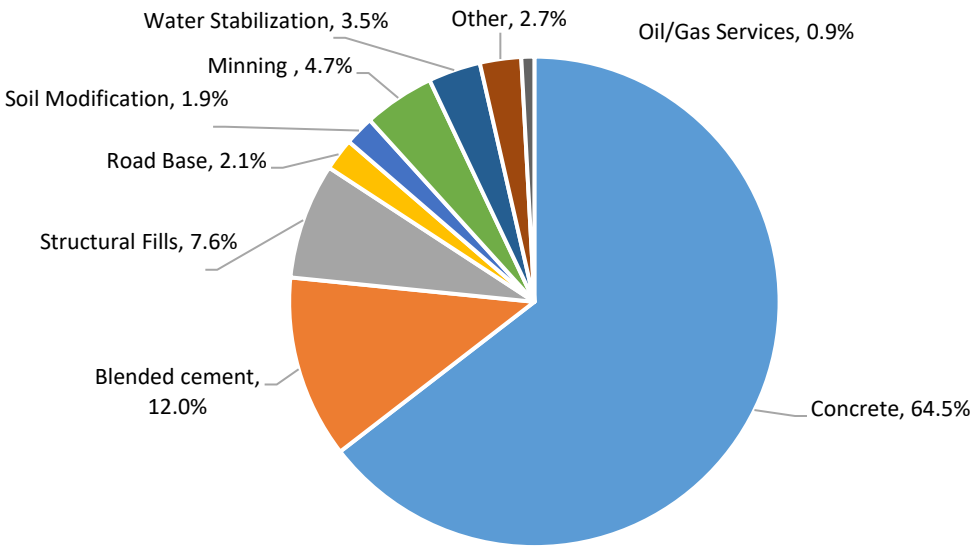

Figure 2-2: Fly Ash Utilization in the United States (American Coal Association, 2016)

CA which is also available in abundance has a much lower utilization in comparison to FA. The ACAA states that only 37% of the CA is utilized as shown in Figure 2-3 (American Coal Association, 2016). The remaining 63% is disposed of in ash dams.

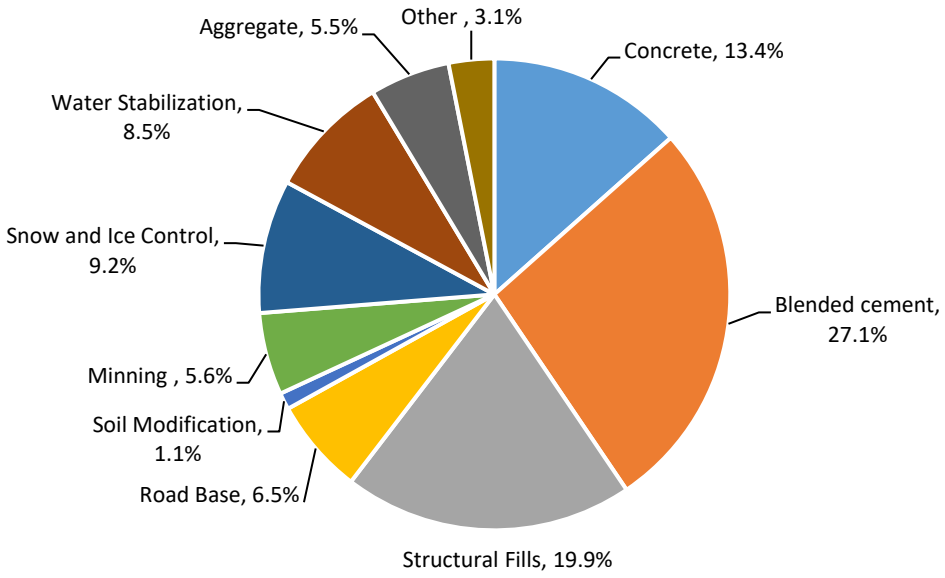

Figure 2-3: Coarse Ash Utilization in the United States (American Coal Association, 2016)

The large number of ash dams is significant and the need for further usage of ash is growing. Given that South Africa is also a water scarce country, effective utilization and management of water resources are vital. Eskom power stations currently have a zero liquid effluent discharge policy (ZLED) (Pather, 2018). This means that all the water used at the power station remains on site. The water is cascaded from a high to poor quality and used until the

water is heavily concentrated with salts and is finally co-disposed of with ash and placed in ash dams. The objective is to dispose of the maximum mass of salts with the smallest possible volume of water. This has led to the co-disposal of brine and FA since the FA is able to act as a salt sink for the discharged effluents and co-disposal will suppress dust particles of FA from forming. The salt sinking phenomenon is observed as the FA-brine interaction reduces the mobility of salts into the surrounding environment. A detailed study investigating the removal of trace elements from brine using FA has been conducted by Fatoba et al. (2011). The study showed favourable results whereby certain elements were removed from the brine upon interaction with the FA. This ultimately reduces the environmental impact of long term storage in comparison to dry disposal.

2.2. Backfilling

Backfilling operations in the mining industry date as far back as the early 1900s when mine wastes were dumped underground. This method was purely adapted and practiced for waste disposal and the environmental or structural implications were not considered. This often led to mine accidents due to ground instability which prompted further research into this field. The addition of OPC to the backfill mixture became prevalent around the 1950s. This lead to significant improvements and understanding of the backfill properties thus leading to the development of the different backfilling methods which are namely rock fill, hydraulic fill as well as the commonly implemented CPB (Sheshpari, 2015).

Backfilling operations have become a fundamental concept in mining as without it, operations would be less safe, less productive and have a shorter life span. Currently, numerous countries such as Canada, China, and Australia utilize mine backfilling as shown in Figure 2.4 (Data obtained from Yumlu (2010)). Many, if not all the environmental problems associated with mines and ash dumps can potentially be combated through mine backfilling. Backfilling has the advantage of utilizing the excess CCPs thus minimizing remediation costs and converting waste into a valuable secondary material. Utilization of the CCPs and brine will also minimize the environmental risk associated with wastewater as well as alleviate the cost associated with treatment as this water could be effectively turned into a paste.

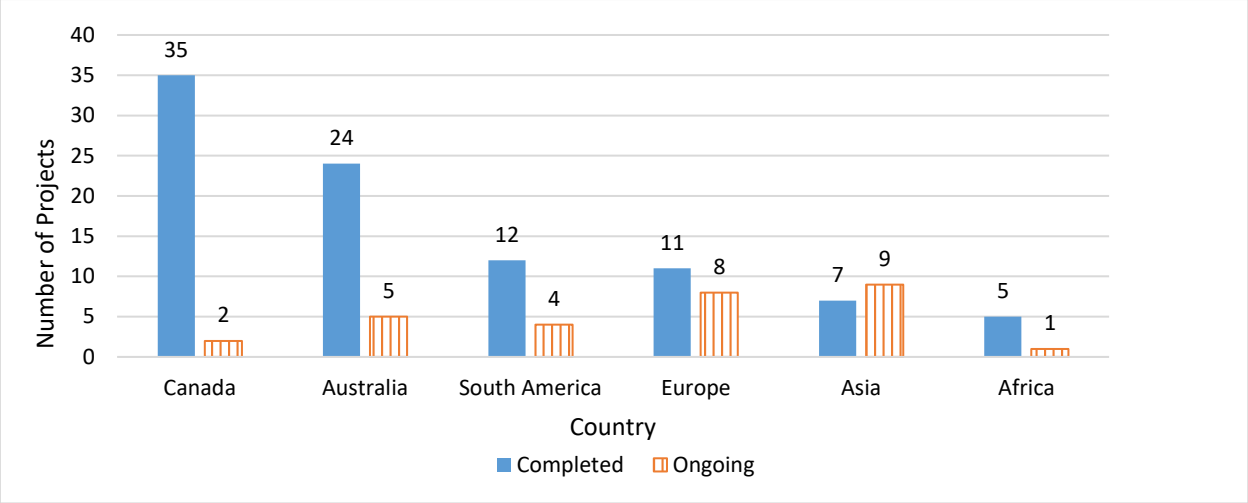

Figure 2-4: Completed and Ongoing Backfilling Projects (Yumlu, 2010)

Fly ash and the other CCPs are suitable for use as a backfill material due to their pozzolanic activity displayed under certain conditions. Pozzolans are siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. These cementitious reactions create an additional binding capacity resulting in increased strength and significantly lower permeability of the CPB. As a result, there is limited movement of contaminants through the solid matrix into the surrounding water bodies. Due to the pozzolanic properties of the CCPs coupled with their lime binding capacity, it is useful in the manufacturing of cement and concrete, building materials and for use as a backfill material. The pozzolanic reaction can only take place in the presence of lime. In backfill applications, lime is often provided by cement addition. Following cement hydration, free lime is released and activates the pozzolanic reaction. The pozzolanic reaction produces an additional cementitious product known as the calcium silicate hydrate gel (CSH) which is an important strength binder. The pozzolanic reaction proceeds according to Eq. 2.1, Eq. 2.2, and Eq. 2.3 below. In Eq. 2.1 and Eq. 2.2, the calcium silicate compounds found in the cement, alite (C_3S) and belite (C_2S), are hydrated to produce the CSH gel and free lime (Robl et al., 2017).

$$2C_3S + 11H \rightarrow C_3S_2H_8 + 3Ca(OH)_2 \quad \text{(Eq. 2.1)}$$

$$2C_2S + 9H \rightarrow C_3S_2H_8 + Ca(OH)_2 \quad \text{(Eq. 2.2)}$$

In Eq. 2.3, the free lime then reacts with the silica in the CCPs to produce the CSH gel. It is more accurate to represent the calcium silicate hydrate gel as $C_xS_yH_z$ as opposed to assigning stoichiometric quantities as there are no strict compositions (Robl et al., 2017).

$$x.Ca(OH)_2 + y.S + z.H \rightarrow C_xS_yH_z \quad \text{(Eq. 2.3)}$$

Where, $C = CaO, S = SiO2,$ and $H = H2O$.

The pozzolanic reaction and the extent to which this reaction occurs is dependent on factors such as the specific area of the pozzolan, the composition of the pozzolan which includes the amount of silica or alkalies present, as well as external factors such as temperature and curing conditions. The use of CCPs and their pozzolanic activity results in a cost decrease as less cement is required which is beneficial for backfilling operations (Mallisa and Turuallo, 2017). This is based on the assumption that cement will always be added which may not be the case.

2.3. Coal Combustion Products

Coal-fired power stations worldwide produce excessive amounts of CCPs. According to the American Coal Association, 60.2 million tons per annum of CCPs were utilized of the total 107.4 million tons produced within the United States (American Coal Association, 2016). Coal combustion products are useful from both an environmental and economic perspective. They have chemical and physical properties that make them suitable for use in engineering structures such as the CPB. However, these chemical properties also have various elements that can be harmful in large amounts and cause concern with regards to leaching. The chemical properties vary between FA, CA and MA and this ultimately determines their further usage. These variations between the different ashes are discussed below.

2.3.1 Fly Ash

The most abundant CCP is fly ash (FA), accounting for approximately 10% by mass of the coal following combustion. After combustion of the coal, the FA particles are suspended in the flue gas and removed through filters. FA accounts for 70 – 90% of the total ash produced. It consists of a fine grey powder that is usually spherical in shape, smooth and amorphous. FA particles are generally small with sizes ranging from 0.5 – 100 μm and are generally heterogeneous, consisting of multiple crystalline phases such as quartz, mullite, and

hematite (Dwivedi and Jain, 2014). Following weathering of ash, the chemical and mineralogical changes that occur resulting from the interaction of atmospheric CO_2 result in phases that are thermodynamically more stable and thus less reactive (Del Valle-Zermeño et al., 2015). This is due to the dissolution and precipitation of minerals, redox reactions, cation exchange and hydration reactions that occur. It has been proposed that the weathering of FA in ash dumps is analogous to that of volcanic ash with abundant aluminosilicate glass-forming clay minerals during weathering. Thus, weathered ash contains contaminants which are less mobile than unweathered ash.

FA is considered the world's fifth-largest raw material resource (Mukherjee et al., 2008). The utilization of FA depends on the chemical properties as each batch of FA is specific to the mineral matter of the coal from which it is formed thus there are varying chemical and physical compositions. FA can be characterized according to its composition, surface chemistry, mineralogy as well as reactivity. Given the large abundance of FA available, it could be re-used to minimize disposal costs or to gain revenue by the sale of another product. FA is commonly used in many industries such as the cement industry (Potgieter et al., 2002), zeolite synthesis (Querol et al., 2002), ceramic manufacturing (Luo et al., 2017), a low cost adsorbent to remove dyes from wastewater (Potgieter et al., 2018) and encapsulate trace metals (Alinnor, 2007). However, these industries only utilize a very small percentage of the total FA available. This is based on the exclusion of the cement industry which does use a greater portion in relation to the other industries.

FA is used in a multitude of backfilling operations. This is due to the pozzolanic activity, high fines content and spherical particle shape which improves strength and workability of cement pastes (Campbell, 1999; Chindaprasirt et al., 2005; Joshi and Lohita, 1997). The chemical composition and morphology show positive applications in concrete (Chancey et al., 2010).

2.3.2 Coarse Ash

The other CCP produced in abundance from the combustion of coal is coarse ash (CA). CA particles, also referred to as bottom ash or slag, fall to the bottom of the coal combustion chamber and typically account for 10 – 20% of the total ash produced (Mahlaba et al., 2011a). CA is heterogeneous and often consists of a mixture of slag, ferrous and non-ferrous

metals, ceramics as well as other non-combustible and residual organic matter (Kim et al., 2005). It is porous, irregular and granular with a much larger particle size than FA; similar to that of gravel. The larger CA particles contain more crystalline and less glassy phases in comparison to FA. It is darker than FA with colours ranging from grey to black. Some studies claim that CA and FA have similar chemical compositions if derived from the same coal with CA having a higher carbon content and thus higher LOI (Argiz et al., 2017; Lan and Yuansheng, 2007). CA particles also have high porosity and are characterized by large particle sizes with approximately 90% retained on a No. 325 sieve (45μm) with sizes ranging between 0.1 – 5mm (Basirun et al., 2017).

CA is typically disposed of using two methods, namely the dry and wet methods. Dry CA is disposed of in landfill sites and ash dumps whereas wet CA is pumped in a slurry form to disposal sites such as ponds or lagoons (Yoon et al., 2009). There is a significantly larger proportion of CA dumped in comparison to FA due to its limited usage in backfilling applications. Furthermore, new coal plants in South Africa use dry ash handling systems whereas older plants use wet ash/slurry systems. CA is utilized mainly in the cement industry (Argiz et al., 2017), road construction (Del Valle-Zermeño et al., 2015) as well as embankments (Kim et al., 2005). CA has a particle size distribution and physical properties similar to that of river sand hence can be used as a substitute in the cement making industry as well as the brick-making industry. Since CA consists mostly of silica, iron, and alumina, it is useful and feasible for concrete production (Rafieizonooz et al., 2016).

An extensive review detailing the potential use of CA as a pozzolanic material has been conducted by Abdulmatin et al. (2018). This study found that unmodified CA is not suitable as a pozzolan however CA that has been ground is suitable. The pozzolanic reactivity of the ash could increase by 27% upon particle size reduction (Cheriaf et al., 1999). At least 25% of the CA particles should be able to be retained on a No. 325 sieve (45 μm). Many other studies were conducted utilizing CA as a replacement of the fine aggregate in cement (Andrade et al., 2009; Kou and Poon, 2009). Overall, CA was not suitable when purely used as a cementitious binder and requires modification. Robl et al. (2017) stated that when CA is used in backfill operations, it should be close to optimal moisture content and free from pyrite as available sulphate will lead to expansion reactions. In cases where CA replacement was increased, workability was reduced.

2.3.3 Brine

Coal processing methods such as gasification and combustion rely heavily on water usage. This water is often obtained from rivers or underground sources and contains a significant amount of soluble salts. Steam generation is required through the combustion and gasification of coal is required in order to rotate the turbines for power generation. This steam needs to be of ultra-pure quality as it is boiler feed water. To achieve this high purity water, pre-treatment of the water is required such as ion exchange or reverse osmosis. Brine is generated as a waste product of this process. Additionally, the resultant steam in the cooling process becomes heavily concentrated with dissolved salts due to evaporation. This is because these salts were initially present in low concentrations, however, due to water loss through evaporation, the stream becomes heavily concentrated with these salts. These salts contain elements such as Na, Mg, Ca, K, SO_4, Cl, As and Pb (Fatoba et al., 2015). These industrial brines are very complex mixtures of salts in varying concentrations which are dependent on the initial water quality or the water treatment process which results in brine production. Brines can be very saline with a total dissolved solids (TDS) in excess of 35 000 mg/l. These salts need to be removed from this wastewater stream to prevent accumulation and in accordance with the ZLED policies most mining operations utilize. This is especially true in inland coal processing operations. Wastewater treatment processes are thus mandatory and include techniques such as reverse osmosis, electrodialysis, ion exchange, and ultrafiltration. It is estimated that for every cubic meter of desalinated water, an equivalent amount of brine is produced (Muftah, 2011).

The wastewater stream can be disposed of in evaporation ponds, via deep well injection or via surface water discharge. Surface disposition occurs whereby the brine is placed in solar evaporation ponds and left to undergo evaporation in an attempt to reduce the volume of wastewater and produce a manageable solid waste product (Petrik et al., 2015). This method is not sustainable for long term usage as it requires a large amount of space and time and is wasteful of water. The solid waste produced can be harvested and sold or disposed of at an approved disposal area (Squire, 2000). Deep well injection disposal discards the brine underground via drilling of wells. This process is costly as the well design and geological constraints must be considered to ensure the brine is not a source of contamination. An environmental impact assessment (EIA) is required which is used to predict the adverse impact on the environment of a particular waste. Surface disposed of brine is released into

groundwater or the sewers. This process dilutes the brine but can cause significant ground and water pollution. Mickley et al. (1993) stated that brine disposal accounts for a significant portion of wastewater treatment costs. The handing of the brine can also be technically challenging (Mahlaba and Pretorius, 2006). It has also been found that current disposal methods are not sustainable and cause a significant environmental threat (Ahmed et al., 2003). The need for cost-effective brine utilization or disposal is necessary.

As current methods are not effective nor sustainable disposal techniques, the use of brine and FA co-disposal is growing as both these wastes exist in abundance. Muriithi et al. (2014) investigated the interaction of co-disposal between FA and brine which showed promising results. The addition of FA to the brine showed an increase in pH (From 4.48 to 11.55) accompanied by a decrease in the major brine constituents such as Na, K, Mg, and SO_4. The converse was true in the case of calcium and chlorine. This suggests that the constituents of the brine can be encapsulated within the FA particles or be precipitated as secondary salts onto the particles. The co-disposal of FA and brine thus has the potential to mitigate the environmental footprint of each constituent (Jewell and Fourie, 2006). Mahlaba (2007) compared the rheological behaviour of pastes with brine and potable water. Pasting with potable water produced a higher bleed formation but lower setting time in comparison to pasting with brine.

2.4. Elemental Chemical Composition of Coal Combustion Products

The chemical composition of the coal combustion products (CCPs) is critical in achieving the desired outcomes of the CPB in terms of environmental and structural suitability. CCPs generally contain varying amounts of SiO_2, CaO, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O along with other trace elements such as As, Cu, Ni, Cr, Pb, Ba, B, Co, Cd, and Mn. FA and CA differ in their chemical composition due to their difference in particle size. As a result, the ash types have different concentrations and subsequent leaching rates. The presence of chemical compounds such as sulphates and alkali earth metals also differ and CCPs containing high concentrations of these elements can be of concern due to their secondary chemical reactions (Malvar and Lenke, 2006). The total concentration of these elements and compounds need to be analysed to ensure there is no harmful environmental impact on the receiving environment upon disposal or secondary use.

A large portion of the elements contained in CCPs is typically found on the surface due to their high melting points and the short time spent in the combustion chamber. Whilst in the combustion chamber, these elements become volatile and react with the surrounding oxygen. Upon cooling, they become crystalline solids and condense on the surrounding ash particles (Kutchko and Kim, 2006). The relative volatility of these elements determines the chemistry and reactivity. Figure 2.5 shows roughly which elements are encapsulated in the various ash types according to their relative volatility (Figure adapted from Robl et al. (2017)). Group 1 elements are those that do not volatilize whereas Group 2 elements are those that volatilize completely in the combustion chamber. Thus, as the flue gas moves up the combustion chamber, these elements condense on the FA particles as a result of the temperature drop.

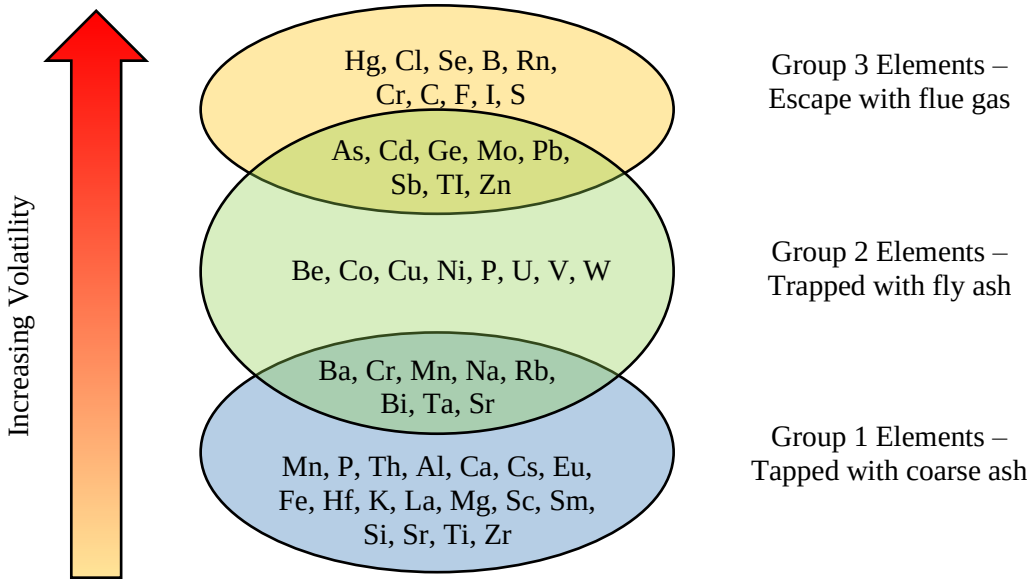

Figure 2-5: Elements in the Various Ash Types According to Relative Volatility

2.4.1. Leaching of Trace Elements and Compounds

Leaching is defined as the process whereby water travels through a solid matrix thereby dissolving analytes within the solid matter and releasing them into the surrounding environment. Leaching can be of concern as harmful elements or compounds can be released into the environment which were previously encapsulated within the ash particles. The extent of leaching of CCPs can be significant due to the very thin surface layer on the ash particles which contains a significant amount of readily available leachable material.

When utilizing CCPs, the mobilization of major and minor elements depends on numerous factors such as complex ion formation, precipitation or dissolution, adsorption, desorption and redox reactions (Cornelis et al., 2008; Gitari et al., 2009). The total amount of and rate of release of the leachable elements are dependent on the total elemental concentration, the distribution of the elements within the ash particles as well as any incorporation of these elements in secondary solids (Jankowski et al., 2006). Factors that affect the leaching of CCPs include elemental concentration, the origin of feed coal, combustion process conditions and pH. The release of these various elements is dependent on the type of leach test conducted and the test conditions. These conditions include factors such as temperature, pressure, extraction fluid, solid to liquid ratio, test duration and the number of extractions (Zandi and Russell, 2007).

Compounds such as sulphates, alkali earth oxides, and chlorides are highly unstable in the presence of water at ambient conditions. These compounds will usually rapidly dissolve to form more stable, less soluble mineral phases which will be precipitated out into solution. Thus, the alkaline earth elements may rapidly dissolve at first and pass into the solution. Following a period of time coupled with an increase in pH, secondary solids may be re-precipitated. Initially, a high leaching rate will be observed followed by a rapid decline. The concentration and leachability of these elements contained in the secondary phases will be controlled by the solubility of that particular phase (Spears and Lee, 2004).

Trace metal and element leaching have always been an environmental concern when dealing with CCPs due to the presence of numerous metals in varying concentrations such as As, Zn, Cu, Cd, Cr, and Pb. Detailed leaching studies have been conducted by researchers in different leaching environments (Choi et al., 2002; Gitari et al., 2009; Izquierdo and Querol, 2012; Jankowski et al., 2006; Jones et al., 2012; Kim et al., 2003; Silva et al., 2010; Ward et al., 2009). However, some studies claim that the results may be unrealistic and not simulate actual conditions as in the case of the toxic characteristic leaching procedure (TCLP) test (Zandi and Russell, 2007). This test utilizes acidic environments which is an unlikely environmental condition (Jones et al., 2012). This has prompted research into testing and analysing the varying leaching tests methods and conditions in order to determine the most optimal test which accurately represents that of the environment that the CPB will be in contact with.

2.4.1.1. Trace metals

A study by Jones (1995) found that elements such as Cd, Cu, Mo, Sb, V, and Zn are enriched on the surface of FA particles and are more easily leached whereas elements such as Ba, Co, Cr, Mn, Ni, and Pb are distributed between the surface and glassy matrix of the ash particles thus exhibit lower leachabilities. Since these elements are enriched in the core of the ash particles, their release is diffusion-controlled and dependant on surface layer dissolution rates. The precipitation of secondary species such as ettringite is found to bind and encapsulate elements such as As, B, Cr, Sb, Se and V (Izquierdo and Querol, 2012). Although an alkaline pH lowers the mobility of most metals, metal mobility may be enhanced in the case of As, Cr, Mo, Sb, Se, V, and W.

Madzivire et al. (2018) found that FA coupled with AMD can neutralize and capture elements such as Fe, Al, Zn, Cu, Co, Mn, and Ni. At a low pH, Fe was the highest leaching element whereas at a higher pH, As was the highest leaching element (Sandeep et al., 2016). Selenium also showed significant leaching at a high pH. Other studies showed that Cr and Mn showed high leaching across the entire pH range (Zhao et al., 2018). Metal mobility is largely dependent on pH with a higher mobility expected at low pHs except in the case of As release (Dutta et al., 2009). Molybdenum is the highest leachable element in alkaline ashes whereas boron is highly leachable in acidic ashes.

Jones et al. (2012) analysed the leaching of metals using two methods. The synthetic groundwater leaching procedure (SGLP) and TCLP tests were utilized. Following the SGLP test, elements such as Se, Mo and As were the most mobile elements whereas, in the TCLP test, Ca, Se, Mo, Cd and As were found to be the most mobile. The same study also showed that calcium is more mobile in CA than FA. Overall, CA generally had a lower leachability in comparison to FA which may be attributed to particle size (Jones et al., 2012). Zandi and Russell (2007) also found that high mobility was found for As, Mo, and Se. These studies confirm that oxyanion forming elements such as As, Mo, Sb, Se, and V are the most easily leachable (Ward et al., 2009). Trace elements such as As, Zn, Pb, Ni, Mo, Cr, and Cu were leached in significant proportions (> 30%) from fresh FA (Nyale et al., 2014).

Ward et al. (2009) investigated the leaching of FA following long term weathering. The study showed that weathered ashes have a lower degree of metal mobility in comparison to

the fresh ashes. This was not the case for Mo which had a higher mobility as a result of the increase in pH. This study suggested that equilibrium between the FA and environment has been reached and that once the readily available leachable material had been removed, the remaining elements remained stable with time. This shows promise for using weathered ashes in CPB applications. Querol et al. (2001) compared open and closed leaching systems at different temperatures to observe the effect on leaching. No considerable differences between these systems were found but high temperature leaching resulted in a greater release of elements. High metal mobility of Ca, S, Mg, B, Mo, Se, Ni, Sn, Pb and Cu were found. Leaching was in the order of B ≥ Mo ≥ Se > Li > Sr = Cr ≥ As = Ba = Cd = V > Sn > Rb = Zn ≥ Cu = Ni = Pb > U > Co > Mn.

Leaching of fresh and weathered FA at different depths was performed by Zielke-Olivier and Vermeulen (2016). Ca, B, Ba, and Al decreased with an increase in depth whereas elements such as Mo, Cu, Si, Cr, and V increased with increasing depths. Elements that remained constant were Fe, Na, K, and Mg. Leachability occurred at a higher rate in the fresh ash in comparison to the weathered ash. This confirms that a large concentration of elements is deposited on the surface of the ash particles. The converse was true in the case of Fe, K, and Mo. These elements are rather encapsulated in the ash matrix and are released gradually during weathering. Concentrations of As, Zn, Pb, and Ni were higher in weathered FA in comparison to fresh FA. This was due to the co-disposal of brine with the weathered FA (Nyale et al., 2014).

2.4.1.2. Ionic Species, Alkali Earth and Alkali Metals

The most predominately leached ionic species are Ca, SO_4^{2-}, Cl and the alkali earth metals (Na and K). This is due to their solubility across a wide pH range (Izquierdo and Querol, 2012). Gupta et al. (2017) found that leaching occurred in the order of Al > Fe > Mn > Zn followed by various other elements. CA has high chlorine content and hence higher leachability. The leaching is equivalent to the total concentration due to the high solubility of the chloride ions (Del Valle-Zermeño et al., 2015; Kosson et al., 1996). FA co-disposed with brine showed an increase in chloride concentration due to the leaching of the soluble chloride salts (Muriithi et al., 2014). However, in other cases, the CSH gel formed by the pozzolanic reaction had the ability to immobilise chlorine and thus lower leachability was observed (Mahlaba et al., 2011a).

Gitari et al. (2009) showed that Ca, Mg, Na, K, and SO_4 were significantly leached from the fresh FA. The study concluded that a large number of soluble salts are easily leached in fresh ashes. pH was the greatest controlling factor in element mobility with B, Mn, Fa, As and Se leaching out at low pHs. Silva et al. (2010) investigated both FA and CA and found that FA has an overall higher solubility thus higher leaching rates are expected due to the smaller particle size.

2.4.2. Sulphate

There are various sources of sulphate of which the largest source is in the mine tailings. These tailings heaps typically contain significant amounts of finely ground sulphide minerals which are dominated by pyrite (Harrison et al., 2010). The presence of sulphide could potentially lead to AMD generation through oxidation of the mine tailings which ultimately reduces the strength, chemical and mechanical properties of the CPB due to changes in the pH and volume. This occurs as, during the chemical reaction, an expansive phase is created which causes internal stress on the CPB thus reducing the overall strength (Kesimal et al., 2004a). Sulphate attack on concrete is very common when such compounds are present in the mine tailings (Benzaazoua et al., 1999). The presence of sulphide, coupled with a high binder content, can be advantageous as a CPB with a higher density is produced, and as a result, higher strength is achieved. However, high sulphide content in the CPB can run the risk of being susceptible to sulphate attack and can potentially weaken the CPB (Kesimal et al., 2004a).

2.4.3. Silica, Alkali Earth Metals and Calcium Oxide

More than half of the chemical composition of class F ashes consists of silica. The silica present is found in three different phases namely, amorphous silica, quartz crystals, and mullite. Quartz is found to increase the strength of the CPB and is preferred over the other phases owing to its low solubility and non-reactive nature. Amorphous silica is more reactive and its presence is equally important due to its pozzolanic activity which also contributes significantly to the strength of the CPB. However, amorphous silica also plays a role in the alkali-silica reaction (ASR).

The ASR is a chemical reaction that occurs in concrete between alkali-hydroxides present in the pore solution and certain types of materials containing reactive siliceous minerals or glass (Harish and Rangaraju, 2011). ASR is of serious concern with regards to the CPB and precautions need to be taken to ensure this does not occur. The alkali ions, such as sodium (Na^+) and potassium (K^+), are usually present in the cement but can also be found in the ash, mine tailings process water, brine or the surrounding environment. These ions are often present in the form of sulphates or hydroxides. When these ion-containing compounds react with water, these ions become soluble and dissolve into the CPB pores. This, in turn, increases the corresponding hydroxide ions (OH^-) concentration. This increased OH^- concentrations dissolves and reacts with the amorphous silica present in the ash forming a gel-like substance. This gel is hygroscopic thus absorbing the surrounding water which causes an increase in volume and the gel begins to swell. This swelling can be significant enough to induce expansion and pressure on the surrounding environment and as a result, causes cracks in the concrete and ultimately failure of the CPB (Lahdensivu et al., 2018). This reaction is however unstable in the presence of calcium ions (Ca^{2+}) in the form of $Ca(OH)_2$. The gel reacts with these ions to form the calcium silicate hydrate (CSH) which is an important strength binder for the CPB. However, over a long period of time, the calcium may be all used up and ASR will begin to occur.

FA and other CCPs with a high silica content and low CaO, Na_2O, and K_2O are preferable due to their pozzolanic activity and ability to mitigate ASR. Ideally, a ratio of silica to aluminium oxide should be ~2 for concrete applications (Akbari et al., 2015). Pozzolanic CCPs are found to decrease the risk of bleeding or thermal cracking and improve strength (Lowe, 2012).

2.4.4. Loss on Ignition

The loss on ignition (LOI), which is a measurement of the unburnt carbon content in the ash is critical in concrete applications. LOI is important as air entrainments problems arise due to factors such as the type of carbon (i.e. activated carbon), the interaction between the ions and the variability of the carbon content. Air entrainment is problematic as the residual carbon can absorb water and chemical admixtures which reduce the efficiency of the concrete and result in an inadequate air-void system. Generally, a maximum of 12% is allowable for class F ashes and 6% for class C ashes (Thomas, 2007). A high LOI is also

found to reduce the effectiveness of the CPB as this increases the water demand in the concrete as shown in Figure 2.6 (Abubakar and Baharudin, 2012; Wang et al., 2009). Care should be taken when utilizing CA which is characteristic of a high LOI in comparison to the other ashes. Many state transportation departments globally specify a maximum LOI value that does not exceed 3% - 4%, even though the American Society for Testing Materials (ASTM) ASTM C618-05 (2005) standard criteria is a maximum LOI content of 6%. This limit is because LOI values greater than 4% have adverse effects on air entrainment. In concrete application, a low and consistent LOI is important in predicting product quality and the control of air entraining admixtures.

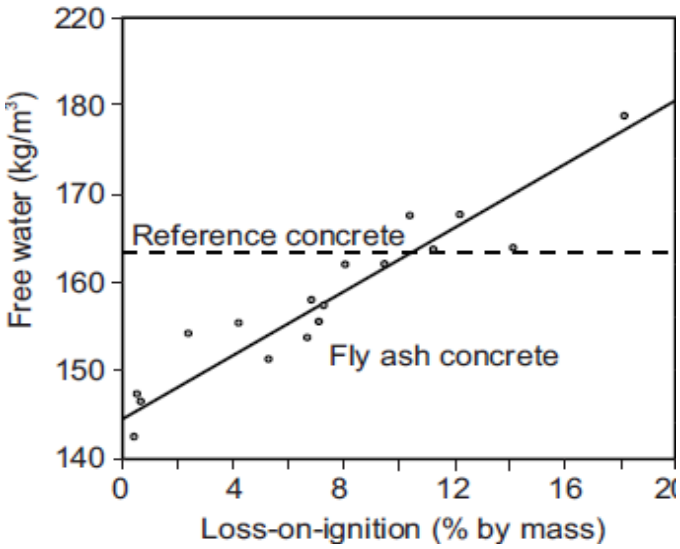

Figure 2-6: Effect of LOI on Water Demand of Concretes at Equal Slump (Thomas,2007)

2.4.5. Class of Ash

There are two main classes of coal ash which are Class F and Class C ashes. These classes arise due to the difference in their elemental composition, heating value, geographical location, and ash content. The variation in the chemical properties of the FA produced from each coal category is shown in Table 2.1 (Ahmaruzzaman, 2010). There are four main categories of coal which are: anthracite, bituminous, sub-bituminous, and lignite. Very little anthracite coal is burned in utility boilers, thus there are only small amounts of literature available on anthracite coal FA and results are not presented.

Table 2-1: Chemical Composition of Fly Ash Produced from Different Coal Types

	Weight Percentage of Component		
Component	Bituminous (%)	Sub- Bituminous (%)	Lignite (%)

SiO_2	20 – 60	40 – 60	15 – 45
Al_2O_3	5 – 35	20 – 30	10 – 25
Fe_2O_3	10 – 40	4 – 10	4 – 15
CaO	1 – 12	5 – 30	15 – 40
MgO	0 – 5	1 – 6	3 – 10
SO_3	0 – 4	0 – 2	0 – 10
Na_2O	0 – 4	0 – 2	0 – 6
K_2O	0 – 3	0 – 4	0 – 4
LOI	0 – 15	0 – 3	0 – 5

According to the ASTM C618-05 (2005) standard, ashes with a combined SiO_2, Al_2O_3 and Fe_2O_3 content of 70 wt% with a low lime content (< 10%) are termed class F ashes whereas a combined content of 50 wt% with a high lime content are termed class C ashes. A comparison between these classes of ash are summarized and shown in Table 2.2 (Thomas, 2007).

Table 2-2: Comparison between Class F and Class C Ashes

	Class F Ashes	**Class C Ashes**
Type of Coal	Anthracite and bituminous	Lignite or sub-bituminous
Hardening properties	Pozzolanic with the addition of cementing agent	Pozzolanic and cementitious
Lime content	Low (1 – 12%)	High (30 – 40%)
Alkali content	Low	High
Sulphate content	Low	High
Sulphate resistance	Increased with 20 – 30 wt% ash	None. May increase sulphate attack
Heat of hydration	Reduced	Only reduced at high content (>50 wt%)
Early-stage strength	Higher	Lower
Alkali-Silica reactivity	Reduced with 20 – 30 wt% ash	Reduced with 40wt% ash
Maximum LOI	12%	6%

Class C ashes are formed from lignite or sub-bituminous coals. Class C ashes are known for their pozzolanic and cementitious properties and often do not require a cementing agent since they are self-cementing in the presence of water. Such ashes contain high amounts of lime (30 – 40%), alkalis and sulphates (Dwivedi and Jain, 2014). Lignite and sub-bituminous coals also contain higher amounts of calcium and magnesium oxide with lower amounts of silica and iron oxides accompanied by a lower carbon content. Some studies have found that class C fly ashes are not suitable in areas where sulphates are a concern as such ash may increase the rate and extent of the sulphate attack (Folliard and Drimalas, 2008; Thomas, 2007). Class C ashes have also been found to have higher operating costs due to the addition of air-entraining agents and higher heat of hydration. Class C fly ashes should consist of no more than 35 wt% in concrete applications (Naik et al., 2003).

Class F ashes are formed from burning bituminous and anthracite coals. These ashes have pozzolanic abilities, however, they require the addition of a cementing agent such as OPC owing to their low CaO content (1 – 12%). South African FA is generally comprised of bituminous or sub-bituminous type coals. Class F ashes have been found to lack the initial early age strength qualities but can be significantly enhanced in the long term. Class F ashes are advantageous because the addition of superplasticisers is not required thus minimising costs.

2.4.6. Particle Size Distribution

One of the most important characteristics of a uniform CPB is the particle size distribution (PSD). This affects the porosity, transportation, workability, and setting of the CPB. It is generally particles that are smaller than 20 µm that have the most profound effect on the CPB, specifically on pumping (Kesimal et al., 2004a).

Fines are defined as those particles having a diameter of less than 20µm. An extensive study on the effect of the fines content on the CPB has been done by Fall et al. (2005). It was also found that the greater the fines content, the greater the porosity of the CPB. Backfills with higher fines content are found to have a lower strength owing to this high porosity of the CPB. The pore size distribution is also affected by the amount of fines content which consequently affects the strength of the CPB. Pore sizes ranging between 1 – 10µm have been found to affect the porosity by the greatest degree. Kiattikomol et al. (2001) found that

the fineness of the CCPs has the most pronounced effect on the pozzolanic activity and hence the ability to produce reaction products.

The content of fine particles increases the overall surface area of the tailings, as a result, higher water and cementation costs are needed which creates a CPB with a higher moisture content (Ke et al., 2015). As the presence of fines is increased, this allows less water to seep through the CPB owing to the low permeability. However, upon setting, the coarse particles can separate from the fines and this forms a non-uniform CPB (Ercikdi et al., 2017). A CPB with at least 15 wt% fines is required to prevent this from occurring (Meggyes and Debreczeni, 2006). Current specifications for use of FA as a pozzolan according to the ASTM C618 requirement is a maximum of 34% to be retained on a 45 μm sieve.

2.5. Backfilling

The backfill material is often a mine composite material containing a non-homogenous mixture of mine tailings, hydraulic binders, and water. It is useful as large amounts of mine waste are able to be disposed of simultaneously. It could consist of varying amounts of FA, CA or a mixture of the two. Other backfills do not utilize mine tailings or potable water, but rather implement brines and CCPs alone. The composition of the backfill is site-specific and designed following extensive testing which reviews both the environmental and structural specifications.

2.5.1. Types of Backfilling Methods

There are three main types of backfilling methods. These include rock backfill, hydraulic backfill and the CPB. Each method has its advantages and disadvantages as shown in Table 2.3. The type of backfill method used is specific to the factors listed below (Hustrulid et al., 2001) –

- The type of mining process;
- Excavation sizes and stope sequences;
- Depth and orientation of mine; and
- Type of material available for backfilling.

Rock backfill can be described as a technology for the transportation of backfill forming components such as rock, stone, gravel, soil or industrial solid waste underground using

labour-intensive methods, gravity or machinery equipment to fill underground mine voids (Sheshpari, 2015). Rock backfilling is most suited for the cut and fill mining method.

Hydraulic backfilling is used when tailings are passed through hydro cyclones or other mechanical means to produce separate clay fractions and sand. The clay produced, also termed slime, is removed and stored or disposed of and generally not used further owing to low permeability. The remaining sand is then hydraulically pumped into the mine voids and can be mixed with binders if necessary. This method is suited for room and pillar or board and pillar underground mining techniques (Sivakugan et al., 2006).

A CPB is a modern backfill method commonly used today. A cemented paste refers to a paste that is a non-segregating, non-settling suspension of solids in a liquid medium with non-zero yield stress. This means that the paste consists of solids that do not separate from the liquid phase and requires a minimum force in order to flow. It is a non-homogenous material made by mixing waste tailings, water, and cement. The solids content usually ranges between 70% and 85%. The water used is typically mine processed water or brine and the binder accounts for 3-7% of the total weight (Sheshpari, 2015). This method is often preferred as it ensures safe and economical disposal of mine waste as additional tailings disposal and rehabilitation costs are not incurred.

Table 2-3: Comparison of Advantages and Disadvantages of Various Backfill Methods

	Advantages	**Disadvantages**
Rock backfill	Flexible and ease of operation	Labour intensive
	Minimal power requirements	Tight packing is not always achieved
Hydraulic backfill	Suitable for all materials of different shapes and sizes	High water consumption
	Simple to operate	Can have uncontrollable flow
Paste Backfill	Dense CPB with high strength	Energy and capital intensive
	Safe deposit of mine waste	High pumping capacity

In order to fully understand the NEB achieved from backfilling, the risks associated with the unfilled void of the abandoned mine needs to be compared to that of the equivalent surface-based ash-brine disposal backfill system. If the backfilled mine disposal operation poses a lower risk than that of the unfilled mine void, a NEB is achieved. A critical comparison between the conventional ash and brine management system and the backfill operation will allow one to determine if a NEB is achieved.

2.5.2. Conventional Ash and Brine Management

A typical ash and brine management system is shown in Figure 2.7. A full description of the process is given below the figure corresponding to the respective labels in the figure. Figures 2.7 and 2.8, as well as detailed process explanations, can be found in Love et al. (2019).

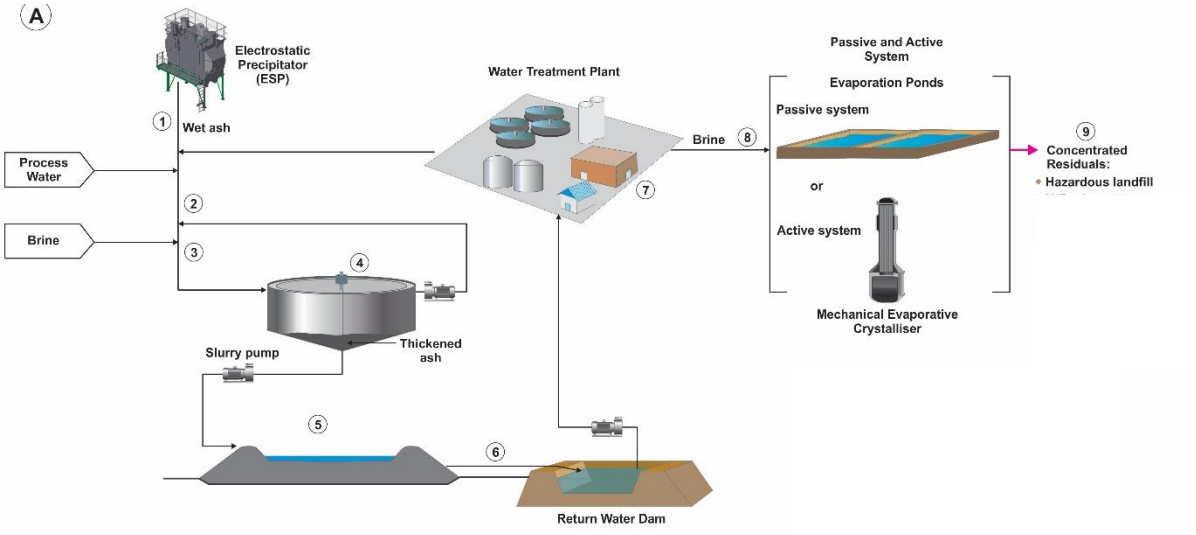

Figure 2-7: Conventional Ash and Brine Management System

A1: Fly ash is formed following the combustion of pulverized coal and is transported downstream via the flue gas stream. The FA is separated from flue gas by electrostatic precipitators (ESP). Other mechanical precipitators or baghouses may be used for this process. The FA is then collected in hoppers found below the ESP.

A2: Water is utilized in a wet ash removal system to convey the FA downstream in a dilute slurry. This water is often processed water from elsewhere in the plant which is being reused. The water to ash ratio in this slurry is typical large ranging between 10 and 20 times. This value does vary between different plant operations.

A3: Brine which is generated from water recovery operations can be added to the FA slurry. The resultant stream often contains a large amount of salts which favours

precipitation and dissolution of contaminants from the ash. This step is optional in plant operation. Dry disposal systems do not have the addition of brine or water.

A4: The ash-brine stream is thickened in a gravity thickener for transportation to the disposal facility. The thickener is used to optimize water content and ensure that operational parameters such as pumping are not compromised by minimising the mass of material required to pump.

A5: The thickened ash slurry is disposed of in an ash dam. The ash sinks to the bottom of the ash dam and forms large beaches around the edges. Excess water in the slurry separates from the ash and is removed through water sluices. A certain amount of water will remain trapped in the ash dam as interstitial water thus the ash dam will remain saturated throughout its lifetime. Long term geochemical weathering reactions occur between the ash and contaminants creating a vast amount of secondary reaction products.

A6: The excess water removed from the ash dam through the sluice is returned to the water dam for treatment and re-use elsewhere in the plant. The production of excess water coupled with the additional water from rain run-off causes these ash disposal systems to have large negative environmental footprints.

A7: The water treatment plant is often mandatory in mining operations to prevent large contaminate disposal. The treated water improves water use efficiency in the plant.

A8: The water treatment plant generates brine. This brine can be utilized in step 3 or is left to undergo further treatment. Two treatment methods exist which can be active or passive. Passive brine management uses lined evaporation ponds that rely on wind and solar energy to evaporate excess water resulting in a higher salinity but lower volume brine. Active management schemes use mechanical evaporators which have a high energy input. However, the residual brine from both methods requires further treatment.

A9: The waste produced from step 8 is usually a hypersaline brine or a dry salt cake. Further disposal requires careful consideration as this waste can be hazardous and contains a large amount of contaminants.

In a typical ash-brine management system, the underground mine void is left unfilled. Over time this mine void will fill with water through surface infiltration. This contaminated water is often acidic and will be pumped out of the mine void to prevent accumulation and sent to the water treatment plant for further treatment.

2.5.3. Ash and Brine Backfilling System

A typical ash and brine backfilling system is shown in Figure 2.8. A full description of the process is given below corresponding to the respective labels in the figure. A much more in-depth explanation of this process can be found in Sivakugan et al. (2006).

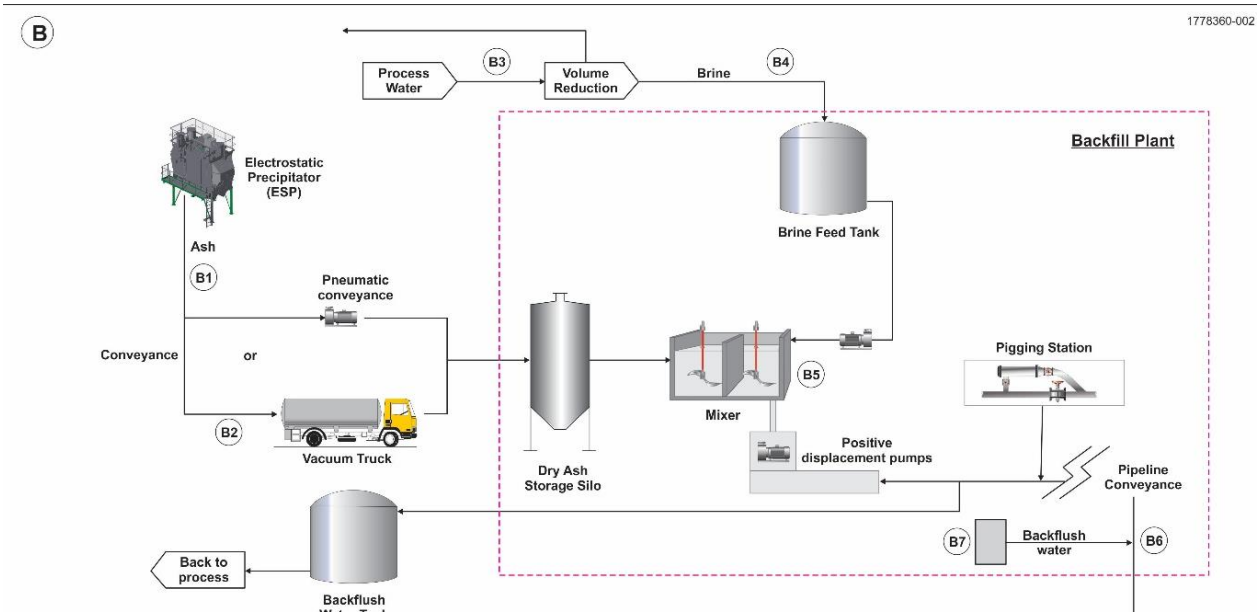

Figure 2-8: Backfilling Process Diagram

B1: Fly ash, which is separated from the flue gas through the ESP, is collected from the hoppers. This ash is in its dry state to ensure the pozzolanic activity of the ash is maintained. The pozzolanic ability of the ash is extremely beneficial for the backfilling operation.

B2: Dry FA is sent to the backfill plant. The method of transportation is dependent on factors such as the distance the ash needs to travel as well as the quantity of ash. The ash is stored temporarily in silos prior to use in the backfill operation. At this stage, additional additives such as lime, gypsum, clays or OPC can be added.

B3: A volume reduction process is used to treat process water through methods such as desalination or thermal evaporation. This is necessary to reduce FA demand and ensure optimal backfill mix proportions are achieved. Clean water is reused in the process and brine is produced.

B4: Brine is transported to the backfill plant and stored in a brine feed tank ready for mixing with fly ash.

B5: Brine and ash are combined in a mechanical mixer according to a pre-determined mix design. This mix design is decided following extensive prior testing to ensure structural specifications can be attained. The resultant mixture is blended to a consistency suitable for backfill objectives. This means that the paste needs to be flowable and/or a high-density slurry that can be easily pumped over long distances.

B6: The CPB is then transported to the underground mine voids via a pipeline and positive displacement pumps. The backfill is injected into the voids through surface boreholes.

B7: Since the CPB is a reactive and cementitious material, various precautions need to be taking regarding the pumping operation. Backflush equipment and pigging stations are installed on the pipeline to prevent line blockages from forming as a result of process interruptions.

Once the CPB has been filled into the mine void, it assumes its resting form as determined by the beaching angle of the material and cures in place. The mine void is filled to the maximum degree possible. As a result, the risk of land subsidence and water ingress into the void is significantly reduced.

2.5.4. Advantages of Backfilling

2.5.4.1 Risk of Metal Leaching

Backfilling is advantageous as the risk of leaching from the brine as well as CCPs is reduced. A detailed review of the leaching behaviour of FA has been done by Izquierdo and Querol (2012). They found that trace metals and a large number of elements are tightly bound to the FA particles and thus will not easily be leached regardless of the nature of the FA. Wang et al. (2016) found that during the cement-making process, cement addition has a positive effect on the immobilization of trace metals. A study conducted by Madzivire et al. (2017) focused on the risk of metal leaching following the use of FA as a backfill material. It was found that backfilling with FA can neutralize and capture 50 – 95% of the metals and other contaminants such as Fe, Al, Zn, Cu, Co, and Mn. It must be noted that these removed contaminants can be remobilized if the CPB is exposed to fresh AMD, water or oxygen as the oxidation of reduced sulphide minerals can form fresh AMD within the CPB voids. It is therefore advised that although FA is suitable for backfilling, the influx of fresh AMD must be avoided to prevent remobilisation of the already captured contaminants. Fatoba et al.

(2011) investigated the FA-brine interaction and showed that the FA was capable of removing some elements from the brine such as B, Na, Mg, Cl, and SO_4. However, some elements such as Ca, Ba, Sr, and K were leached from the FA leached into the brine solution.

2.5.4.2 Water Recovery

Approximately 90% of the process water used in mining operations can be recovered through filtration and thickening before the CPB material is made. Approximately 10% use of FA will result in a 3% reduction in water costs following the cement application (Thomas, 2007). This forms a CPB with a low permeability which inhibits the diffusion of oxygen into the CPB thus reducing the formation of AMD (Ercikdi et al., 2017). A CPB with low permeability is also favoured to prevent the passing of surface water through the backfill material which could lead to the release of potentially harmful elements or compounds.

2.5.4.3 Rheology

Rheology refers to the study of flow or deformation. Rheology is important in terms of backfilling as it refers to the characteristics of the paste which would allow determination of the economic feasibility such as the pumping requirements to transport the paste. FA addition improves workability and rheological characteristics such as pumping and decreases bleeding. These phenomena are observed due to increased dispersion and cohesiveness of the particles which reduces segregation (Naik et al., 2003). Since FA particles are spherical in shape, they act as miniature ball bearings within the CPB thus providing a lubricant effect. Similarly, the pumping ability is improved due to a decrease in frictional losses. As a result, there is less wear on the equipment. CA, on the other hand, reduced the workability when used as a substitute for river sand in concrete (Rafieizonooz et al., 2016; Singh and Siddique, 2016). However, Senapati and Mishra (2012) found that the addition of CA reduced the pumping power requirement. The use of both FA and CA improves the CPB texture since the presence of the irregularly shaped particles enhances the interparticle friction which is responsible for obstructing the flow of fresh paste (Rafieizonooz et al., 2016).

2.5.4.4 Chemistry

Coal FA addition has been found to have a reduced heat of hydration. This is because the slower reacting FA generates less heat per unit of time as opposed to the hydration of the

faster reacting OPC. As a result, the temperature rise when using FA as opposed to OPC will be lower. The pozzolanic reactions that occur with the CPB have a lower heat of hydration than the reactions occurring with cement, resulting in a decreased risk of thermal cracking (Zasiah et al., 2011). This is especially beneficial for use in large masses of CPBs since not only is the heat dissipated as quickly as it develops, but the reduced thermal cracking will result in a higher strength CPB due to the pozzolanic reaction products. Class F FAs are generally more effective than Class C FAs in reducing the heat of hydration.

Class F FA has been effective in inhibiting or reducing expansive reactions resulting from the ASR. This is because the total alkali content is reduced by replacing some of the cement with FA. There is also a reduction in the CaOH content of the CPB through the formation of the CSH gel and reduction in pore solution alkalinity through alkali binding by the pozzolanic reaction products. There is an additional refinement of pore structure and pore size distribution in hydrated CPB resulting in reduced permeability and a denser CPB (Harish and Rangaraju, 2011). This is also because class F FAs have a lower alkalinity and are hence more susceptible to combatting ASR. Since many CCPs are alkaline materials, they have the ability to neutralize acidic groundwater and inhibit the production of AMD. AMD production is reduced due to a smaller surface area of rock for the reactions to take place on (reduction of contact between groundwater and mine compartments), as well as decrease water flow through the CPB and the addition of neutralising materials.

Furthermore, the implementation of FA in the CPB will reduce the CO_2 emissions as less cement is required in manufacturing (Akbari et al., 2015). It has been estimated that 7% of the world's CO_2 emissions are linked to cement manufacturing thus the lime content replaced with FA will significantly reduce this percentage. Replacement of cement by one tonne of FA will reduce CO_2 emissions by the same magnitude (Malhotra, 1999).

2.5.4.5 Mining

The use of CPBs could not only rehabilitate abandoned mines but also has the potential to reduce the current environmental impact of existing mine sites. Backfilling provides a safe working environment for miners through surface stability and improved mine ventilation (Cui and Fall, 2016). Backfilling also controls surface subsidence which is often more severe in shallow depth mines (Deng et al., 2016). Mineral recovery is improved by reducing ore dilution. Thus, more ore reserves are made available as the ore pillars which were previously left underground can be replaced by the CPB acting as secondary ground support pillars thus

increasing the recovery ratio of minerals in adjacent openings (Ke et al., 2015; Xu et al., 2018). This could benefit both abandoned and active mine sites. Furthermore, the risk of rock bursts is reduced as the pressure is now distributed more evenly. In addition, surface pollution is mitigated through disposing of tailings underground. The new legislation also specifies that surface disposal ash dams need to be lined which could add additional costs, thus backfilling will mitigate this cost.

2.5.5. Disadvantages of Backfilling

2.5.5.1. Capital Intensive

The process of designing and implementing a CPB can be extremely energy and capital intensive due to dewatering, filtering, and pumping. The thickened paste slurry requires high pumping pressures due to the high density (Ercikdi et al., 2017) and as a result, pumping maintenance is necessary. Transportation costs are also high depending on the rheology of the paste especially since these pastes are characterized by high densities. The mine tailings need to be dewatered prior to use in order to become a paste which can be expensive. This process generally requires a lot of manpower and equipment as a new independent plant is formed. Essentially, a new plant is formed on-site containing all the equipment necessary to produce the paste.

Air entrainment costs become significant when considering the addition of FA to the CPB. When FA is used, the addition of an air-entraining agent is required to ensure the freeze-thaw durability of the CPB. This is due to the particle sizes and the unburnt carbon content in the ash which absorbs the mixture (Naik et al., 2003). Binder costs are very significant when utilized in CPB. Binders are said to account for a significant portion of the backfilling project with costs in the region of 75% of the total project (Grice, 1998). Huge cost savings can be attained by reducing the binder proportion. However, this can compromise the strength of the CPB. This study aims to achieve maximum strength development with minimal binder proportion.

2.5.5.2. Pumping Requirements

Rheology, workability, and transport of the CPB into the mine voids are an important technical indicators and constitute a large portion of the costs. These factors play a significant role in the design of the piping and transportation system. An extensive study

performed by Qi et al. (2018) evaluated the pumping requirements of the CPB. The study showed that the pressure drop increased with an increase in solids content, cement to tailings ratio and the inlet velocity of the CPB. However, the circuit shape had the most profound effect. Wu et al. (2015) found that increasing the volumetric flow rate and pumping pressure as well as increasing the pipe diameter with a fixed volumetric flow rate can reduce the pressure drop. Positive displacement pumps are often used which can be costly especially for smaller companies.

2.5.5.3. Legislation

A limitation associated with backfilling is the current legislation. FA is classified as a hazardous waste and as a result, there are many legislative constraints associated with further use. These constraints are implemented to ensure the intended use for the waste is beneficial. The current legislation in South Africa is set out by the Department of Environmental Affairs (DEA) under GN. 715 of 2018 which specifies that a FA user needs to apply for a waste exclusion. The National Environmental Management: Waste Act, 2008 (Act 29 of 2008) (NEM: WA) outlines procedures and guidelines in applying for a waste management license following an environmental impact assessment to ensure the waste will be used in an environmentally beneficial manner. These procedures can be a costly and time-consuming task which may hinder small scale users from the re-use of their FA in an environmentally acceptable manner.

2.5.6. Properties of the Backfill Material

Many factors affect both the short- and long-term strength, stability, and suitability of the CPB. These factors are grouped into intrinsic and extrinsic factors as stated by Ercikdi et al. (2017). Intrinsic factors are those related to the chemical, physical and mineralogical characteristics of the CPB which include the mine tailings, binder, and FA as well as the ratio in which these components are mixed to form the CPB. Extrinsic factors are those which relate the interaction of the CPB with its surrounding environments such as the geographical location of the mine and the type of adjacent rock. Various intrinsic and extrinsic factors with regards to backfilling are shown in Table 2.4 below.

Table 2-4: Intrinsic and Extrinsic Factors for Backfilling

Intrinsic Factors	**Extrinsic Factors**
Chemical properties of FA – Particle size distribution, specific gravity	Stope size and geometry
Water/cement ratio of the CPB	Groundwater conditions
Binder type	The temperature of the curing conditions
Water pH	Drainage conditions of the surrounding rock

Of the two factors stated above, the intrinsic factors are the ones that can be easily manipulated to achieve the desired outcome. The intrinsic factors are often modified based on the extrinsic factors so that a CPB with the correct specifications is produced as each case is site specific. The presence of certain intrinsic factors often has a greater effect on the CPB such as mix design. Both the FA and CPB have defined factors that can influence one another thus making them dependent cofactors. The mechanical and rheological characteristics of the CPB are dependent on the physical, chemical and mineralogical properties of the tailings, binder type and ratio used. The characteristics of the CCPs used and the CPB as well as their effect on backfilling are analysed in Section 2.6.

2.6. Design of the Cemented Paste Backfill Applications

Mine backfilling or pasting is suitable due to its economic and environmental benefits. Paste technology involves the immobilization of ash by creating a paste-like slurry consisting of brine and ash which hardens over time due to the pozzolanic activity of the ash. A paste can be defined as a homogeneous, viscous mixture of solids and liquid which does not bleed nor segregate, with the ability to harden. The implementation of paste technology produces a material with low permeability which significantly reduces the re-mobilization of entrapped salts and thus acts as a salt sink. Pasting is able to reduce the environmental impact of hazardous waste and minimise mobility of pollutants through a combination of both physical and chemicals factors such as solidification and stabilization.

2.6.1. Composition

Previous studies state that the main CPB components such as binder and tailings significantly affect the strength and durability (Fall et al., 2005; Kesimal et al., 2004a). The

ratio in which these constituents are combined is also of importance. Composition affects the CPB in terms of strength, density, permeability, workability, and transportation system. The CPB consists of a mixture of solids, water and binder.

2.6.1.1. Solids Content

Solids content refers to the fine aggregate or the larger coarse aggregate particles which are used in concrete applications. The coarse aggregate is typically gravel, crushed stone or crushed bricks (Mansur et al., 1999). In the case of backfilling, a combination of CCPs or FA alone often makes up the solids content. Solids contents between 70% and 85% have generally been chosen.

The optimal water to cement ratio is dependent on the fines content. Decreasing the fines content has had a positive effect on the CPB mixture however there needs to be at least 15 wt% of the fine particles to ensure the CPB forms colloidal particles and remains as a paste (Kesimal et al., 2004a; Xu et al., 2018). An increase in the solids content has been found to decrease the bleeding rate and slump of the CPB (Yang et al., 2017). However, a higher solids content causes a decrease in the workability of the paste as the water content is decreased (Deng et al., 2016). However, high solids content often leads to a longer setting time. It has been found that to reduce underground pollution, the bleeding rate should be 15% with a minimum solids content of 70% (Yao and Sun, 2012).

2.6.1.2. Binders

Binders such as OPC, FA or blast furnace slags (BFS) can be used in a CPB. Binders constitute approximately 3% – 7% CPB (Sheshpari, 2015). The higher the binder composition, the higher the strength of the CPB. This is because an increase in binder content leads to increased hydration and pozzolanic reaction products such as CaOH and as a result, increases the buffering capacity of the CPB towards sulphate attack (Fall et al., 2005; Kesimal et al., 2005; Xu et al., 2018). However, large binder dosages are not economically viable, and an increase in binder dosage increases the surface area of the tailings which are fully covered by the hydration products. Thus, there is a reduction in the tailings surface area available for further oxidation (Ercikdi et al., 2017).

Binders have been found to have a direct correlation with resistance to the deterioration and mechanical strength of the CPB. Backfills containing a binder such as OPC are said to have a lower bleeding rate than uncemented backfill mixtures. Studies by Belem et al. (2002) found that CPB containing a binder of at least 5% significantly reduced the pore size causing a reduction in the saturated hydraulic conductivity and increased the water retention capacity of the CPB.

Studies have been conducted to reduce the amount of OPC by geopolymer binders in order to reduce CO_2 emissions (Akbari et al., 2015). Geopolymer binders utilize the phenomena that alkaline-rich metals react with Al-Si containing materials to produce a strong alumino-silicate complex, thus the raw materials could be FA compounds. This method, however, requires additional activators such as sodium silicate and sodium hydroxide in their study. Overall, the geopolymer binder had comparable strength to that of OPC.

2.6.1.3. Water

The water used in the CPB can either be clean water, mine processed water or brines. Mine water which has been used in mining operations is often dewatered thus removing most of the water to produce a highly concentrated slurry. Typically, a high water content is required with a cement to water ratio of 2.5% – 7%. This is owing to the ease of transport of the slurry as this is one of the main operational parameters. Studies by Yang et al. (2017) have found that a cement to tailings ratio of 1:10 to be the most suitable backfill composition in terms of mechanical and rheological characteristics. As the volume of water increases, the slump values also increase and as a result, transportability is easier.

Brines are more commonly used than mine processed water for CPB applications as they are often rich in Ca, Na, sulphates, and chlorides. Mahlaba et al. (2011) showed that the chemical composition of the brine is an important design parameter. The composition determines the paste rheology as well as strength development. Typical brine compositions vary, however, Mahlaba et al. (2011b) suggested that brine with a salinity of 40 000 – 60 000 mg/l should be utilized for optimal workability. This value may differ depending on the ash or brine used.

2.6.1.4. Backfill mixtures

FA mixed with various industrial brines produces a high-solids paste that hardens over time. The resultant product has low water permeability and good strength development. Some studies have been conducted with varying backfill compositions and different aggregate as well as binder substitutions. FA has been found to be suitable as a backfill material (Palarski, 1993; Sheshpari, 2015). Chen et al. (2017) studied the use of phosphogypsum and phosphate tailings in the CPB, however, a low UCS was achieved. Nurgesang et al. (2016) studied the effect of adding mullite to the FA. The results were a CPB which increased in UCS from 14 Mpa to 71 Mpa with the addition of 40 wt% mullite. Qi et al. (2015) investigated the effect of varying mix proportions on the resistivity and UCS. Both parameters increased with an increase in FA content. Mahlaba et al. (2011b) showed that using a higher salinity brine decreased the paste workability. Table 2.5 shows the mix proportions for concrete mortars with ash substitution used in designing a higher strength mortar. These compositions are used when replacing FA with concrete in structures which require high strength and stability.

Table 2-5: Mix Proportions for Concrete Mortars

	Amount of Constituents (Mehta, 2004)		
Constituents (kg/m^3)	Low Strength (28 Day UCS: 20 MPa)	Medium Strength (28 Day UCS: 30 MPa)	High Strength (28 Day UCS: 40 MPa)
Water	120-130	115-125	100-120
Cement	100-130	150-160	180-200
Fly ash	125-150	180-200	200-225
Fine aggregate	800-900	800-900	800-900
Coarse aggregate	1100-1200	1100-1200	1100-1200
Water:Cement Ratio	0.40-0.45	0.33-0.35	0.30-0.32

2.6.2. Workability

Workability refers to the ease of transportation, placement, and flow of the CPB without any segregation. One of the essential elements required for the utilization of paste for backfilling is the ability to transport the paste underground. Similarly, the ability to discharge the paste

through the surface boreholes and the ability of the paste to flow without segregation once placed underground is important. Water demand which refers to the water requirement of the paste and is another important parameter that determines workability. The water demand ensures that the desired slump and pumping capacity is achieved. Factors that affect workability include the size, shape, and texture of the solids in the CPB. Other factors such as the fineness of the FA or cement used as well as the carbon content affect workability. Low fineness and high carbon contents have an adverse effect on workability. Using high replacement levels of CA can reduce workability due to the higher carbon content and low porosity. As a result, water demand will be higher. This will also lead to higher bleeding rates (Andrade et al., 2009).

A general guideline is that the CPB must contain at least 15 wt% of its particles finer than 20 µm to ensure it remains as a paste and can be pumped (Mahlaba et al., 2011). Uncemented samples have been found to have a higher chance and rate of bleeding than CPBs (Kesimal et al., 2004a). Density also affects workability in terms of transportation. Low density slurries may seem to be more effective due to the ease of pumping over long distances. However, they may have the risk of having poor consolidation and volumetric filling efficiency (Munro and Smirk, 2018). High-density slurries are energy intensive as pumping costs are high. Therefore, slurry paste thickening should be executed to the point where pumping and flow properties remain manageable. The final discharge density does not have a significant effect on the CPB but does on the economic constraints of the operation.

2.6.3. Permeability and Porosity

Permeability and porosity are important parameters of the CPB investigated as they allow one to determine diffusion controlled leaching behaviour. The permeability reflects the rate at which water will seep through a material in a given period of time. It is dependent on the size and shape of the ash particles, the degree of compaction and the viscosity of the water or brine used. Permeability is related to the pore sizes of the backfill paste. There are multiple different pore sizes with four main size distributions. These are large capillary pores (10 nm – 10 μm), middle capillary pores (50 – 100 nm), meso-pores (4.5 – 50 nm) and gel micro-pores (< 10 nm). The CSH gel is characterised as a gel microspore that does not account for the transport of fluids, but rather, the larger capillary pores are responsible for the mass transport of fluids (Robl et al., 2017). Manmohan and Mehta (1981) compared the

pore size distribution of the CPB with and without the addition of FA. Their study showed that at 28 days, the paste containing FA had a higher pore volume than the control sample. However, after a period of a year, the pore volume of the FA paste decreased drastically to below that of the control sample. This shows that the pozzolanic activity of the FA and the presence of reaction products was able to significantly refine the pore structure of the CPB thus reducing permeability. This was confirmed by Zhao et al. (2018). Hardened CPB pastes typically have a permeability of 10^{-5}-10^{-8} cm/s (Conner, 1990). The utilization of FA in concrete has found to produce a cementitious backfill material with a low permeability which is favourable. This is because FA particles are spherical in shape which allows for more dense packing and a decrease in air entrainment of the concrete. A dense backfill paste also has a high favourability for pozzolanic reaction (Ahmaruzzaman, 2010).

The porosity of the CPB depends on the water to cement ratio, degree of hydration, amount of cementitious material as well as the reactivity and the curing time (Jain and Neithalath, 2009). Rong et al. (2017) showed that the porosity of cement mortars decreased as curing time increased as a result of increased cement hydration products. The porosity also has an effect on the UCS, in general, an increase in porosity decreases the strength (Ouellet et al., 2007). The UCS of the CPB decreased exponentially as the porosity increased. Changes in porosity are a result of solids concentrations, with a higher solids concentration leading to a lower porosity (Liu et al., 2018).

2.6.4. Leachability

Leaching from a porous solid material follows the laws of mass transport due to gradients in concentration, chemical potential or pressures. It is a combined process of chemical interactions between the solid matrix, pore solution, and surrounding water. Leaching plays an important role when assessing the potential effects of waste disposal on the environment. The chemistry within and surrounding the CPB will change over time and thus the release of trace elements will vary over time intervals thus making leaching predictions an important parameter to ensure long term suitability over a range of different environmental conditions. The Leachability of the CCPs disposed of in ash dams containing FA or CA can be of concern and is discussed in Section 2.4.1. However, it must be noted that the release of metals and soluble oxides from the CCPs, when implemented in a backfill paste, could still occur especially when the CPB is in contact with water, soil or air for prolonged periods of

time. Flooding of the CPB can lead to the formation of unsaturated zones which causes sulphide oxidation which could potentially lead to trace metal leaching (Hamberg et al., 2018).

The leaching of ions from the CPB occurs due to a concentration gradient between the solid CPB and the surrounding water. The pore solution of the CPB is typically known to be alkaline in nature and is characterised by a high pH. When the CPB is in contact with the surrounding groundwater, the lower ion concentration of this water in comparison to the pore solution creates this concentration gradient which causes ions to diffuse out of the material. This concentration gradient is the driving force of ions to be transported through the monolithic material via diffusion. As the diffusion occurs, an equilibrium between the inner pore solution and monolithic material needs to be maintained. As a result, acidic water or solution which comes into contact with the CPB can be detrimental to the CPB and cause cracking (Bengtsson, 2017). The internal and external factors which affect the leaching behaviour of the CPB are shown in Figure 2.9 (Figure adapted from Van der Sloot et al. (2009)). Internal factors affecting leachability include porosity, permeability, and particle size. These factors are all dependant on the material in which the backfill is composed of, mix design of the CPB and the surrounding environment.

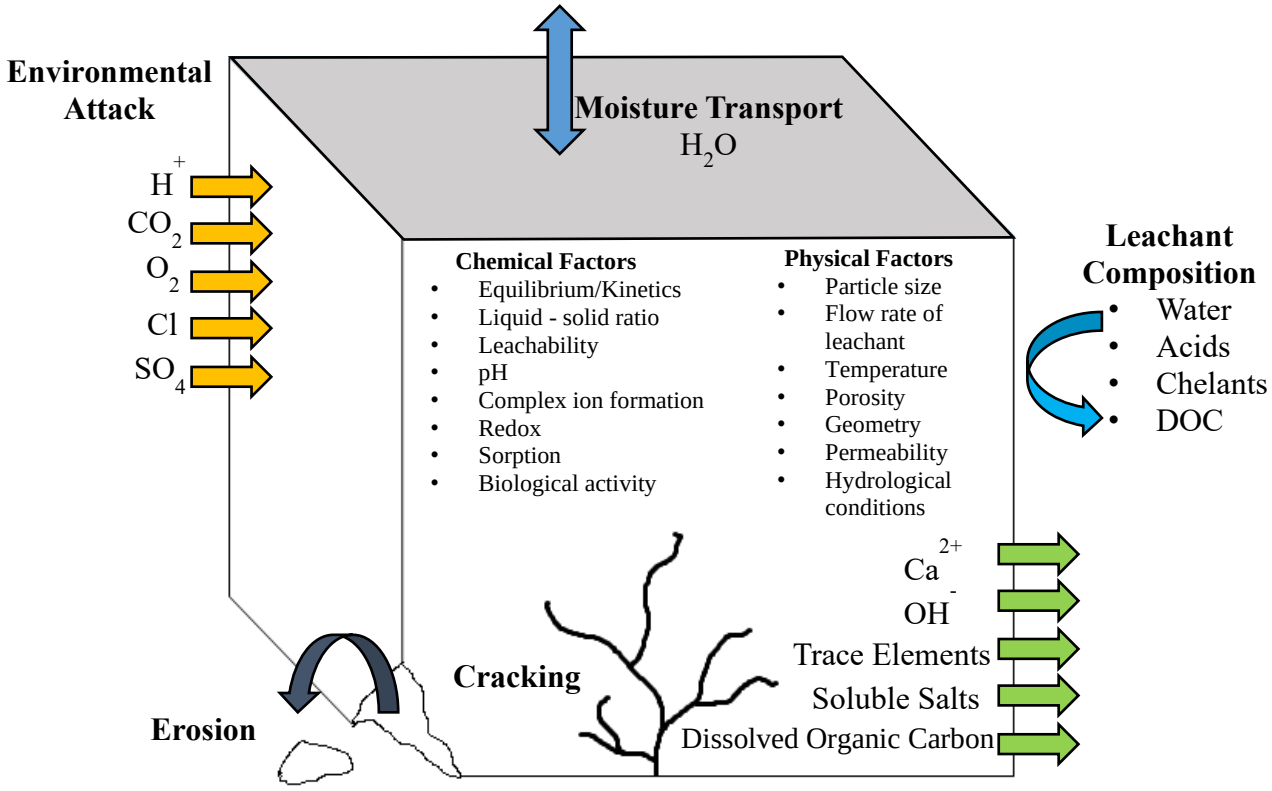

Figure 2-9: Internal and External Factors affecting the Leaching Behavior of the Cemented Paste Backfill

Studies have shown that no significant leaching of the CPB occurs upon cement addition because a cementitious layer forms around the ash particles preventing water seepage (Ahmaruzzaman, 2010; Benzaazoua et al., 2008). Although it has been found that the CPB can encapsulate trace elements, the solubility is dependent on the surrounding environmental conditions. If a particular element has a high concentration in the brine of CCPs, leaching may increase over a while if favourable conditions are experienced thus contaminating the environment. However, this element may also be encapsulated if unfavourable conditions are achieved. In general, solidification of the monoliths reduces permeability thus minimising the production of secondary minerals and resultant leachability (Paria and Yuet, 2006).

2.6.4.1. Leaching Tests

Leaching tests are conducted to determine the release of elements under a specific set of conditions. These tests are used to simulate a similar environmental condition or to expose the waste material to a broad range of different experimental conditions in order to derive leaching data. These tests allow the user to determine equilibrium data or kinetic data to determine additional parameters such as diffusion coefficients which are useful in predicting long term behaviour. The rate of leaching is dependent on the type of tests and test conditions as well as the source and type of CCP used. A detailed review of the various leaching tests is given by Tiwari et al. (2015).

Multiple leaching tests could be performed, each simulating different environmental conditions to which the CPB could be exposed to. The tests commonly used when analysing the leachability of the CPB include the toxic characteristic leaching procedure (TCLP) (EPA SW-846 Method 1311), a synthetic precipitation leaching procedure (SPLP) (EPA SW-846 Method 1312), deionized water leaching procedure (DWLP), static leaching procedure (SLP) test and the tank leaching test (TLT) (EA NEN 7375:2004).

The TCLP, SPLP and DWLP tests are used to determine the mobility of both organic and inorganic contaminants present in liquid, solid or multiphase waste. These tests utilize similar procedures with different extraction fluids. A mass to volume ratio of 1:20 with a contact time of 18 hours in which the solid is immersed in a specific extraction fluid is the

basis for these leaching tests. The solution is then analysed for element concentration. The extraction fluids vary whereby the TCLP uses a buffered acetic acid with deionized water or sodium hydroxide (NaOH), the SPLP uses sulfuric and nitric acid in a 60:40 ratio whereas the DWLP uses deionized water. The SPLP test is used to simulate exposure to acid rain resulting from airborne nitric and sulfuric acids. These tests require the sample to be crushed to a sample size of < 9.5mm. Since element mobility in CPB is pH dependent, leachability is often higher in the TCLP test in comparison to the SPLP due to the acidic pH. Since these tests require the sample to be crushed, the surface area is larger and particle size distribution is different. Thus these tests may not always be an accurate representation of the environmental conditions as well as element mobility. This method may be more effective in determining the total metal mobility as opposed to the leachability which will actually be observed in that environment.

The SLP test evaluates the leaching of a solid with known geometry immersed in a specific amount of leaching solution (approximately 2 cm of fluid around all sides of the monolith). The solution is often the same as that of the SPLP which consists of 60% sulfuric acid and 40% nitric acid. This test simulates weathering of the CPB for long term exposure to acid rain. The leaching solution is continuously tested with no leachate renewal. This allows the determination of long term leaching behaviour and the total concentration of elements leached out from the monolith.

The TLT is a semi-dynamic batch leaching test whereby a monolithic mass of low permeability is fully immersed in a leaching solution (typically deionized water). It is used to determine the mass transport from monolithic materials as a function of time. The leachant is changed periodically following specified time periods. The TLP is similar to that of the SLP test however, the extraction fluid differs and the leaching solution is replenished. The leaching is determined cumulatively. This test often requires much more time than the TCLP test due to the smaller surface area to volume ratio. The governing characteristic of the CPB which determines the leachability is the permeability and porosity of the CPB. Table 2.6 shows the advantages and disadvantages associated with each leach test method. Ground methods are indicative of the reaction products found in the pore solution whereas tank test methods are indicative of the mobility of metals or elements out of the CPB.

Table 2-6: Advantages and Disadvantages of Monolithic Leaching Tests

Tests Method	Advantages	Disadvantages
TCLP	• Quicker and simpler • Inexpensive	• No kinetic effects • Chemical reaction products ignored • Unrealistic simulated environment • Particle size reduction required • Sample ground thus increased surface area and leachability is overestimated
TLT	• Diffusion parameters can be calculated • Mass transfer rates	• Longer period of time • Precipitation of secondary reaction products may occur
SPLP	• More accurate representation of environmental conditions	• Data cannot be extended to other scenarios • Particle size reduction required
SLP	• Long term leaching behaviour	• Non-standard test method

2.6.4.2. Leaching Behaviour

Few studies have been conducted on the leaching behaviour of the CPB following the implementation of CCPs. A summary of the elements released under different environmental conditions following use in the CPB is shown in Table 2.7. Lu et al. (2016) investigated the metal release of cement clinkers in three different environments such as groundwater, seawater, and acid rain. This study found that metal release was highest in seawater followed by groundwater and lastly acid rain. The leaching behaviour of FA and CA used as replacements for cement and sand was conducted by Kadir et al. (2016). The study found that arsenic was the highest leaching metal in all ash types and different leaching tests. In the case of samples containing only FA, higher leaching rates of Cu, Ni, Cr, and Pb were observed in comparison to the control sample. The study also showed that a higher leachability of elements was found using the TCLP tests as opposed to the SPLP test. This is because pH is the controlling factor of metal mobility and the TCLP test has a much more acidic pH. The SLP tests showed the lowest leaching rate.

Jiao et al. (2011) evaluated the long term leaching of the CPB. The study showed that the concentration of As increased and then showed a rapid decrease following a period of 60 days. This was due to ions adsorbing or precipitating onto the CPB again. A similar trend was found upon analysis of Ba ions. In general, longer soaking time leads to an initial increase in leachability followed by a decrease. In all cases, the CPB did not serve as a potential source of contamination thus concluding it is feasible to be implemented into underground mine voids. Benzaazoua et al. (2008) performed a similar investigation of the CPB in an aggressive environment and found that there was no significant element release that could have an adverse effect on the environment.

Hamberg et al. (2015) studied the effect of leaching in both fresh and weathered ash CPB on As, Ca, Fe, Si and S using gold mine tailings. Results for the weathering of the CPB showed that leaching increased steadily until a period of 24 days and then stabilized. The study showed a slight increase in sulphur which is due to the oxidation process. Coussy et al. (2011) also studied the effect of As leaching in FA based CPB. Arsenic leaching was initially high, however, at lower pHs, the leaching decreased and was stabilized.

Gupta et al. (2017) investigated different laboratory batch leaching procedures with regards to FA and FA bricks containing cement, sand, lime, and gypsum. The batch processes were tested according to the TCLP, SPLP and the DWLP test. The study showed that the SPLP and DWLP test procedures are most representative of natural environmental conditions as unrealistic pH values were not attained. The highest leaching elements were Al, Fe, and Mg. Chen et al. (2009) found that Ni and Cr exhibit low leachabilities as they are encapsulated within the CSH gel. Hamberg et al. (2018) investigated the use of FA coupled with gold mine tailings. The study showed that following weathering of the CPB, the cumulative release of Ni, Zn, Fe, and Cu was lower in the CPB than when compared to the release of the tailings alone.

Qi et al. (2015) found that following 7 days of curing, the concentration of Si, Fe, Al, Ca, Na and K as well as the pH decreased with an increase in FA content. Overall, metals in CCPs are not leached out following cement addition as these metals become encapsulated in the solidified cement due to cement hydration and calcination. As a result, leachability and metal release are reduced. Specifically following the calcination process, elements such as As, Cd, Pb, and Zn are fixed (Zhang et al., 2009). Higher concentrations of elements

observed in the pore solution are due to the dissolution of FA or the reaction products following the pozzolanic reaction. These include products such as portlandite ($Ca(OH)_2$), the CSH gel, ettringite and monosulphate phases (Qi et al., 2015). Species such as Fe^{3+}, K^+, Na^+ and Ca^{2+} decreased in the pore solution whereas species such as Al^{3+} and Si^{4+} increased due to the pozzolanic reaction. Some studies found that the addition of FA to the CPB could lower the leachability of some elements in comparison to the cement only backfills (Kadir et al., 2016; Kamali et al., 2008; Yao and Sun, 2012). Overall, the disposal of CCPs in CPB could have adverse effects on the receiving environment if the pH is not closely monitored as pH is the greatest controlling factor of element mobility.

Table 2-7: Release of Elements following Backfilling

Ash Type	Type of Test	Elements leached	Elements not leached	References
FA	TCLP	As, Cr, Pb, Cu, Ni	Fe, Mn	(Kadir et al., 2016)
	SPLP	As, Pb	Ni, Fe, Mn	
CA	TCLP	As, Zn, Ni	-	
	SPLP	As, Pb, Zn, Cu and Cr	Ni, Fe, Mn	
FA	TLT	As, Fe, Si, Ca	S	(Hamberg et al., 2015)
Slag	Humidity cells	Ca, Si, Fe, Zn, Mn	As, Cu, Pb	(Benzaazoua et al., 2008)
FA, gangue waste	TLT	As, Cu, Cr	-	(Chan et al., 2009)

2.6.5. Unconfined Compressive strength

The UCS is used to determine the performance of cementitious materials under mechanical stress. It is an important design parameter when designing backfills or when considering the replacement of cement with CCPs in the use of concrete mortars since the material must provide support. The strength required is dependent on the end-use and cement mortars require much higher strengths than when compared to the strength required for CPB. Strength evaluations are shown below for both uses. Strength development is dependent on the physical, chemical and mineralogical properties of the tailings, the amount of water,

water chemistry and lastly, the type of binder and proportion of binder used (Benzaazoua et al., 2004). Xu et al. (2018) found that the UCS increased with an increase in solids content. A 28-day UCS test showed that a solids content of 70% had a 50% greater strength than a CPB with a solids content of 65%. Such phenomena are experienced as higher solids content increases the compactness of the CPB resulting in a CPB that has closely bonded hydration products.

2.6.5.1. Cement Mortars

The concretes made from various ashes had comparable strengths following cement mortar bar tests. Cement mortars utilize ash substitution. However, the 28 day UCS decreased following increasing amounts of ash substitution accompanied by an increase in water demand (Argiz et al., 2017). CCPs show increased strengths following 28 days due to the pozzolanic reaction occurring. In general, the UCS increased with a decrease in the water to cement ratio as the binder content is higher (Kesimal et al., 2005).

CA is commonly used as a substitute for river sand in concrete with favourable results (Singh and Siddique, 2015). The UCS was not significantly affected by the substitution of CA. However, the adsorption of water was greater upon the incorporation of CA due to the high carbon content. The substitution of CA showed a reduction in permeable pore space and increase resistance to abrasion. Argiz et al. (2017) found that mortars consisting 35% CA showed poor strength evolution in comparison to the MA mortars and found this to be the upper limit for CA substitution. However, in the same scenario, mortars with CA showed higher strengths than mortars consisting of only FA and cement. After 90 days of curing, the compressive and splitting tensile strength of CA concrete mixtures was almost comparable to that of the control concrete mixture (Singh and Siddique, 2016). The same study found that at 28 days, CA has a lower strength than the control concrete sample. The presence of the CSH gel resulted in a delay in the hydration process and thus lower strength. The pozzolanic reaction also did not occur at 28 days also contributing to the lower strength observed. Aggarwal et al. (2018) had similar findings with the 90-day UCS development being higher than that of the 32 day UCS.

FA cement showed different findings with regards to the UCS. Argiz et al. (2017) determined the strength differences between FA and CA. FA cement mortars had a higher

early strength when compared to CA mortars. However, ground CA mortars showed comparable strength to that of FA thus showing that particle size was significant in strength development. Besides the UCS, additional strength properties such as the modulus of elasticity and flexural strength were a maximum with a FA replacement of 50% (Al-Manaseer et al., 1988). There is also a low risk or alkali-silica reactivity in CPB with FA solids contents greater than 50%. The UCS is found to decrease with increasing FA content but the difference in strength between the FA substitute concrete and control samples decreases as curing time increases (Durán-Herrera et al., 2011). This suggests that although the initial strength is lower in the FA sample, strength development is significant in comparison to that of the control sample. The delayed strength development is more pronounced at higher ash replacement levels.

MA mortars constructed with CA were used to replace the fine aggregate in the concrete mixture whereas FA was used as a cement replacement. Rafieizonooz et al. (2016) found that following 91 days of curing, all MA samples gained greater than 95% compressive strength of the control sample. After 181 days, all MA samples showed compressive strength which was comparable to that of the control sample. Table 2.8 summarises the 28-day UCS values for CCPs used in concrete mortar applications. The percentages of FA and CA expressed below are in terms of the total cement percentage replacement and fine aggregate replacement, respectively. These strengths are however dependant on other factors such as the water to binder ratio and type of fine or coarse aggregates used.

Table 2-8: 28 Day Compressive Strength Tests for CCPs implemented in Concrete Mortars

CCP	UCS (MPa)	Composition	References
FA	83	45% FA	(Poon et al., 2000)
FA	54	25% FA	(Argiz et al., 2017)
FA	36.8	15% FA	(Durán-Herrera et al., 2011)
FA	35	20% FA	(Huang et al., 2013)
FA	39	20% FA	(Saha, 2018)
MA	46	8% FA; 2% CA; 90% OPC	(Argiz et al., 2017)
MA	69.52	12.5% CA; 12.5% FA	(Soofinajafi et al., 2016)
MA	26.49	20% FA; 25% CA	(Rafieizonooz et al., 2016)
MA	25.01	20% FA; 75% CA	(Rafieizonooz et al., 2016)

CCP	UCS (MPa)	Composition	References
CA	58	25% CA; 65% Cement	(Argiz et al., 2017)
CA	30.43	20% CA	(Aggarwal et al., 2018)
CA	32	100% CA	(Kou and Poon, 2009)
CA	18.91	25% CA; 25% Sand	(Aggarwal and Siddique, 2014)
CA	43.40	50% CA	(Sandhya and Reshma, 2013)
CA	46.2	60% CA	(Maliki et al., 2017)

2.6.5.2. Cemented Paste Backfills

The CPBs required different specifications than that of concrete mortars. Since high FA content backfills require a lower binder dosage, typically 4 – 7%, the UCS is generally lower in the range of 0.5 – 1 MPa (Hamberg et al., 2015). Typically, a 28-day UCS of 0.7 – 2 Mpa is required in order to ensure slope stability and for use in CPB (Brackebusch, 1995). Following 92 day testing, UCS between the range of 0.5 – 3 MPa is expected (Benzaazoua et al., 2004; Grice, 1998; Kesimal et al., 2004a; Ouellet et al., 2007).

Qi et al. (2015) found that the UCS increased with an increase in FA content with 7 –, 14 – and 28 – day strengths of 3.57 MPa, 5.8 MPa, and 7.8 MPa. This is due to the greater content of reaction products and compaction of the pore structure. Various researchers have different limits for UCS. Mahlaba et al. (2011b) stated a limit of 500 kPa to be the lower limit which was higher than the limit set out by Potvin et al. (2005) and Hamberg et al. (2015) of 200 kPa. Li and Fall (2018) investigated the effects of sulphate content on the strength development of the CPB. Results showed that the ash with the lowest sulphate content had the highest UCS. Typical UCS values for CPB composed of various materials are presented in Table 2.9.

Table 2-9: UCS of Various CPB

Composition	28 Day UCS (MPa)	References
FA; coal gangue; cement; water	7.8	(Qi et al., 2015)
FA; Brine	1.65	(Mahlaba et al., 2011b)
FA; Brine (High salinity)	3.00	(Mahlaba et al., 2011b)
Construction demolition waste	1.74	(Chen et al., 2018)
Oil shale	1-5	(Uibu et al., 2016)

Composition	28 Day UCS (MPa)	References
Mine tailings, OPC	1.51	(Li and Fall, 2018)
Mine tailings, OPC	1.82	(Xu et al., 2019)
Mine tailings, OPC	1.5	(Liu et al., 2018)
Gold tailings, FA, OPC	0.2	(Hamberg et al., 2015)

2.6.6. Setting Time

The high initial strength of the CPB is desirable as early strength gain is important as it speeds up the mining processes and is a good indication of long-term strength development. The setting of the CPB is a percolation process whereby particles are bound together through the formation of reaction hydration products which contributes to the hardening process of the paste (Bentz, 2008; García et al., 2008). Setting time needs to be monitored to ensure the CPB does not segregate and there is no excess bleed water. The effect of CCPs on the setting time of the CPB is dependent on the composition of ash, quantity of ash or binder added, water to cement ratio and temperature. The setting time is proportional to the amount of ash used. Generally, longer setting times are expected with greater ash substitution. By varying the brine to FA mixing ratios, pastes with varying setting and curing times can be achieved. Higher water to cement ratios requires longer setting times (Bentz, 2008). CA showed a shorter setting time than FA due to the slower hydration rate (Argiz et al., 2017). This phenomenon could be accounted for since FA has a greater amount of cement hydration retarders such as ZnO, Pb_2O, Cu_2O and Cd_2O (Murat and Sorrentino, 1996). Cd and Zn are found to increase the setting time of the CPB and lower the strength (Yin et al., 2012). This is due to the adsorption of these metals by the OPC (Murat and Sorrentino, 1996). The converse is true for Cr and Pb. ZnO has a negative effect on the CPB. Low calcium ashes have a higher effect on the setting time of the CPB than higher calcium ashes. This is because the hydraulic activity is increased with an increase in calcium content.

2.7. Conclusion

Mining and the extractive metallurgical industries are a major economic sector in South Africa and many countries around the world. As a result, numerous waste products and environmental concerns have arisen following the extensive use and long-term application of mining. The substantial amounts of CCPs, brines and abandoned mines created as a result of mining have created a platform for backfilling to be an environmentally and economically

feasible solution to combat some of these problems. Due to current legislation and the classification of CCPs, ways in which to utilize these products are needed. Waste can be effectively reused and abandoned mines can be rehabilitated through backfilling.

Extensive research has shown that the use of CCPs, which exhibit pozzolanic activity, is extremely beneficial in backfilling applications. The use of industrial brines and the ionic components present coupled with the CCPs have a profound influence on the environmental suitability and strength development of the CPB. Brine and FA interactions have shown that the majority of the components from both constituents can remain encapsulated following co-disposal as a monolithic material. As a result, the leachability of the CCPs is reduced. Strength development is significant following long term implementation of CCPs with UCS values in comparison to concrete samples. Thus the CPB is beneficial from an environmental, structural and economic viewpoint. Backfilling has shown positive results in improving land stability and utilising vast amounts of waste.

In the context of backfilling and following an extensive review of previous research, numerous studies have investigated the use of individual CCPs (Such as FA only) on factors such as the UCS, leachability and various rheological parameters. However, limited research has been conducted on utilising multiple ash types, such as a mixture of FA and CA, coupled with brine to create a CPB. This study aims to close this research gap and investigate the environmental and structural parameters of the CPB with regard to utilising different ash types and quantities. Currently, there are also no specified guidelines dictating the use of CCPs in backfilling which this study aims to determine.

3. Materials and Experimental Procedure

3.1. Introduction

The previous chapter of this thesis (Chapter 2) critically examined and reviewed previous literature on the CPB and the environmental concern associated with FA, CA, and brine. It is evident from the literature that there is a need for an alternative and sustainable co-disposable method of both ash and brine. The results of the previous chapter have led to the experimental design described in this chapter. This chapter is divided into two sections,

namely the statistical analysis and the experimental analysis. The statistical analysis will be presented in Section 3.2 whereas the experimental and analytical techniques used in the practical experimentation will be presented in Section 3.3. The experimental procedure described in Section 3.3 is formulated based on the findings of the statistical analysis in order to confirm or disprove the hypotheses stated in Section 3.2

3.2. Statistical Analysis

A statistical analysis was performed on sixty-seven different ash samples across South Africa to determine if trends existed between the different ash types (FA, CA or MA) as well as between the different ash states (fresh or weathered ash). These ashes were analysed according to the South African GN R.635 standard for the total elemental composition by XRF (majors) and acid digestion (to determine the trace elements in the ashes). Furthermore, these ashes were analysed using the Australian Standard Leach Procedure (ASLP) to determine the pH, TDS, and EC.

This analysis aimed to relate the chemical composition of the different ash types or states to the environmental and structural suitability in the CPB. This was done through the construction of various flowcharts which serve as a guideline for preliminary examination of an ash before designing a CPB. These flowcharts provide guidelines for use and are based on the initial elemental compositions and state of the ashes. Furthermore, this analysis aimed to predict the leaching behaviour of these different ashes based on the total elemental concentration. This was performed only for ashes whereby data was obtained for fresh and weathered ashes from the same location. This statistical method of analysis further examined the difference in the behaviour of the different ash states and types in terms of leachability.

3.2.1. ANOVA

An Analysis of Variance (ANOVA) is a statistical method of analysis that is used to determine whether there are any statistically significant differences between the means of two or more independent and unrelated groups. An ANOVA is essentially an extension of a t-test for two independent samples with two or more groups. An ANOVA compares these groups in order to determine the significant interactions between the independent variables on the dependent variable. The independent variable is a categorical variable with two or more groups whereas the dependent variable is a continuous variable. In this study, the

independent variable was the ash state (fresh or weathered ash) which was then further sub-divided into ash groups (FA, CA or MA). The continuous dependent variable was the elemental chemical compositions and the leachability of these ashes for each major oxide or element. The ANOVA allowed determination of whether differences in the means of the chemical composition or leachability of the different ash states and types existed. This method of analysis is useful in interpreting experimental outcomes (Ostertagova and Ostertag, 2013). It must be noted that an ANOVA does not specify where such interactions or differences exist and which groups are different. Further analysis requires a post hoc test which will allow a more in-depth examination into where the differences between the ash groups arise.

An ANOVA tests two hypotheses to determine if significant differences between two or more groups exist. These hypotheses are based on the homogeneity of variances (H_o). The homogeneity of variances is an assumption in which the variances (the spread of data around the mean) of the independent groups are equal. For simplification, consider two independent variables, A and B. The two hypotheses are as follows –

- Null hypothesis – The sample means are all equal. No significant differences occur between the means of variable A or variable B.

$$H_o = \mu_A = \mu_B$$

- Alternate hypothesis – There is a significant difference between the means and not all sample means are equal.

$$H_o \neq \mu_A \neq \mu_B$$

The p-value is useful in interpreting the statistical results. It is a number between 0 and 1 that is used to determine the probability that the null hypothesis is true. A significant level of 95% was chosen, thus a p-value of less than 0.05 would mean that the null hypothesis should be rejected and the alternative hypothesis is supported thus there is a significant difference in the means of the groups. The results will be reported in the format –

$$[F(a, b) = c, \text{p} = d]$$

Where, a and b are the degrees of freedom for the respective independent and dependent variables, c is the F value and d is the p-value.

The F value is useful as it explains the ratio of two variances. Variances are a measure of dispersion which states how far the data is scattered from the mean. Larger F values represent greater dispersion which in this case, is undesirable. However, in the case of statistical significance, group means will be different from one another and hence there will be high variability among the means. Essentially, the ANOVA coupled with the p-value and F value will determine whether sample means between the different groups are equal or not.

The ANOVA is based on the following important assumptions listed below –

- The groups are independent of one another and unrelated;
- The dependent variable in each group should be normally distributed. Technically, the residuals need to be normally distributed. However, both tests should yield the same results. The testing was determined through the Shapiro-Wilks test as well as graphically using the QQ plot;
- There should be equality in variances. In order to test for equality of variances, the Levene's test of homogeneity was utilized;
- There should be no significant outliers in the data set. An outlier is defined as a recorded data observation that stands further away from most of the other data points. This often occurs due to error measurements. John Tukey's method of leveraging the interquartile range has been used to determine the presence of outliers. This method applies to most ranges since it does not depend on assumptions of data distribution. Moreover, this method ignores the mean and standard deviation, thus making it resistant to being influenced by the extreme values in the range; and
- The data should not be normally distributed hence factors such as the skewness and kurtosis need to be analysed. Skewness is a measure of symmetry hence the data should be symmetrically distributed (skewness = 0). Kurtosis is a measure of the degree of tailedness in the frequency distribution thus indicating if there is more data on the left or right of the distribution. Similarly to the skewness, kurtosis should be 0 or close to 0.

3.2.2. Two-Way ANOVA

A between-subjects experimental design was performed whereby a single observation contributes to a single point in the data set. A two-way ANOVA is commonly implemented as many data sets often have more than one independent variable. A two-way ANOVA will be considered for this study between the type and state of ashes on the chemical

compositions and leachability of the ashes. Approximately sixty-seven ash samples were analysed according to Table 3.1 below.

Table 3-1: Different Ash Types and States Analysed in Two Way ANOVA

	Fresh	**Weathered**	**Total**
Fly Ash	17	8	25
Coarse Ash	16	6	22
Mixed Ash	10	10	20
Total	43	24	67

The leachability and concentration data of the various ash states and types were analysed to determine percentage changes following weathering as shown by Eq. 3.1. The percentage change determined how these parameters (Leachability or concentration) changed as different ash types weathered, such as if there was an increase, decrease or no change. A positive value denotes that leachability was increased in the weathered state whereas negative values denote that leachability decreased as the ash weathered.

$$Change\ in\ Parameter(\%) = \frac{Fresh\ ash\ value - Weathered\ ash\ value}{Fresh\ ash\ value} \times 100\% \qquad \text{(Eq. 3.1)}$$

Furthermore, the leachability was examined based on the initial total concentration (mg/kg) of a particular element in order to determine the elemental percentage leached. This was performed according to Eq. 3.2.

$$Percentage\ Leached\ (\%) = \frac{\text{Total elemental concentration} - \text{Leached value}}{\text{Total elemental concentration}} \times 100\% \quad \text{(Eq. 3.2)}$$

The leachable concentration was converted from an mg/l to mg/kg value using E.q. 3.3.

$$Leachable\ Concentration\ \left(\frac{mg}{kg}\right) = \frac{\text{Leachability}\left(\frac{\text{mg}}{\text{l}}\right) \times \text{Volume leachant (l)}}{\text{Mass of solid sample in test (kg)}} \times 100\% \quad \text{(Eq. 3.3)}$$

R studio was used as the statistical analysis software tool. Various packages within R Studio were utilized to perform the specific statistical tests. Different tests were utilized in order to ensure all assumptions were obeyed. If the assumptions were exceeded, non-parametric tests

were conducted to determine significance. Due to the data sets being unbalanced, meaning not all groups have the same number of observations, a type III sum of squares was utilized. The results were expressed visually using side-by-side boxplots and interaction plots. The code used to perform the statistical analysis in R studio can be found in Appendix L.

3.2.3. Non-parametric tests

In cases of data sets where the two way ANOVA assumptions were exceeded, non-parametric statistical tests were performed as outlined by Field et al. (2012). These tests are robust hence they do not require certain assumptions to be met such as normality and homogeneity of variances. Non-parametric tests include trimmed means, rank-based ANOVAs, median tests, and M-estimators. These tests are all outlined by Feys (2016) and Wilcox (2012) and prove to be effective methods of statistical analysis. Such methods were adapted from the WRS2 package in R Studio. The following robust statistical tests were performed –

- Trimmed means (t2way) uses mean calculations by discarding 10% of the probability distribution at high and low ends;
- Median tests (med2way) is used as a robust measure of central tendency thus is independent of outliers;
- M-estimators (pbad2way) use weighted means which excludes the effects of outliers; and
- Rank-based ANOVA (raov) is essentially a robust ANOVA which is an alternative to the least-squares method of analysis.

It must be noted that these robust methods of analysis did not take the place of the standard ANOVA; rather, these methods were utilized as an additional test method to that of the standard test. If the results were indeed similar, that provided support for the accuracy of the standard ANOVA. However, if the results were noticeably different, this prompted a closer examination of the data to see if unusual observations have occurred.

3.2.4. Post Hoc Tests

Following the ANOVA, the p-value was examined to determine if there were significant differences between the data groups. This p value determined if there is an overall difference in the means of the data set. However, from the ANOVA, it is not possible to determine

which exact groups in the data set are affected and where these differences arise. This requires the need for a post hoc test. Post hoc tests are statistical tests performed between the subgroups in the data set following the ANOVA. These post hoc tests perform multiple pairwise comparisons to determine which samples means differ from one another and as a result which groups are statistically significant. Tukey's Honest Significant Differences (HSD) was used as a post hoc test used in this study and is very useful in determining where the significant differences between the groups lie. The test utilizes the same assumptions as that of the ANOVA.

3.2.5. Plots

Boxplots are useful in summarizing the distribution of a numeric variable. The boxplot provides information about the minimum and maximum points as well as the first, second (median) and third quartile of the data set. Boxplots are commonly used as a visual representation because if there is no overlap of the quartiles among the different groups, the difference among centres is more likely to be significant, and there would be enough evidence to reject the null hypothesis and conclude the alternative one. Interaction plots are also used as a visual representation of the interaction between two or more groups. Parallel lines mean no interaction exists whereas non-parallel lines indicate that an interaction does indeed exist. Once the ANOVA was performed and the post hoc test completed, the data were analysed using the box plot and interaction plots. Trends and predictions about the ash were based and discussed following the graphs. A summary of the methodology performed during the statistical analysis is shown in Figure 3.1.

3.2.6. Relationship between Parameters

The relationship between the leachable fraction and the total concentration of all elements was examined. This was conducted in order to determine if a relationship existed between these two parameters i.e Does a higher total concentration result in a higher leachability? This relationship will allow further analysis into predicting the leaching behaviour and thus mobility of these elements. The statistical relationship is also known as the correlation between two variables which in this case is the leaching and total concentration, was done through analysing the Pearson correlation. The Pearson correlation (r) is a number between -1 and 1 that indicates the extent to which two variables are linearly related. A negative value denotes a negative relationship whereby when one variable increases, the other variable

decreases. Consequently, a positive relationship denotes a relationship that when that when one variable increases, the other variable also increases. A value of 0 means that there is no correlation whereas a value below -0.5 or above 0.5 indicates a notable correlation between the two parameters, and values below those values suggest a less notable correlation.

In the case where the data was not normally distributed or when there is the presence of outliers, this may provide an incorrect or distorted relationship between the two variables. In this instance, the Spearman's rank correlation (r_s) was used which is a non-parametric test that can be used in conjunction with the Pearson's correlation coefficient. If there is a small difference between these correlation coefficients, it can be said that outliers are not influencing the results. However, if these values are different, it would mean that the outliers are substantially influencing the results. Hence, the decision was made as to whether to remove the outliers are keep them in the data set based on these two correlation coefficients. The ANOVA methodology is shown in Figure 3-1.

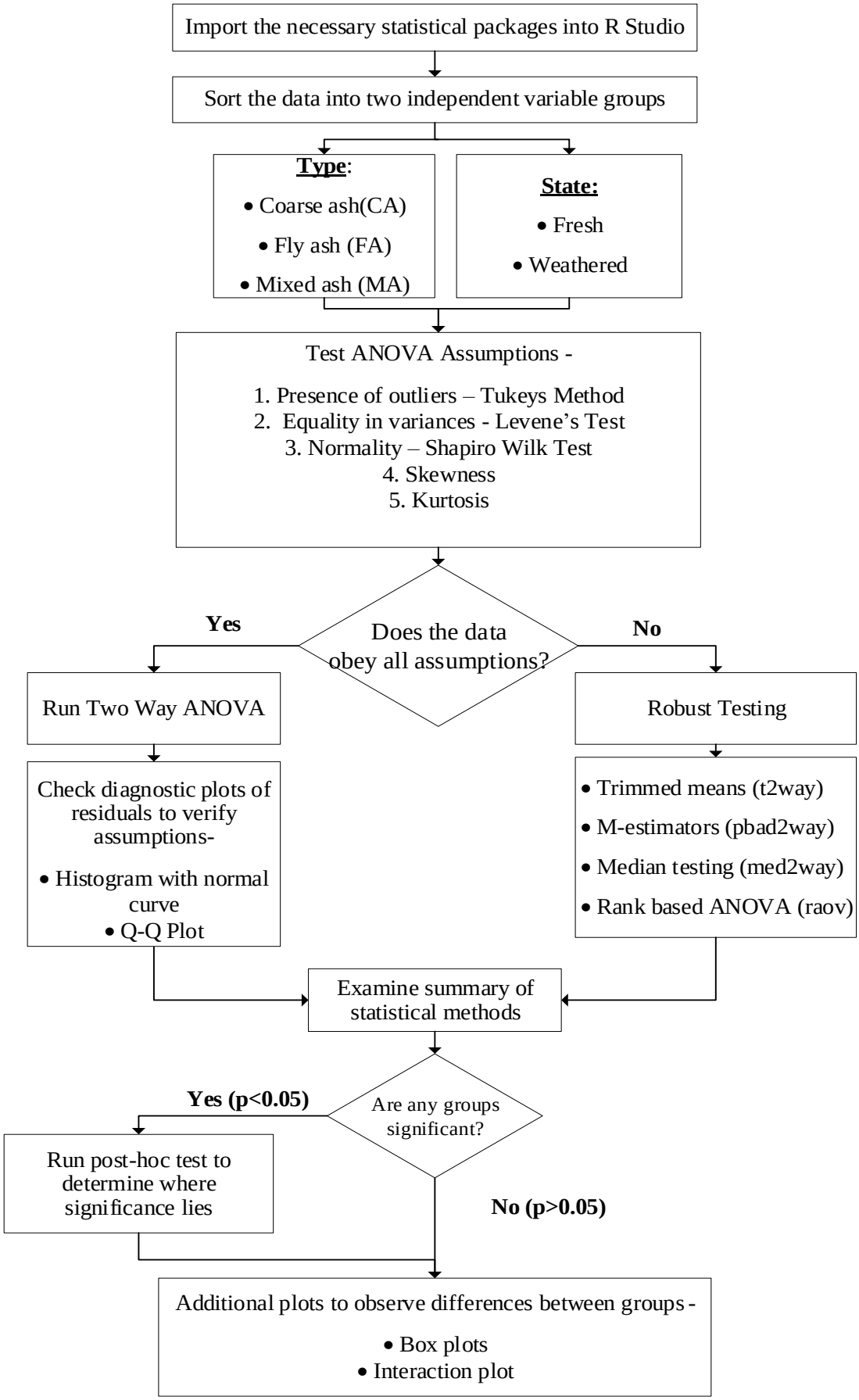

Figure 3-1: ANOVA Methodology

3.3. Experimental Methodology

A large amount of literature has been reviewed in order to gain insight into the re-use of CCPs in CPBs. The physical and mechanical properties, as well as the environmental and structural requirements of the CPB, have been studied to ensure sufficient knowledge is gained following the experimental design. Following a review of the available literature, a combination of CCPs coupled with brine to produce a CPB have not been extensively studied. This experimental methodology in this study aims to improve the knowledge of CPBs which implement CCPs in varying proportions. Environmental and structural parameters such as leachability and strength will be investigated following different mix designs to determine the most suitable ash type.

All tests and experiments performed were conducted with the utmost care in the laboratory. Wherever possible, the ASTM standard test procedures were utilized to ensure a valid and comparable result is attained. Information of the material specifications, test procedure, set up as well as the implementation of the experiments can be found below. The results of the various characterization tests can be found in Section 4.1.

3.3.1. Materials

The materials used in the study to construct the CPB include fly ash (FA), coarse ash (CA), brine and ordinary Portland cement (OPC).

3.3.1.1. Solids

FA and CA were obtained from a coal mine in South Africa. Two different sources were used for comparison. The ashes were kept in sealed containers to prevent the ingress of air and stored at room temperature until needed. OPC used in this study achieved the requirements set out by ASTM C150-07. The bulk ash was analysed using X-ray fluorescence (XRF) using a Philips 2404 Wavelength Dispersive spectrometer fitted with a Rh tube. LOI determination was done by placing the ashes in a furnace at 950°C for two hours and measuring the percentage mass loss.

Two additional classified ashes were analysed in strength determination in order to determine the effect of particle size. These include DuraPozz and PozzFill. DuraPozz is a classified FA that is characterized by its very fine particle size. PozzFill is an unclassified

ash product produced from pulverized fuel ash. It is beneficial in concrete applications due to its unique particle size distribution and chemical composition. Both ashes were obtained from Ash Resources (Lafarge) in South Africa and were used in strength determination experiments.

The particle size distributions (PSD) of the ashes were determined using the Malvern particle size analyser 2000. At least 15% of the FA particles need to be <20μm to ensure a stable paste is formed. This is to ensure the pozzolanic requirements for class F specified by ASTM C618 is met. Higher degrees of fineness also have a better effect on the slumping of pastes. The CA used was unmodified.

3.3.1.2. Brine

Brine was synthetically produced in order to simulate actual brine produced from a desalination plant. The brine was characterized using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The ICP-OES was conducted using a Spectro Arcos whereas the ICP-MS was conducted using a PerkinElmer NexION300X. The brine was stored in a sealed plastic container at ambient temperature until further use.

3.3.1.3. Sample Preparation

The desired solids content of 68% and liquid content of 32% was chosen based on the study conducted by Mahlaba and Pretorius (2006). The study found this to be the suitable mix design of those investigated and that in this range, the CPB remains a non-segregating paste regardless of the brine composition. The solids (ash and OPC) were first mixed to ensure a homogeneous uniform powder was attained. This is because the setting of cement is fairly prompt. The liquid medium (brine) was then added to the solids and mixed until a non-segregating paste was formed. After the desired paste consistency was reached, the paste was manually poured into moulds of the required size. After filling the moulds, the mixture was tapped and rodded to remove any air bubbles. The samples were demoulded and cured in a water bath until required for further testing.

In Table 3.2, the mix designs are given which contain OPC, FA, CA, and brine as shown expressed as approximate mass percentages. A water to cement ratio (w/cm) of 0.5 was

maintained for all mix designs. In all circumstances, each set was prepared in duplicate to eliminate the experimental error. All mix designs for each sample number were created from a single batch for consistency. Samples 7 and 8 were constructed for unconfined compressive strength testing only.

Table 3-2: Cemented Paste Backfill Mix Designs

#	Sample Name	Cement (%)	Fly ash (%)	Coarse Ash (%)	Total solids content (%)	Brine (%)
1	FA1	5	63	0	68	32
2	MA1	5	31.5	31.5	68	32
3	MA2	5	42	21	68	32
4	MA3	5	21	42	68	32
5	MA4	5	50	13	68	32
6	CA	5	0	63	68	32
7	PozzFill	5	63	0	68	32
8	DuraPozz	5	63	0	68	32

3.3.2. Experimental Procedures

Various experimental procedures were employed on the constructed CPB. These tests allow for further analysis of the environmental and structural performance of the monolith.

3.3.2.1. Scanning Electron Microscopy

The scanning electron microscope (SEM) is a type of electron microscope that is used to analyse a sample surface. SEM images have a characteristic three-dimensional appearance and are beneficial for examining the surface structure and morphology of the sample. SEM analysis was performed on both the FA and CA before use as well as on the cured CPB to examine the morphological changes. Specimen preparation includes drying the sample in an oven at 100 °C and making it conductive to electricity by sputter coating it with gold as ash alone is not conductive to electricity. Furthermore, Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed. EDS is useful in determining the elemental analysis or chemical characterization of a sample at specific areas.

3.3.2.2. UCS Test

The CPB paste was poured into cube moulds of 100mm x 100mm. After demoulding the monoliths, the samples were allowed to cure for 14, 28 and 52 days in a water bath. Following the curing of the monolith at the specified time period, unconfined compressive strength (UCS) testing was conducted. The UCS was conducted using a mechanical cube press foot test with a preload of 10 N prior to data collection beginning at a compression rate of 2.5 mm/min to failure. This was in accordance with the ASTM C109/ C109M-16a standard method of testing. The test was conducted in triplicate and an average result was recorded. Figure 3.2 shows a sample of the CPB prior to and after demoulding.



Figure 3-2: UCS Sample Blocks

3.3.2.3. Tank Leaching Test

The semi-dynamic tank leaching test (TLT) was conducted to simulate flooded CPB material. The tests were conducted in accordance with the USP EPA Method 1315. Method 1315 considers the continuous leaching of water-saturated monolithic material by the use of an eluent filled tank that is periodically renewed with leaching solution. Both the sample size and vessel dimensions are specified so that a specific liquid to area ratio (L/A) ratio of 10 can be maintained. Monoliths were cast in cylindrical moulds with a height of 6 cm and a diameter of 6.5 cm as shown in Figure 3.3. The CPB samples used for this test were FA, MA1, MA3, and MA4. The CA and MA2 CPB samples disintegrated once in contact with water and thus were not analysed further. This suggests that the cementitious phases in these mixtures dissolved upon water percolation and exhibited poor binding properties due to the large mass proportion of CA. The fresh leaching solution was changed at nine predetermined intervals according to Table 3.5. The pH, conductivity and total dissolved solids (TDS) was measured for each time interval and analytical samples are collected and preserved for

atomic adsorption spectroscopy (AAS) analysis. Prior to sample collection, the solution was filtered through a 0.45 µm membrane and acidified. Eluate concentrations are plotted as a cumulative release as a function of time. This test is useful in determining the mechanism of diffusion-controlled ion release that occurs at the external boundary of the material (Hamberg et al., 2017). The following procedure was utilized in the TLT –

- The monolith blocks were demoulded.
- Each monolith sample was placed in a sealed glass jar, with at least 2cm of water covering the sample along all exposed sides. A L/A ratio of 10cm^3 of solution/cm^2 of solid was maintained.
- After the pre-determined time intervals in Table 3.3, the eluent was drained and preserved for further analysis. The leachate was thoroughly stirred before collection and the monolith was immediately placed in a fresh leachate.
- The pH, EC, TDS and ion concentration of the stored leachate was measured.
- The tank was filled with the same quantity of water for consistency.

The mass transfer of elemental release from the monoliths was calculated according to Eq. 3.4.

$$M_{ti} = \frac{C_i \times V_i}{A} \quad \text{(Eq. 3.4)}$$

Where M_{ti} (mg/m^2) is the elemental mass released during the leaching period (i), C_i (mg/l) is the elemental concentration during period i, V_i(L) is the leachate volume and A (m^2) is the exposed surface area.

Table 3-3: Tank Leach Test Leachate Renewal

Sample Number	Interval Duration (Days)	Cumulative Leaching (Days)
1	0.08	0.08
2	1	1
3	2	2
4	5	7
5	7	14
6	14	28
7	14	42
8	7	49
9	14	63



Figure 3-3: Monolith TLT Samples

3.3.2.4. Weathering Cell Test

The weathering cell test is a simplified version of the commonly used humidity cell test specified by ASTM D5744-96. The test utilizes a similar procedure which requires less material than the ASTM method as set out by Cruz et al. (2001). This test aims to accelerate the weathering process of the CPB in order to evaluate the reactivity and long-term environmental performance. This test was also performed as it enhances evaporation and reduces the degree of saturation of the monolith thus avoiding reactivity inhibition due to the lack of oxygen (Coussy et al., 2011).

Approximately 70 g of the crushed CPB sample was used for analysis. The samples are exposed to weekly cycles of one day leaching, three days of ambient air exposure, another day of leaching and lastly two days of air exposure. Leaching was performed by immersing the crushed sample in 50 ml of deionized water and stirring for 2 hours. The leachate was removed by vacuum filtration and then acidified for further analysis. The analysis included pH, TDS and EC determination as well as AAS to determine elemental concentrations. Approximately 10 cycles were performed to reach a pseudo steady state. Results are presented as the leached concentration per mass of solid material (mg/kg) as shown in Eq. 3.5.

$$C_c = \frac{\sum(C_i \times V_i)}{S} \qquad \text{(Eq. 3.5)}$$

Where C_c is the cumulative leached amount (mg/kg), C_i is the elemental concentration in the leachate during interval *i* (mg/l), V_i is the leachate volume (L) and S is the sample weight (kg). The TLT and weathering cell tests can be effectively compared by using the liquid to solid (L/S) ratio (Volume of liquid in contact with a dry solid material). The leachate concentrations (mg/l) are multiplied with the defined L/S or L/A ratio of the test which

results in the mass released per kilogram of solid (mg/kg). This ensures proper comparison of results obtained for the same material during different leaching experiments.

3.3.2.5. Acid Neutralization Capacity Test

The acid neutralization capacity (ANC) is an important parameter used to estimate the buffering capacity of the CCPs and CPB mixtures as it provides information on further utilization of FA and CA. This can be used to predict the long-term behaviour of the CPB mixtures since precipitation/dissolution of metals is directly affected by the buffering capacity. The ANC of the CCPs can be used to predicate the reactivity with acids and to determine the leaching characteristics as a result of changes in pH (Yan et al., 2000). Since leachability is pH-dependent, the ANC will indicate the leaching resistance of the CPB mixtures as the ability to neutralize acids will allow prediction of which species are able to accept and neutralize protons.

This method is divided into two stages as set out by the European standard method prEN14429. Firstly, a preliminary test to evaluate the acid consumption was performed to determine the amount of acid addition required to attain 9 different endpoint pH values. These pH values range between 3 and 11 as a pH of 11 is typically that of the natural FA and CA. In this pH range, most of the cementitious phases are dissolved (Coussy et al., 2011). The test was carried out by placing 15 g of each crushed CPB sample in rinsed polyethylene bottles with 135 ml of deionized water to attain a L/S of 9. After stirring for a period of 1 hour, pre-determined amounts of 2.5 M nitric acid (HNO_3) were added to each bottle and stirred. The pH was measured and adjusted with more HNO_3 if necessary to attain the desired endpoint pH. A final L/S ratio of 10 was reached following acid addition. The total amount of HNO_3 added to attain the required pHs was recorded and used to construct a titration curve. The main ANC test was carried out using the titration curve to prepare 150ml acid solutions of different pHs. The test involved using 9 batches of each sample containing 15 g of ground CPB samples placed in 250 ml polyethylene bottles. Each bottle was filled with 150ml of nitric acid solution to attain a pH between 3 and 11 and stirred for a period of 8 days in order to reach equilibrium. A L/S ratio of 10 was maintained. The pH, EC, and TDS of the leachates were measured followed by ICP-MS and ICP-OES analysis after filtration using a 0.45 µm pore membrane filter and acidification. The ANC test was

conducted in duplicate thus a total of 18 ANC tests were conducted for five different CPB samples (FA, MA1, MA2, MA3, and CA).

3.3.2.6. Rheology

The rheology of the paste refers to parameters that affect transportability such as the bleed of the CPB. Bleed water or bleeding is defined as the phenomena observed during the settlement of the CPB whereby water separates from the pastes and forms a layer at the top. In this test as described by ASTM C940 - 98a, the freshly mixed paste was poured into a 1000 mL graduated cylinder with a final volume of 800 ml. The bleeding rate was measured by dividing the final bleed water by the initial water volume. The height of the bleed water was recorded after 24 hours. The bleed formation is undesirable because it may require further treatment if it does not become reabsorbed by the ash matrix/CPB. However, if quick settling and minimal bleed formation are observed, the paste may stiffen inside pipes during transportation before disposal.

The next chapter (Chapter 4) will present and discuss the results of this study. The results of the statistical analysis performed on the various ash types and states as well as the experimental analysis carried out on the FA, CA and brine CPB monoliths will be presented and discussed in Chapter 4. The various decision making flowcharts are also presented which enable or guide the user to screen any ash for potential further used based on specific compounds or properties.

4. Results

This chapter examines and discusses the results of the statistical analysis as well as the experimental methodology. Section 4.1 presents the raw data results based on the characterisation tests conducted on the ashes and brine. Section 4.2 presents the results of the statistical analysis whereas Section 4.3 presents the results of the experimental work.

4.1. Preliminary Analysis

The preliminary characterization includes the results of the XRF, ICP-MS, ICP-OES and SEM analysis of the ashes and brine. Table 4.1 summarises the chemical composition and physical characteristics of the ashes and OPC used in this study. It can be seen that all ashes have a high silica (SiO_2) content which exhibits cementitious properties. However, the ratio between CaO and silica is low thus the need for an additional cementing agent such as OPC is required. All ashes satisfy the requirements of being Class F ashes which displays pozzolanic activity.

Table 4-1: Elemental Composition of Coal Combustion Products

	FA	**FA1**	**CA**	**CA1**	**PozzFill**	**DuraPozz**
SiO_2	59,44	34,41	41,34	42,4	55,26	55,22
Al_2O_3	26,66	17,51	16,51	17,73	31,91	31,86
Fe_2O_3	7,35	2,09	5,96	4,28	3,86	3,27
MnO	0,09	0,02	0,07	0,04	0,04	0,04
MgO	0,85	0,67	0,48	0,93	1,13	1,12
CaO	2,79	2,56	1,58	4,00	4,34	3,88
Na_2O	0,06	0,07	0,07	0,08	0,2	0,27
K_2O	0,78	0,3	0,49	0,34	0,65	0,73
TiO_2	1,24	1,01	0,75	1,06	1,62	1,66
P_2O_5	0,39	0,23	0,16	0,32	0,40	0,42
Cr_2O_3	0,02	0,03	0,01	0,06	0,05	0,05
NiO	0,01	0,01	0,00	0,01	0,01	0,01
LOI	0,37	42,00	33,00	28,00	0,54	1,23

The PSD of the ashes is shown in Figure 4.1. It can be seen that the CA has a different particle size distribution with a greater coarser fraction in comparison to the FAs which is expected. PozzFill has the smallest PSD followed by FA, DuraPozz and CA.

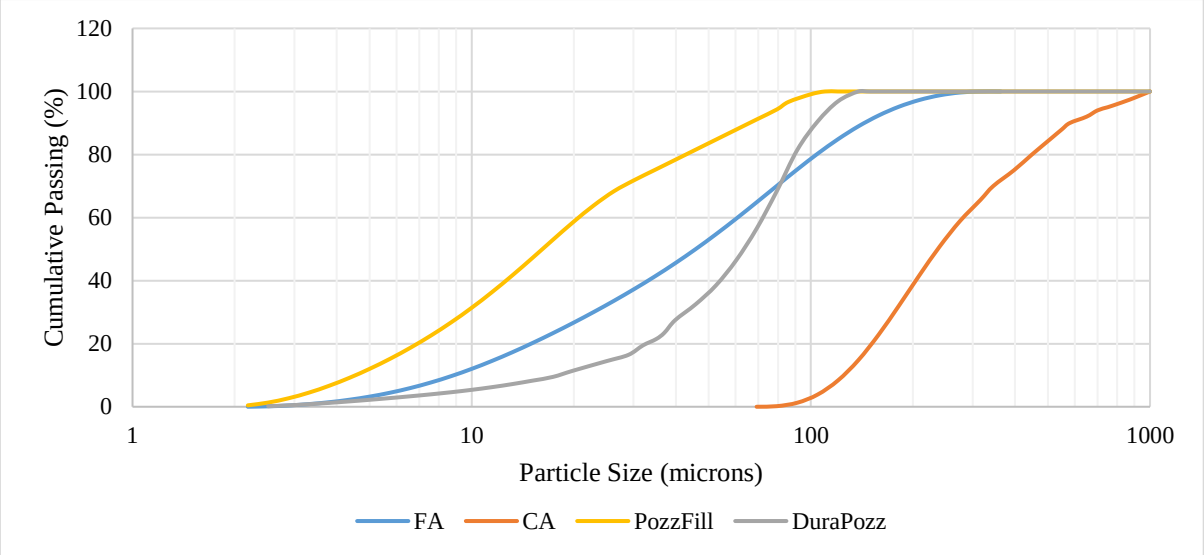

Figure 4-1: Particle Size Distribution of Various Ashes

Typical brine compositions based on a literature review are shown in Table 4.2. An average of these chemical compositions was used as the basis on which the brine solution was prepared.

Table 4-2: Chemical Composition of Brine

Composition (mg/l)	This Study	(Fatoba et al., 2015)	(Muriithi et al., 2014)	(Sonqishe, 2008)	(Fatoba, 2010)
Na	2988	4475	3355	4719	4805
Mg	108	75.4	112	198	163
K	8.68	56.4	78.8	115	106
Fe	7.01	0.043	0.068	3.3	0.24
B	0.81	1.39	0.154	1.6	2.24
Al	1.47	0.016	0.023	2.8	0.045
Ca	105	101	210	112	107
Cr	0.009	0.0063	0.023	0.4	0.014
Ni	0.011	0.057	2.5	0.4	0.12
As	0.013	0.0036	0.076	BDL	0.0068
Ba	0.090	0.029	0.15	0.1	0.057
Pb	0.007	0.0009	1.6	0.1	0.0039
pH	11.83	7.75	8.48	7.8	7.75
EC (mS/cm)	12.39	16.69	-	15.83	17.19
TDS (g/l)	6.07	8.35	-	7.92	5.40

4.2. Statistical Analysis Results

A robust statistical analysis was performed on each of the compositional elements, metals and compounds found in the various coal combustion products (CCPs). The ashes under consideration were fly ash (FA), coarse ash (CA) and mixed ash (MA) which consisted of both FA and CA in varying proportions. A detailed compositional, leachability and leachable concentration fraction analysis following weathering of these ashes was performed. A statistical analysis of variance (ANOVA) was conducted in order to determine if significant differences exist between the different ash groups or the state of the ashes i.e fresh or weathered. The ANOVA was conducted on the total elemental composition (major oxides) as well as the leachability of fresh and weathered ashes. The term leachability refers to the total leachable fraction of the ash under consideration. The results from the ANOVA were then used to determine trends between the means of the different ash states and types. Thereafter, the results were analysed whereby the leachability, total elemental concentration and the elemental chemical mass composition of the ashes were compared to relate the leaching behaviour to either the total concentration or the total elemental composition. The elemental chemical compositions expressed in this chapter are approximate mass percentages (%) unless stated otherwise. These include SiO_2, CaO, Na_2O, K_2O, Al_2O_3, Fe_2O_3, TiO_2, MgO and MnO. The leachability and the total concentration data were expressed in mg/l and mg/kg, respectively. The raw data which includes the leachability and concentration data, percentage changes and correlation coefficients between the fresh and weathered state can be found in Appendix A – K.

Flowcharts were constructed for the elements and compounds which have a significant effect on further use in CPB applications. These flowcharts are useful in deciding whether a specific ash containing a certain proportion of a particle element or compound can be implemented effectively in the CPB. These serve purely as guidelines, as each case is site-specific and will require additional testing before implementation. Flowcharts and guidelines are only proposed for ashes that have a significant difference between the state or type of ash or pose a risk if implemented in the CPB.

The following annotations have been used and implemented for the flowcharts –

- Dashed lines on the flowcharts are indicative of the preferable/advisable route.

- Asterisk (*) symbols on the plots are indicative of statistical significance. Table 4.3 summarises the significance level with the corresponding symbol.

Table 4-3: Significance Level Annotations

Level of significance	Symbol	P value
95%	*	$p \leq 0.05$
99%	**	$p \leq 0.01$
99.9%	***	$p \leq 0.001$

Waste classification according to SANS10234 (Based on the Global Harmonised System) takes into account the physical, health and environmental standards. This allows correct classification of potentially hazardous substances and mixtures, including wastes, in terms of their intrinsic properties. Since FA and CA are classified as a hazardous substance, a GN R. 635 waste assessment is performed to determine the type of waste and the correct barrier design requirements for disposal. The waste assessment as shown in Figure 4.2 is performed against four levels of thresholds for leachable and total concentration. The relevant terminology used is as follows –

- LC = Leachable concentration in waste (mg/l)
- TC = Total concentration in waste (mg/kg)
- LCT = Leachable concentration threshold limits (LCT0, LCT1, LCT2, and LCT3)
- TCT = Total concentration threshold limits (TCT0, TCT1, and TCT2)

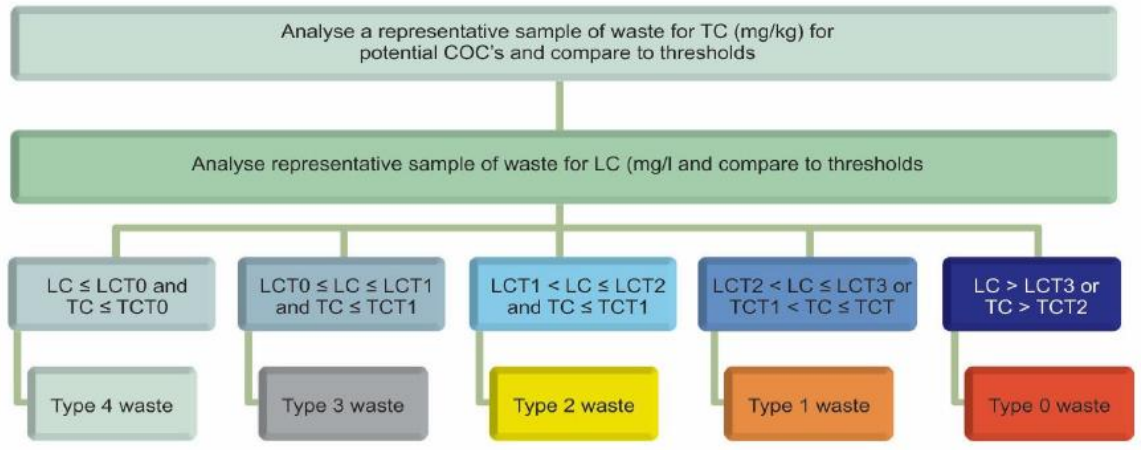

Figure 4-2: Waste Assessment Flow Diagram According to GN R. 635

Table 4.4 shows how each type of waste is further classified in terms of disposal. Each type of waste has different containment barrier design requirements prior to disposal. Although the waste will not be disposed of in a landfill, the waste assessment is performed as a

motivation of the risk level associated with the disposal of CCPS and to assess the potential impact on the receiving environment.

Table 4-4: Waste Type Classification

Type of Waste	Level of Risk	Description
4	Low	Very low-risk waste. It can be disposed of.
3	Low	Low potential for contaminant release. It requires some level of control and ongoing management to protect health and the environment.
2	Moderate	Considered low-risk waste with some potential for contaminant release. It requires proper control and ongoing management to protect health and the environment.
1	High	Considered high-risk waste with high potential for contaminant release. It requires a high level of control and ongoing management to protect health and the environment.
0	Extreme high	Considered very high-risk waste with a very high potential for contaminant release. It requires a very high level of control and ongoing management to protect health and the environment. A Type 0 waste can also not be landfilled.

4.2.1. Oxides

The chemical composition of the CCPs is critical in achieving the desired outcomes of the CPB in terms of environmental and structural suitability. FA, CA and MA differ significantly in their chemical composition and their further use. However, some studies claim that CA and FA have similar chemical compositions with CA having a higher LOI (Argiz et al., 2017; Lan and Yuansheng, 2007). The major oxides occurring in CCPs are silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3), calcium oxide (CaO), sodium oxide (Na_2O) and potassium oxide (K_2O). Oxides occurring in smaller proportions are titanium dioxide (TiO_2), magnesium oxide (MgO) and manganese oxide (MnO).

4.2.1.1. Silicon Dioxide

More than half of the chemical composition of class F ashes consists of silica-containing minerals, which may not necessarily be SiO_2. The silica present is found in two different phases namely, amorphous silica and quartz crystals. Quartz is found to increase the strength of the CPB and is preferred over the other phases owing to its low solubility and non-reactive nature. Amorphous silica is more reactive and its presence is equally important due to its pozzolanic activity which can also contribute significantly to the strength of the CPB. However, amorphous silica also plays a role in the ASR and care should be taken with regards to high amorphous silica content ashes in backfilling applications. The ashes analysed are class F ashes thus they have high mass percentages of silica. The variation in mass percentages is analysed following weathering of FA, CA and MA. Upon statistical analysis of the SiO_2 content in the various ashes, a significant difference was found between

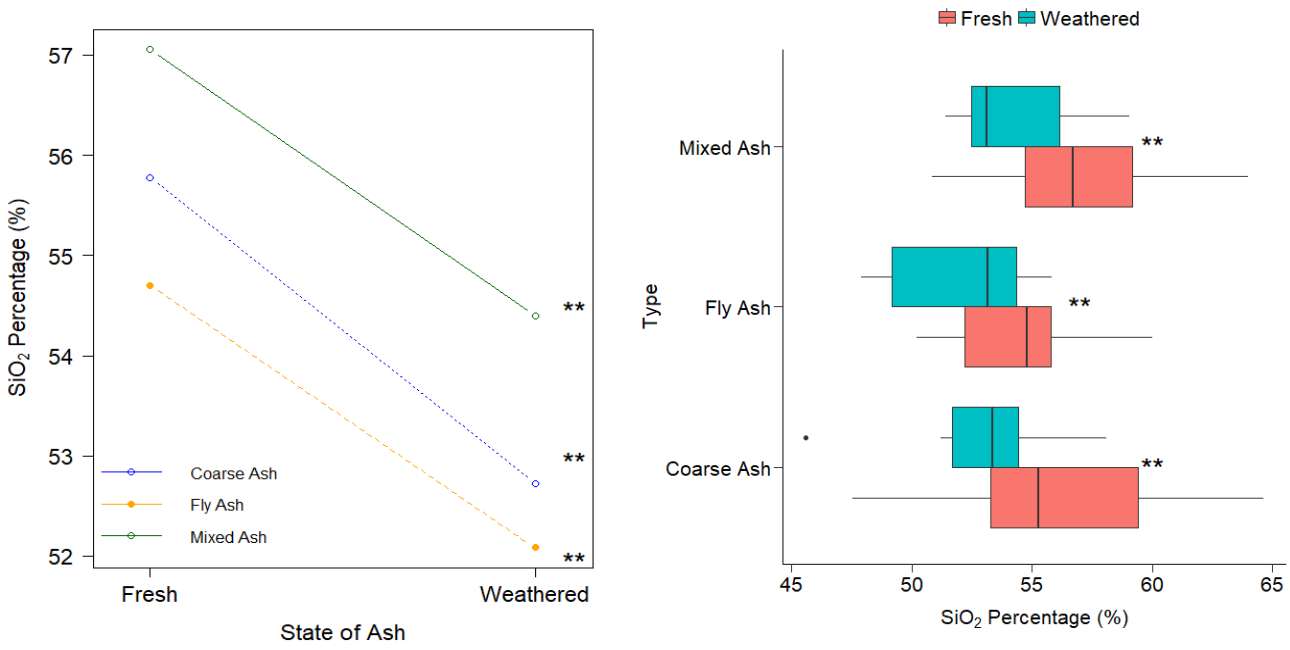

Figure 4-3: Interaction and Bar Plot of SiO_2 Variation Between the Different Ash States and Types

the state of the ashes [F(2, 58) = 7.548, p = 0.0079].

Fresh ashes have a higher SiO_2 content than weathered ashes as shown in Figure 4.3. Fresh FA, CA and MA ashes have approximately 2.62%, 3.06%, and 2.66% higher SiO_2 content than the respective weathered ashes. From Figure 4.3, it can be seen that all ash types follow this relationship with MA having the highest SiO_2 content. Campbell (1999) and Zevenbergen et al. (1999) reported similar findings. Generally, all ashes seem to have similar SiO_2 percentages, but lower concentrations are often found in CA. This is because FA is

more reactive due to the finer-grained particles as opposed to the larger CA particles (Ward et al., 2009). The mass percentage decrease is in a similar order of magnitude for all ash types. This decrease could be attributed to the pozzolanic effect, the ASR reaction or potential leaching due to the breakdown of the glassy matrix.

4.2.1.1.1. Silicon Leachability

The leachability of silicon (Si) follows a different relationship to that of SiO_2. There is a decrease in leachability of 39% for CA whereas FA and MA show an increase of 23% and 28%, respectively, following weathering of the ashes. The decrease in leachability observed for CA could be attributed to the glassy matrix of the ash still remaining intact and thus the silica has not yet reacted. Alternatively, CA has a larger particle size thus leachability would take a longer time to occur. Consequently, the higher leaching of MA and FA could be due to the relationship between the leachability and the elemental composition. Both weathered MA and weathered CA show a positive linear relationship whereby the silica leachability increases as the SiO_2 content increases.

The Si leachability is low for all ashes (<10 mg/l). The leachability of silica is dependent on the solubility of quartz (SiO_2) at pHs lower than 10 and the solubility of wairakite ($CaAl_2Si_4O_2.2H_2O$) at higher pHs (Tiruta-Barna et al., 2006). According to Figure 4.4, an increase in the leachability is observed for FA. The aluminosilicate gel would have formed prior to week 7, however, this gel has a low solubility thus resulting in a higher leachability for FA and MA. Currently, there are no limits minimising the leachability of silica thus no precautions need to be taken when using high silica content ashes.

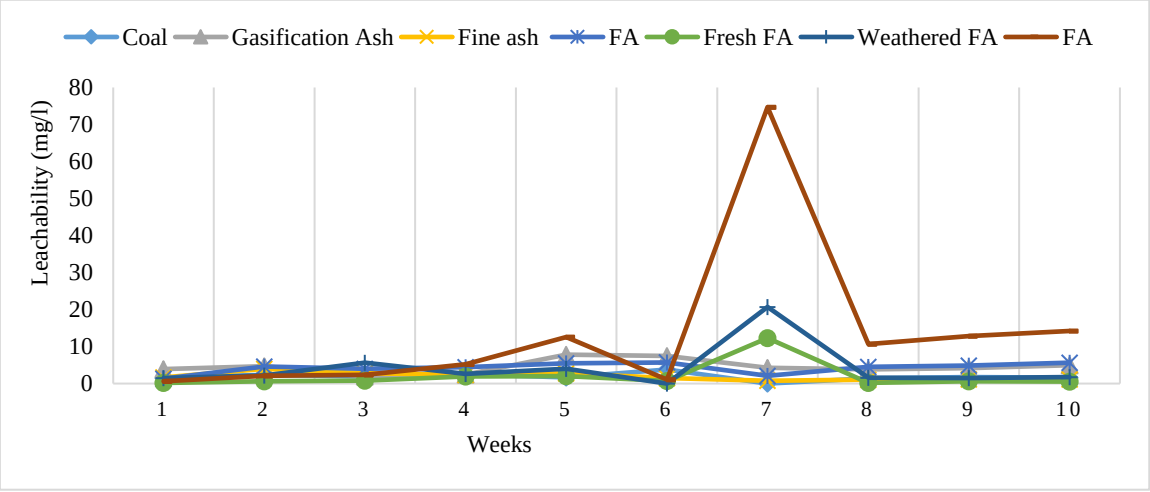

Figure 4-4: Humidity Cell Leachability of Silicon

4.2.1.1.2. Silicon Dioxide Flowchart

The flowchart shown in Figure 4.5 for the use of SiO_2 represents general guidelines to be used when considering the use of CCPs with varying SiO_2 content in the CPB. These guidelines are potential mitigation steps to minimise ASR. The following outlines the theory behind each decision choice –

- SiO_2 content – Silica is an important and necessary constituent as it shows pozzolanic activity thus provides additional strength to the CPB concrete. It was also found to be the most beneficial constituent required for the prevention of the ASR (Malvar and Lenke, 2006). As the amount of silica increases, the Ca/Si ratio of the CSH gel decreases. A lower ratio has been found to increase the binding capacity of the alkalis. Thus, the total amount of soluble alkalis available for ASR is reduced (Fengyan et al., 2006). This also results in lowering the alkalinity of the pore solution (Shehata and Thomas, 2000). This phenomenon occurs as the CSH gel has a negative surface charge, thus has a higher affinity towards the alkalies present in the pore solution. As a result, higher percentages of silica are desired (Malvar et al., 2002). The CSH also has a high affinity towards arsenate which is beneficial (Phenrat et al., 2005). As stated above, fresh ashes would be considerably better to use owing to the higher silica content in relation to the weathered ashes. A silica content greater than 50% is required thus all ashes under consideration are suitable for use.
- Type of ash – Generally, class F FAs are preferred as opposed to class C ashes. This is due to the high silica concentrations and low lime concentrations which are found to be better at mitigating ASR. This was confirmed by studies done by Shehata and Thomas (2000) who stated that low silica and high lime ashes also have greater alkali contents thus contributing to ASR.

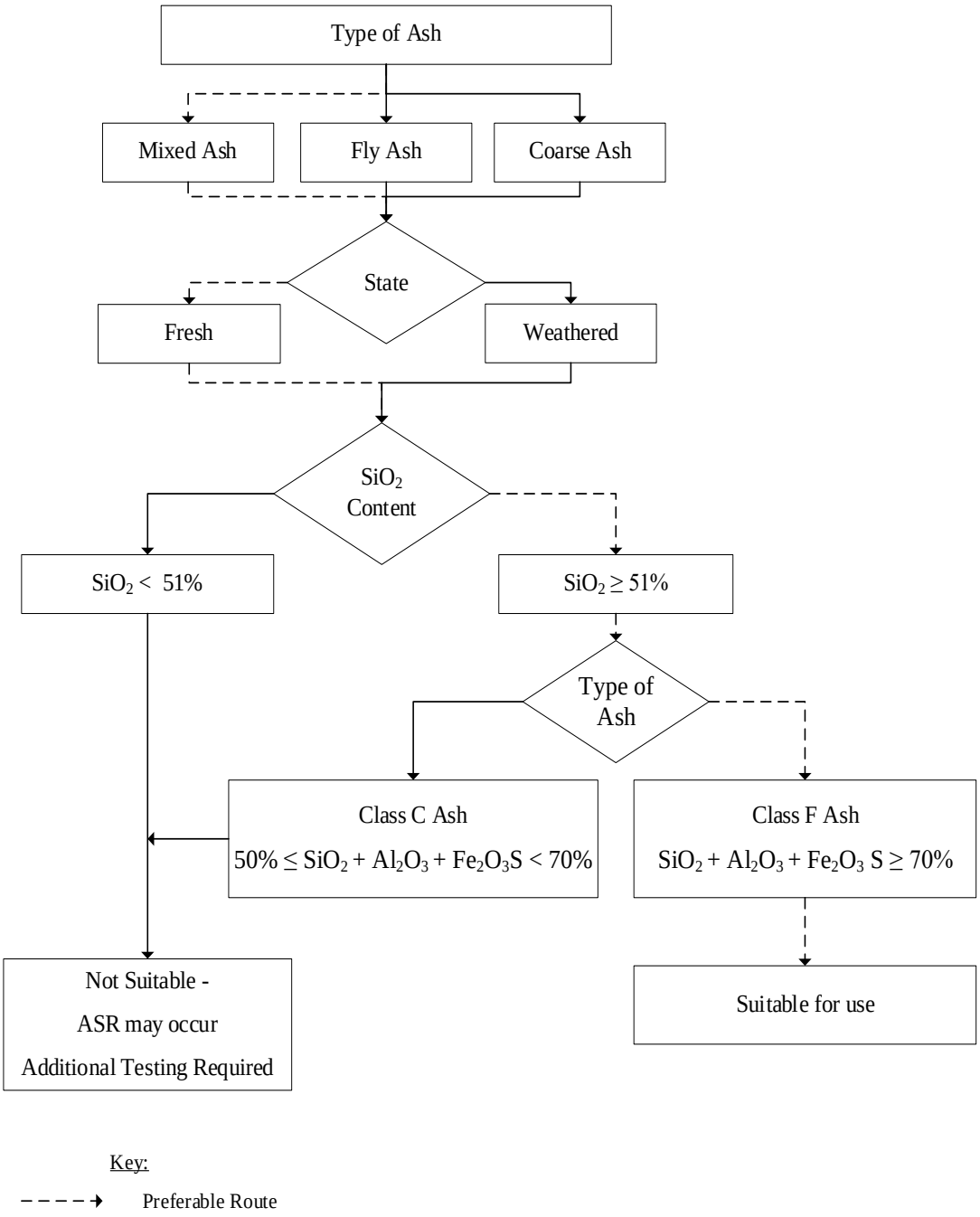

Figure 4-5: SiO_2 Decision Flowchart

4.2.1.2. Calcium oxide

Calcium is present in CCPs in multiple compounds namely lime, anhydrite, calcite and within the glassy matrix of the ash particle. The calcium content is probably the best indicator in determining how the ash will behave in the concrete (Shehata and Thomas, 2000). This is due to factors such as settling time and reactivity. Statistical analysis of the CaO content in the various ashes showed no significant differences between the ash state or type. However, from Figure 4.6, it can be seen that weathered CA and FA have a higher CaO content than fresh ashes. Mixed ash has a very minimal change between the fresh and weathered states with weathered MA having the lowest CaO content.

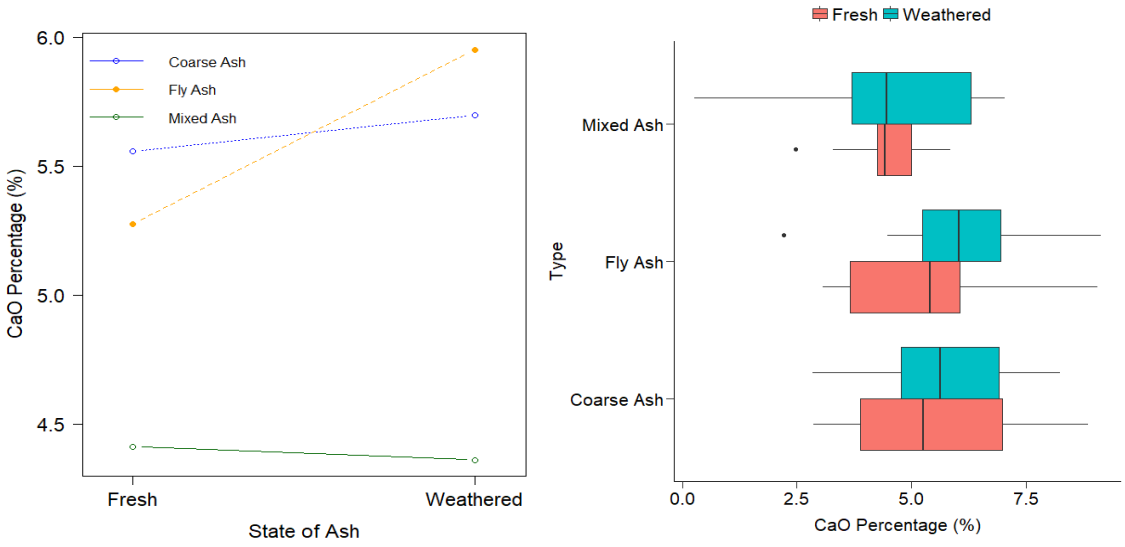

Figure 4-6: Interaction and Bar Plot of CaO Variation Between the Different Ash States and Types

It was found that the increase in CaO content as the ash weathers which could be due to the precipitation of calcium-containing secondary solids. Such solids include calcite, ettringite, and gypsum. These compounds form due to hydration and carbonation reactions. Ettringite requires sufficient water, Al, SO_4 and Ca to form at pHs greater than 11 (Hassett et al., 2005). Another possibility for the increase in CaO could be other ions leaching out of the sample thus it would appear that the ash has a higher CaO content (Campbell, 1999).

4.2.1.2.1. Calcium Leachability

CA shows a change in leachability of 11% whereas FA and MA show a decrease in leachability of -84% and -56%, respectively. CA has a higher CaO content and consequently, a higher Ca leachability due to the dissolution of the calcium secondary containing solids or the presence of free lime. Figure 4.7 shows that fresh FA (FFA) has a much higher

leachability in relation to the other ashes as a result of the free lime content. The decrease in leachability observed following weathering for FA and MA is expected due to the dissolution of free lime of these highly alkaline ashes. There is no definite relationship between the leachability and CaO content besides in the case of fresh MA and FA whereby higher CaO contents seem to result in a higher leachability. Ward et al. (2009) found that TCLP leachability tests often have higher Ca contents (25%) than reality due to the low solubility of calcium-containing salts. From Figure 4.8, the sudden decrease in leachability observed in the initial weeks is attributed to the release of Ca containing compounds such as calcium sulphates, whereas the slower decrease in leachability is due to the less soluble forms such as calcite. There are no limits regarding calcium leachability but Izquierdo and Querol (2012) state that Ca content is important as it controls the leachability of trace metals. Calcium is necessary for the precipitation of ettringite and other secondary phases which have a positive effect on the capturing and retaining of potentially harmful elements such as, Cr or Se.

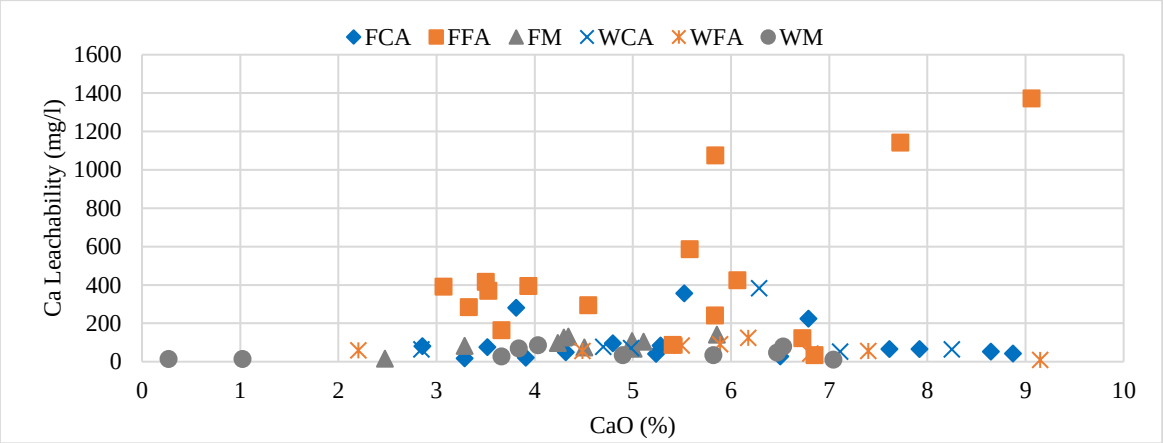

Figure 4-7: Relationship between Ca Leachability and CaO

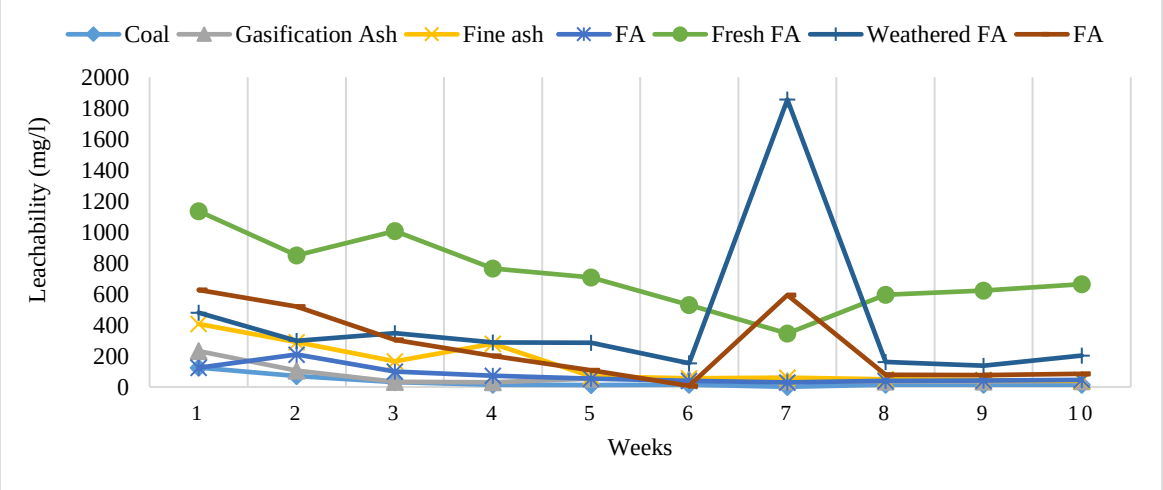

Figure 4-8: Humidity Cell Leachability of Calcium

4.2.1.2.2. Calcium Oxide Flowchart

The CaO content has been found to have the most pronounced effect of all compounds or elements analysed in mitigating the effects of ASR (Malvar et al., 2002). Figure 4.9 represents general guidelines to be used when considering the use of CaO in the CPB and potential mitigation steps to minimise ASR. The following outlines the theory behind each decision choice –

- Type of ash –

  From the analysis above, it was found that all ash types and states are suitable and fall within the lower limit which is specified at less than 10% CaO content. This confirms that high silica class F ashes with low CaO contents and are suitable for use in the CPB.

- Calcium oxide content –

  Studies which were done by Shehata and Thomas (2000) which showed that various coal ashes with CaO contents higher than 20% have very low efficiency in dealing with ASR. Utilization of low CaO content ashes has fewer problems as high CaO ashes have much faster settling times leading to flash setting (Wattimena et al., 2017).

- Replacement level –

  The amount of ash replacement in the CPB is highly dependent on the CaO concentration. High CaO, class C ashes are not preferable as such ashes may require a higher replacement level in the CPB which may not be acceptable from a strength perspective. Thomas and Folliard (2007) stated that higher replacement levels of ash could be used in exceptional cases where there was found to be high aggregate reactivity or high alkali levels. Alternatively, lower replacement levels could be used in the less reactive and low alkali concentration cases. Generally, a minimum replacement of 25% is required.

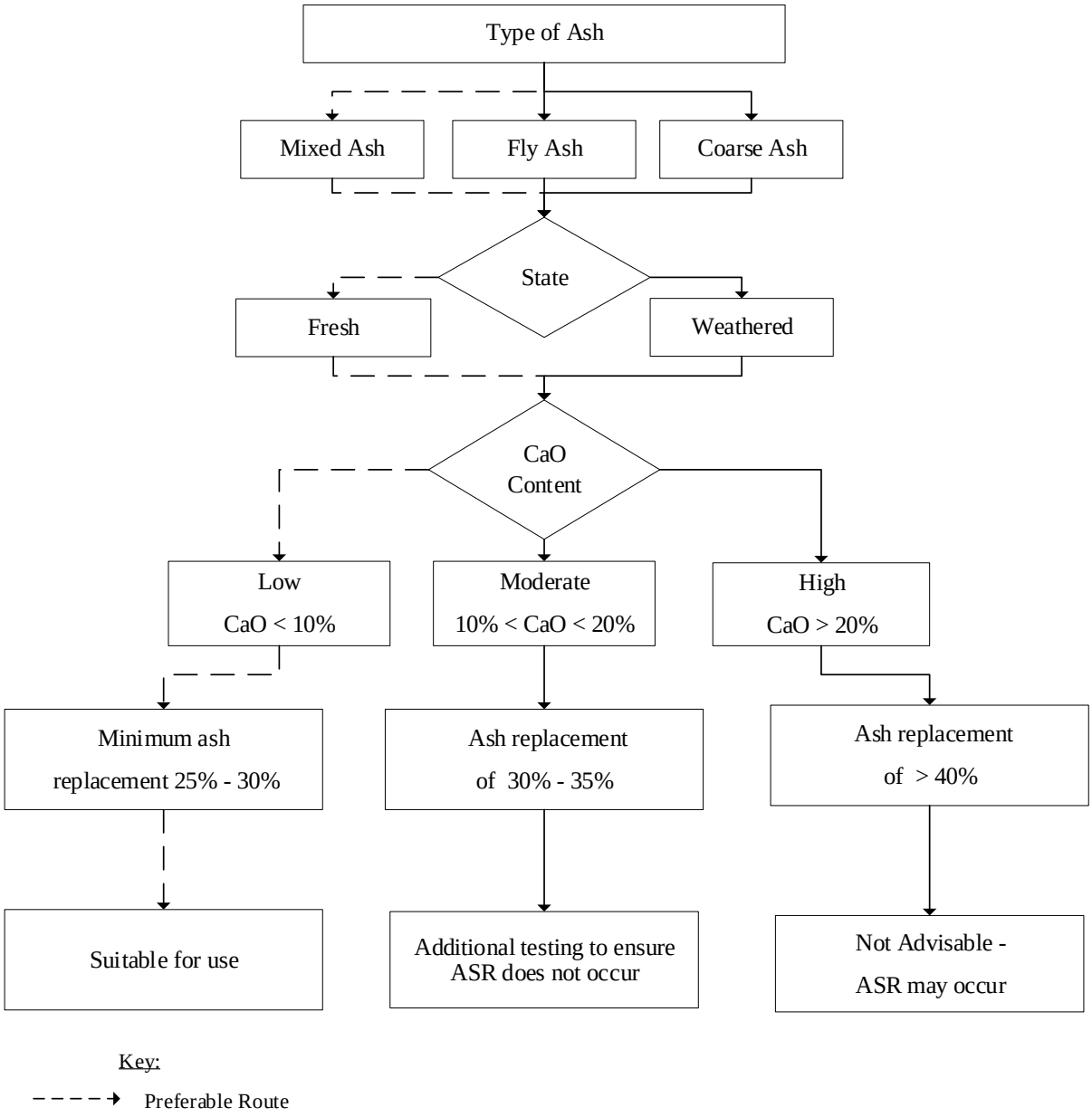

Figure 4-9: CaO Decision Flowchart

4.2.1.3. Alkali Oxides

Sodium (Na) and potassium (K) are often present in coal ashes and OPC in their oxide forms, Na_2O and K_2O, respectively. These oxides are often grouped together and termed alkalis due to their similar chemical behaviour. It has been desired that their content be limited in both the CPB and CCPs due to their detrimental effects such as concrete cracking as a result of ASR. The K_2O content is commonly converted to a Na_2O equivalent so that the total alkali concentration can be expressed. This conversion in order to determine the total equivalent alkali content is shown by Eq. 4.1. (Thomas and Folliard, 2007).

$$Na_2O_{eq} = Na_2O + 0.658K_2O \quad \text{(Eq. 4.1)}$$

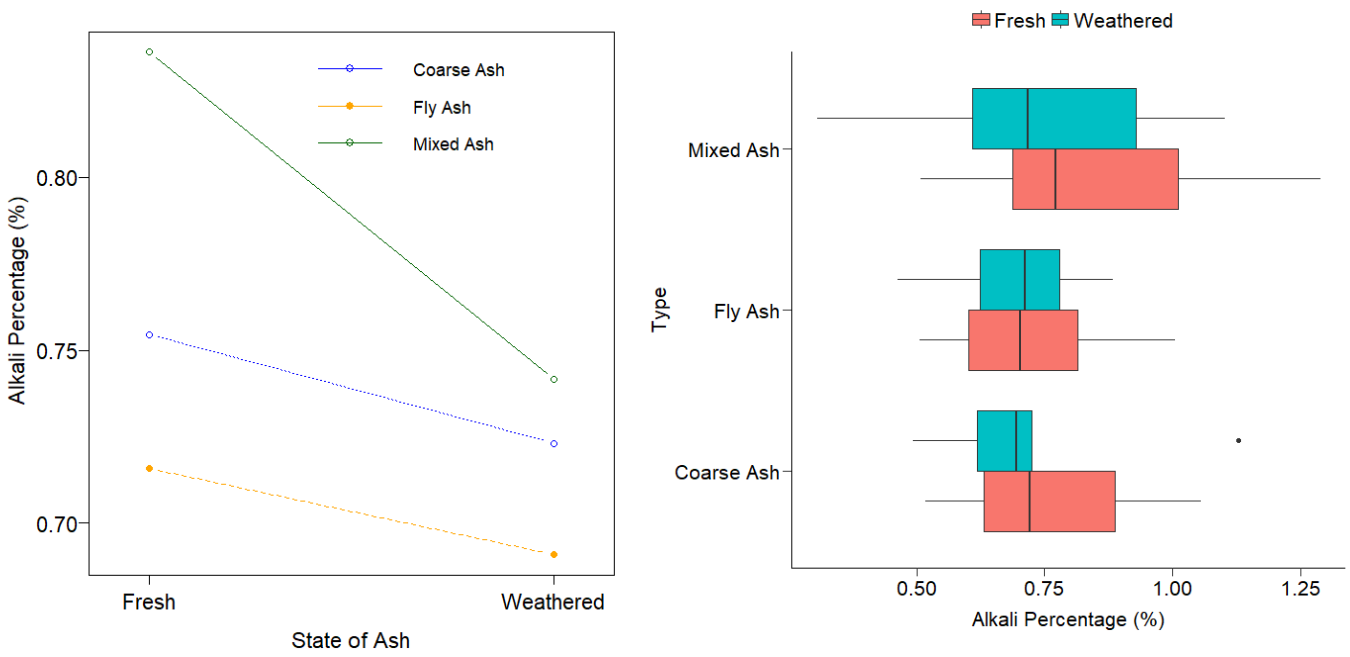

Figure 4-10: Interaction and Bar Plot of the Alkali Variation between the Different Ash States and Types

Statistical analysis on the Na_2O, K_2O, and Na_2O_{eq} was performed individually to observe the individual differences as well as the total alkali content differences. Following the statistical analysis of the Na_2O and Na_2O_{eq} content in the various ashes, no significant differences were found. However, a significant difference was found between the state of the ashes for the K_2O content [$F(2, 61) = 4.122$, $p = 0.0467$]. Fresh ashes have a higher K_2O content than weathered ashes. All ash states and types follow this relationship as shown in Figure 4.10. The decrease in the K_2O content following weathering was greater than the increase in Na_2O, thus overall there was a decrease in the alkali content. There was a very minimal change in leachability (<0.1 mg/l) and thus this was assumed to be negligible.

Table 4-5: Na_2O and K_2O Oxide and Leachability Percentage Changes Following Weathering

	CA	FA	MA
Na_2O (%)	0.01	0.04	-0.04
K_2O (%)	-0.06	-0.11	-0.05
Na_2O_{eq} (%)	-0.032	-0.025	-0.10

Table 4.5 shows that there is a minimal percentage change in the oxides. Consequently, there was also a minimal change in the leachability. The leachability of Na and K is due to the

dissolution of the soluble phases of NaCl and KCl because these compounds are independent of pH (Tiruta-Barna et al., 2006). Zevenbergen et al. (1999) stated that the higher percentages of Na_2O in the weathered ashes could be as a result of co-disposal with brine.

4.2.1.3.1. Alkalis Flowchart

Figure 4.11 represents general guidelines to be used when considering the use of alkalis in the CPB and potential mitigation steps to minimise the ASR. All ash states are suitable for use since there are minimal variations between the fresh and weathered state. The following discusses the theory behind each of the guidelines –

- Alkali content –

  The alkali content should be below 1.5% due to the risk of ASR. The level of ash replacement increases as the alkali content increases. Ashes with alkali concentrations in excess of 5% are not effective at a 25% replacement level (Thomas et al., 2012). However, high replacement levels may have lower strengths. Generally, class F ashes have lower alkali contents. Class F ashes are also known to have alkalis present which are not readily available for reaction whereas class C ashes have higher alkali concentrations present in the pore solution available for reaction. Both fresh and weathered ashes in this study have alkali contents below the advisable limit of 1.5%.

- The alkali content in the cement –

  A maximum limit of alkalis present in the cement or OPC should be 0.60% according to ASTM C150 specifications. Higher concentrations can contribute to ASR (Idorn, 1991).

  One important mitigation step is to avoid a source of external alkalis ingression. Environments containing seawater or de-icing salts should be avoided as well as areas in which industrial wastewaters have high alkali contents. In such cases, additional precautions such as the implementation of protective barriers or coatings should be utilized (Farny and Kerkhoff, 2007).

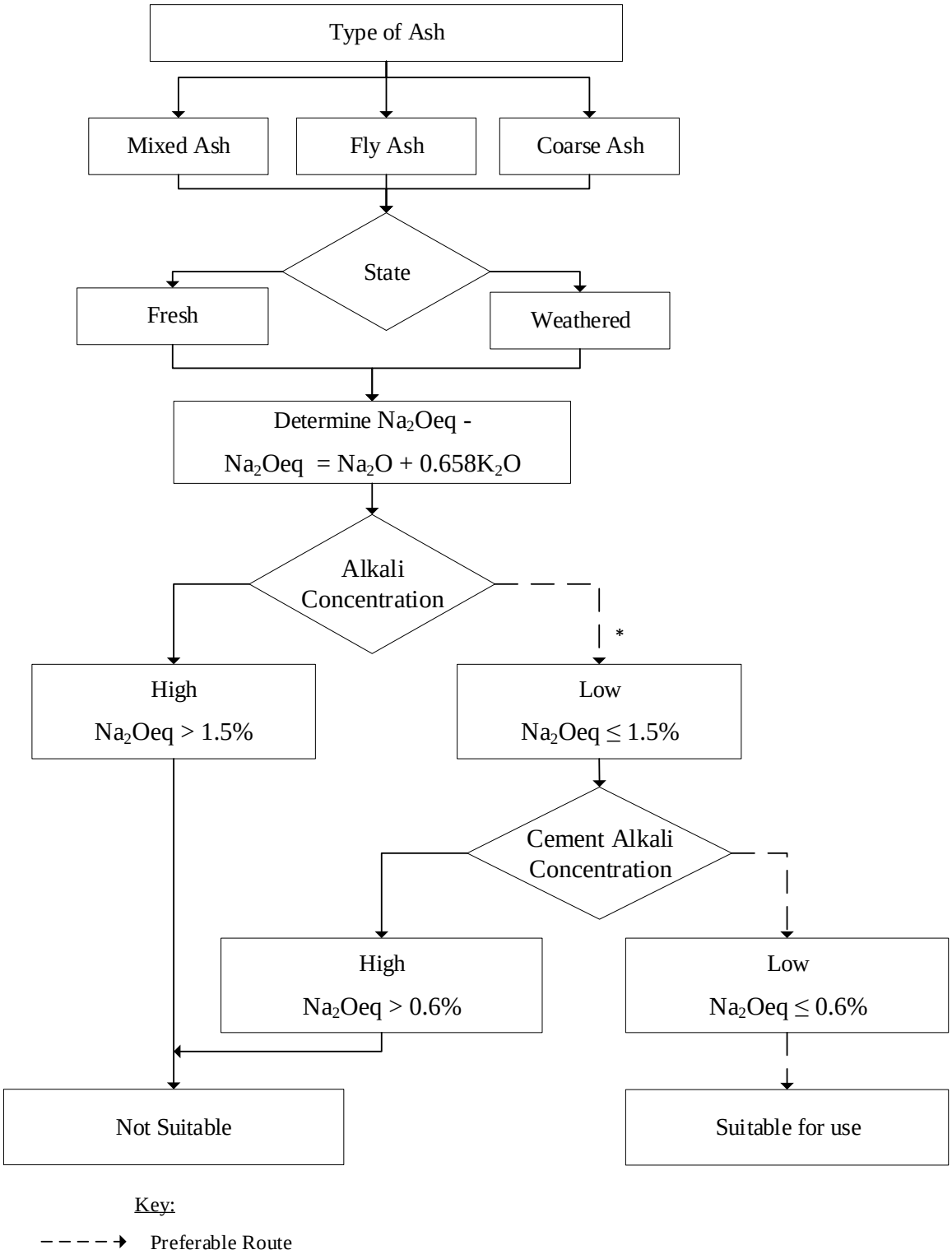

Figure 4-11: Alkali Content Decision Flowchart

4.2.1.4. *Aluminium Oxide*

Statistical analysis of the Al_2O_3 content showed no significant difference in either the state or the type of the ash. Figure 4.12 shows that the Al_2O_3 content decreases as ash weathers for MA and FA. However, the converse is true in the case of CA.

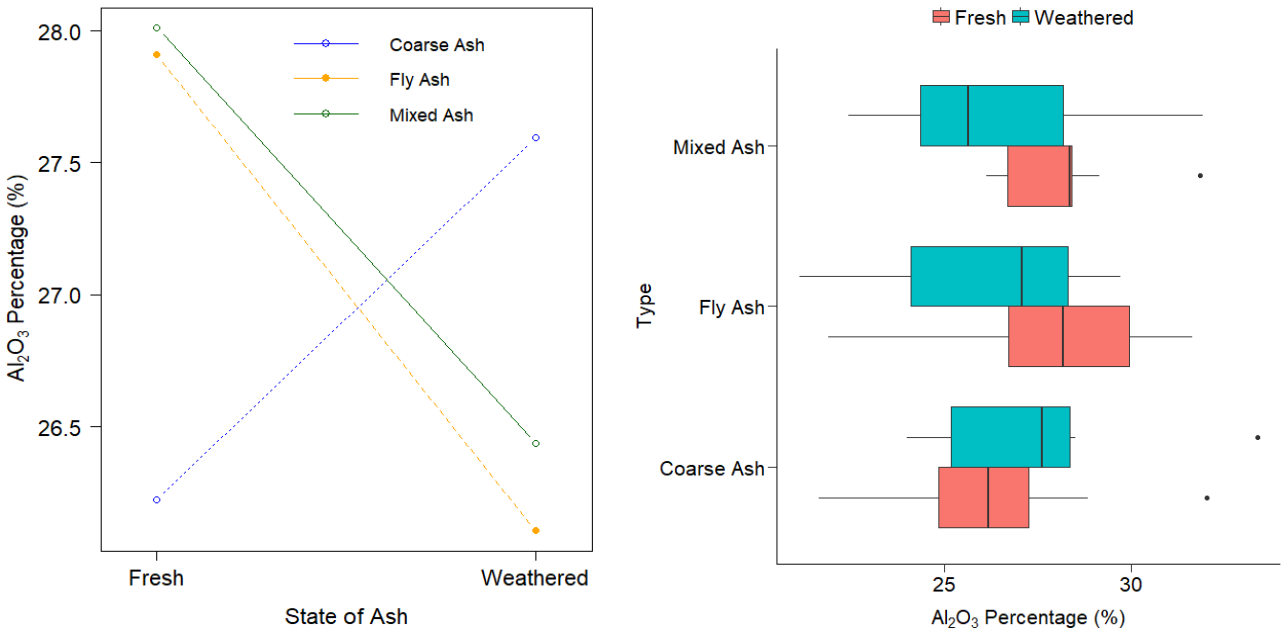

Figure 4-12: Interaction and Bar Plot of Al_2O_3 Variation Between the Different Ash States and Types

Gibbsite (Al_2O_3) is poorly leached considering its abundance in CCPs. This is due to the slow dissolution rates of the glassy matrix and the amorphous aluminosilicates phases. Since the pH of the ashes under consideration is alkaline (See Section 4.2.8), the decrease in Al_2O_3 content is most likely due to the leaching of aluminate ($Al(OH)_4^-$). The weathering process would have led to the dissolution of the ash matrix and thus the release of major elements (Eze et al., 2013). The presence of Al_2O_3 is necessary as it contributes to the pozzolanic effect. The combined SiO_2 and Al_2O_3 content have been found to have a positive effect on the pozzolanic activity of the CPB (Malvar and Lenke, 2006). Consequently, higher Al_2O_3 content would be desired and this would be achieved by utilising fresh MA. Silva et al. (2010) found that the Al_2O_3 content is higher in fresh FA in comparison to CA which is confirmed by this study. However, there are no well-defined guidelines or limits on the Al_2O_3 content since it is considered insoluble and fairly non-reactive in nature.

Leachability of Al with regards to FA followed the same relationship whereby fresh FA had a lower leachability in the weathered state as shown in Figure 4.13. In some cases, the leachability may increase due to the formation of the CSH gel. Leachability is greatly

dependent on the pH, and the change in leachability could also be due to the dissolution of ettringite (Lagerblad, 2001). There is no defined relationship between the Al_2O_3 content and the leachability of Al.

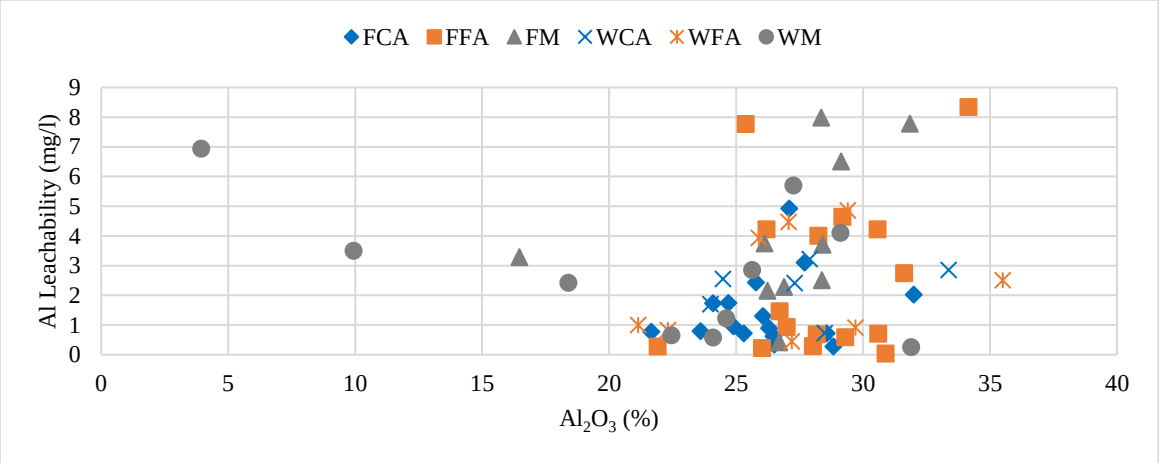

Figure 4-13: Relationship between Al Leachability and Al_2O_3

4.2.1.5. Iron Oxide

Iron oxide is responsible for the colour of the coal ash. It has been found to have minimal effect on the usage of the CPB and is often present as non-reactive hematite and magnetite. Statistical analysis of the Fe_2O_3 and total Fe content showed no significant difference between the state and type of the ash. There is a small decrease (< 1%) in the Fe_2O_3 and Fe content of the CA and FA following weathering. This is due to the spinel structure which creates highly stable compounds that are resistant to weathering and thus not easily released (Izquierdo and Querol, 2012). Fresh CA has a higher Fe_2O_3 content than fresh FA due to the tendency of Fe to segregate in CA materials (Silva et al., 2010). The slight decrease in Fe content could be attributed to oxidation processes.

There is a minimal change in leachability following weathering according to Figure 4.14. This is confirmed by studies by Kim et al. (2003) and Ward et al. (2009).

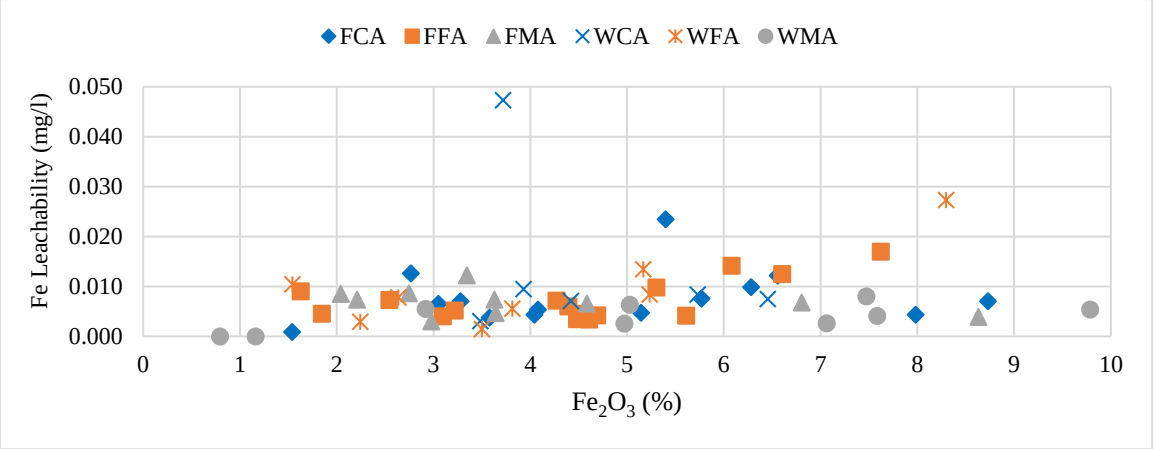

Figure 4-14: Relationship between Fe Leachability and Fe_2O_3

Since Fe_2O_3 is a pozzolan and contributes to the pozzolanic effect, high concentrations would be desirable. The content of Fe_2O_3 is more important to ensure the sum of the major oxides is greater than 70% i.e $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$. Fernández-Jiménez et al. (2007) noted that Fe_2O_3 does not significantly contribute to the compressive strength of the CPB and thus its presence need not be limited or increased. However, sorption mechanisms of iron oxides may reduce the mobility of certain elements as iron provides sites for metal binding (Izquierdo and Querol, 2012). There are no other well-defined guidelines or limits for the content of Fe_2O_3 or Fe.

4.2.1.6. Other Oxides

Other oxides that occur in coal combustion products include titanium dioxide (TiO_2), magnesium oxide (MgO) and manganese oxide (MnO). There were no statistically significant differences for any of the other oxides in the different ash states or types. These oxides form a very minimal part of the CCPs composition with changes of less than 1% in the weathered state. TiO_2, MgO, and MnO all have total elemental composition percentages of less than 3%. The elemental Ti, Mg, and Mn had low leachability. Leachability of Ti, Mg, and Mn was less than 0.23 mg/l, 86 mg/l and 0.30 mg/l, respectively. This may be due to the high alkalinity of these ashes which contributes to low solubility. There is no relationship between the leachable fraction in the leachable and the total elemental composition.

There was a decrease in leachability observed for CA and FA with regards to Mg. Mg is usually trapped within the glassy fraction of the FA, thus upon weathering this matrix has broken down leading to the release of Mg. The maximum limit of MgO in the ash is limited to 5% according to the standards set out by ASTM C618. This is to ensure the detrimental

expansion effects by the production of $Mg(OH)_2$ is avoided. The hydration of MgO to $Mg(OH)_2$ results in a volume expansion of 118% often occurring long after the cement has hardened which causes concrete cracking and structure failure (Rehsi, 1983). Since MgO is one of the earth alkalis, it contributes significantly to the pH. The MgO content in all ashes is well below the required limit (< 1.7%) and can be implemented effectively in the CPB.

All ashes seem to have a similar TiO_2 range, thus all could be implemented effectively. High TiO_2 percentages are desired owing to the photocatalytic effect. The photocatalytic effect has self-cleaning properties due to redox reactions as well as the ability to inhibit the polluting effect of NO_x in the atmosphere (Folli et al., 2010). The Mn content in the ashes is below the limits for both leachability and concentration and occurs in very small proportions thus were considered to have a negligible effect.

4.2.1.7. Summary of Major Oxides Leachability and Total Elemental Composition

The relationship between the leachability and the total elemental composition expressed as a percentage of the major oxides was analysed through the use of correlation coefficients such as the Pearson coefficient (r) and the Spearman coefficient (r_s). Upon analysis of the correlation coefficients, it can be seen that there are no relationships between the leachability and elemental composition when an average value is used as the correlation coefficients are not greater than 0.5. However, when the individual ash states and types were analysed separately, the following relationships between leachability and elemental composition can be deduced from the correlation coefficients –

- Weathered MA follows a linear relationship whereby the Si leachability increases as the SiO_2 content increases ($r = 0.84$, $r_s = 0.50$)
- Weathered CA follows a linear relationship whereby the Si leachability increases as the SiO_2 content increases ($r = 0.68$, $r_s = 0.51$)
- Weathered FA follows a linear relationship whereby the Fe leachability increases as the Fe_3O_2 content increases ($r = 0.78$, $r_s = 0.50$)
- Weathered CA follows a strong linear relationship whereby the K leachability increases as the K_2O content increases ($r = 0.77$, $r_s = 0.84$)
- Fresh MA follows a linear relationship with regards to Ca as the Ca leachability increases as the CaO content increases ($r = 0.70$, $r_s = 0.60$)

- Fresh MA shows a strong positive linear relationship whereby the Na leachability increases as the Na_2O content increases ($r = 0.69$, $r_s = 0.83$)

It can be seen that the weathered ash has a positive linear relationship with respect to the leachability and total elemental composition of Si, Fe and K. Initially, in the fresh ashes, the internal glassy matrix of the ashes remains intact and there is no relationship between the two parameters. The lower leachability in the fresh ashes is due to these elements being tightly bound to the glassy matrix. However, once this glassy matrix has broken up due to chemical weathering, the leachability increases and becomes dependant on the availability which is determined by the total elemental composition. Since Si, Fe and K are known to be associated and encapsulated within the glass fraction of FA and CA, this linear relationship is expected and only becomes prevalent once the glassy matrix has been broken down and leachability is thereafter dependant on the composition and the total element concentration of these components and hence is availability controlled.

It can also be seen that in the fresh ashes, a linear relationship is observed between Ca and Na and their respective major oxides. Conversely to the findings of the weathered ashes, Ca and Na are deposited on the surface of the ash particles and hence are high leachability is expected in the fresh ashes as their elements are readily available. As a result, these fresh ashes show a positive linear relationship whereby a higher leachability is expected as the elemental composition increases. Once the readily available constituents have been removed through surface wash off, there is no apparent relationship between leachability and concentration. All the points stated can be confirmed from the findings stated above.

4.2.2. Semi Metals

Semimetals or metalloids display characteristics of both metals and non-metals. They possess metallic properties to a small degree and are not malleable. They make up a small percentage of CCPs. The semimetals analysed in the different ashes include boron (B), germanium (Ge), arsenic (As), antimony (Sb) and tellurium (Te). The concentration of all semi metals increased in CA upon weathering and decreased for FA and MA. Phosphorous was not analysed further as the mass change in the phosphorous content was less than 0.05% and thus was considered negligible. Phosphorus is very insoluble in CCPs and often occurs in calcium phosphates. High phosphorus contents should be avoided as high concentrations

in water can lead to excessive eutrophication. The percentage leached out from the ashes for the semimetals is shown in Table 4.6. The total concentration (mg/kg) was compared to that of the leachable concentration (mg/kg) to determine the elemental percentage of the total concentration which leached out into the solution.

Table 4-6: Total Percentage of Semi Metals Leached out from CCPs

Element	B (%)	Ge (%)	As (%)	Sb (%)	Te (%)
Fresh FA	6,95	0,04	0,63	6,14	0,27
Fresh CA	8,11	0,04	2,76	8,40	0,96
Fresh MA	17,42	0,03	1,09	5,13	0,26
Weathered FA	4,52	0,03	1,19	7,53	0,33
Weathered CA	3,79	0,02	1,90	9,46	0,44
Weathered MA	4,91	0,08	2,95	3,93	0,30

4.2.2.1. Boron

Statistical analysis of the B concentration in the various ashes showed a difference between the state of the ashes [F(2, 54) = 5.226, p = 0.00842]. Fresh MA had a leachable fraction of B than the weathered ash and had the greatest variation between the different power station locations. The limits, LCT0 and TCT0, were exceeded in certain ashes particularly in fresh FA and MA. However, the total concentration and leachable amount remained below LCT1 and TCT1. Hence, these ashes under consideration can be typically classified as Type 3 waste.

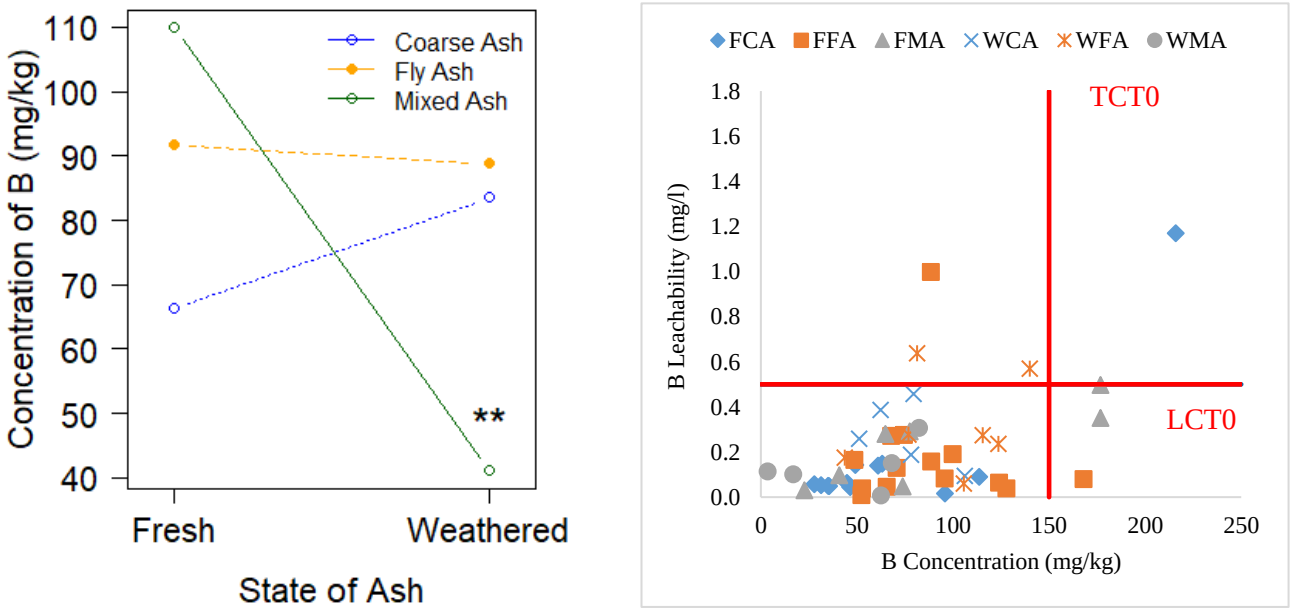

Figure 4-15: Relationship Between Total B and the Leachable Fraction

Figure 4.15 shows that there is a positive relationship between leachability and the total concentration whereby higher total concentrations result in a higher leachability especially in the case of fresh mixed ash ($r = 0.84$, $r_s = 0.86$). Similar finding was reported by Jankowski et al. (2006). Ward et al. (2009) found that B is released in higher concentrations in comparison to all other elements. B is readily leachable, however, the co-precipitation of B with compounds such as $CaCO_3$ has been found to capture B especially in alkaline ashes (Jankowski et al., 2006). This is why a fairly low percentage release of B is observed (< 20%) which could be attributed to B being bound in a mineral phase. Most researchers regard B as being the most mobile trace element in CCPs. Consequently, the fresh ashes had a higher percentage released than the weathered ashes.

4.2.2.2. Arsenic

Arsenic present in coal is in the form of As-bearing pyrite. Following the combustion process, arsenic is deposited on the surface of the FA particles as soluble arsenate species. Since As is an oxyanion, leachability is pH dependent. Leachability can be quite complex and varies over a wide range. Van der Hoek et al. (1994) found that As release in acidic fly ashes increases with an increase in pH but the converse is true in alkaline ashes. The decrease in As and other oxyanionic species released in alkaline ashes could be attributed to the precipitation of ettringite. Calcium arsenates are the most effective at controlling arsenic mobility (Cornelis et al., 2008). Thus, high calcium ashes have a higher chance of these arsenates precipitating in comparison to low calcium ashes. However, phosphate and carbonates may also encapsulate arsenic. Arsenic concentrations in the CCPs analysed showed low concentrations (<14 mg/kg) and low leachability (<0.01 mg/l). However, LCT0 and TCT0 were exceeded in certain individual ashes especially in the case of fresh FA. TCT0 was mostly exceeded however LCT0 was exceeded in one instance. This is shown in Figure 4.16. The total As released is also low (< 3%). It can also be seen that a lower total arsenic concentration results in a lower leachability in the case of weathered MA ($r = 0.70$, $r_s = 0.70$). Refer to Appendix E for detailed data.

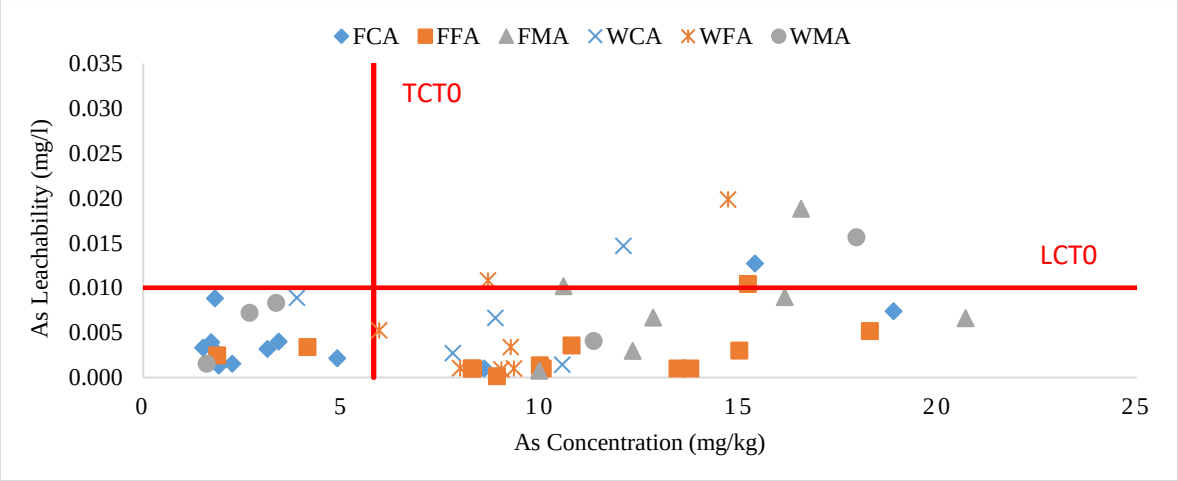

Figure 4-16: Relationship Between Total As and the Leachable Fraction

4.2.2.3. Antimony, Tellurium, and Germanium

Antimony (Sb) is released as a volatile species following the combustion of coal. It differs from the other oxyanionic species as it does not condense on the FA particles as a soluble product but is rather bound to the silicate phase (Kim et al., 2003). As a result, the release of Sb follows a similar relationship to that of Si with higher leachability in the weathered ash state. Furthermore, Ward et al. (2003) stated that at alkaline conditions, the release of Sb is higher than at acidic pHs. The study found similar results whereby the release of Sb in alkaline ashes was in the range of 4 – 12%. As shown in Figure 4.17, although Sb has a lower concentration in comparison to Ge, the leachability was higher due to the higher pH.

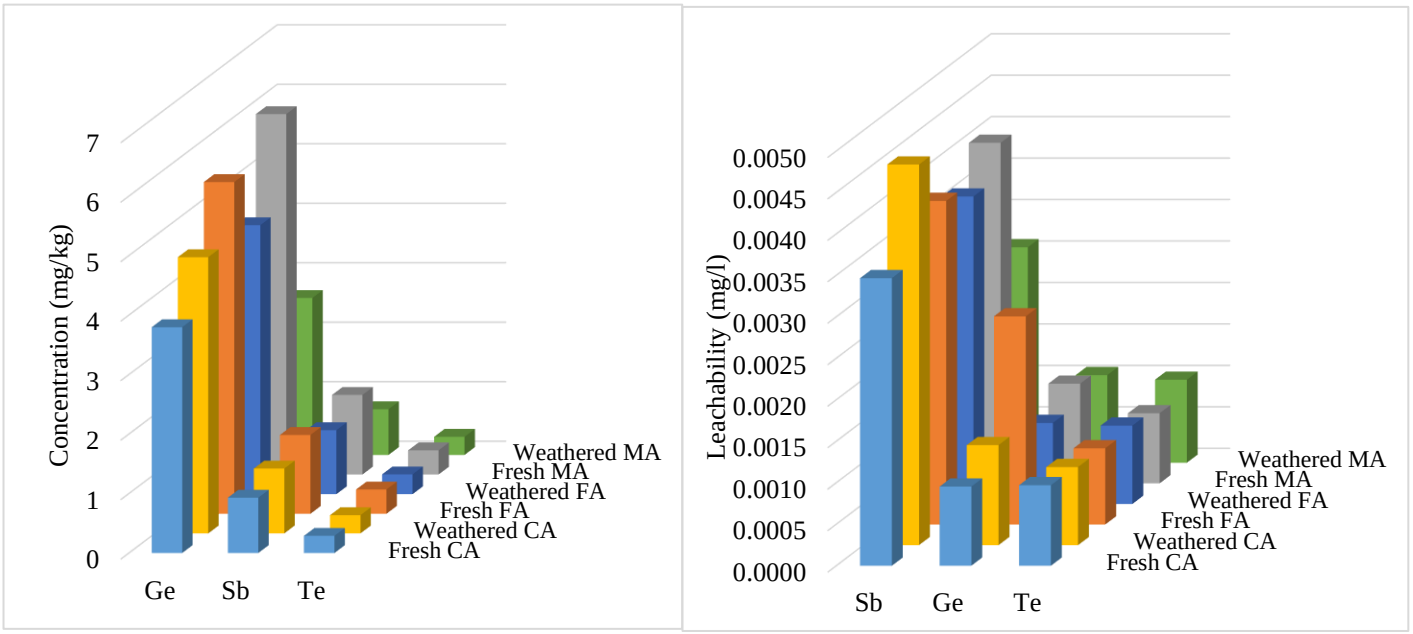

Figure 4-17: Leachability and Concentration Relationship of Ge, Sb and Te

Tellurium (Te) and germanium (Ge) occur in small proportions thus there is limited information regarding their occurrence in CCPs. Due to the low total elemental concentrations and low leachability of Sb, Te, and Ge as shown in Figure 4.17, these elements are not deemed to be of concern. In the weathered ash states, CA shows an increase in the concentration and leachability of Ge, Sb and Tb, while FA and MA has a decrease. Te showed a higher release in CA in comparison to FA. Upon analysis of the relationship between the leachability and the concentration, there was no relationship between the ash states and types except in the case of weathered MA. Weathered MA showed a positive linear relationship where higher leachability was observed as the concentration of Ge and Sb increases. Since the leachability and concentration are low, this observation is not of concern. However, overall it can be said that weathered ashes show a more prominent relationship between the leachable fraction and the total elemental concentration in the case of semi metals.

4.2.3. Basic Metals

Basic metals which were analysed include gallium (Ga), tin (Sn), thallium (TI), lead (Pb) and bismuth (Bi). Basic metals follow the same trend as observed upon analysis of the semi-metals as all concentrations increase in CA and decrease in FA upon chemical weathering. Mixed ash also shows a decrease in all metal concentrations except in the case of Sn. The percentage leached out of basic metals is shown in Table 4.7. The leachability is low in all basic metals.

Table 4-7: Total Percentage of Basic Metals Leached out from CCPs

Element	Ga (%)	Sn (%)	TI (%)	Pb (%)	Bi (%)
Fresh FA	1,13	0,36	0,15	0,002	0,05
Fresh CA	0,43	0,66	0,31	0,005	0,17
Fresh MA	0,94	0,26	0,14	0,002	0,04
Weathered FA	0,99	0,35	0,16	0,002	0,04
Weathered CA	1,10	0,30	0,17	0,002	0,05
Weathered MA	0,53	0,50	0,32	0,004	0,18

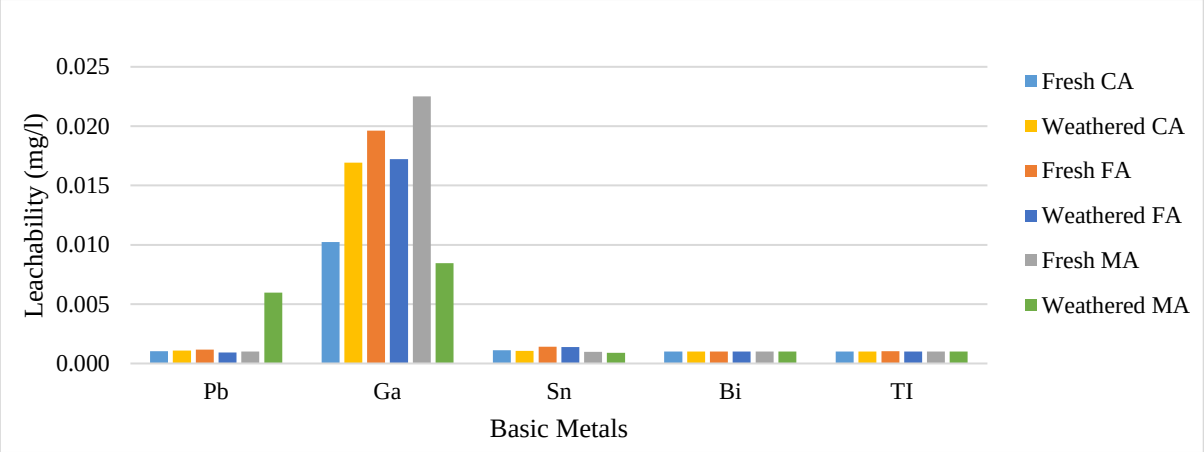

Figure 4-18: Leachability of Basic Metals

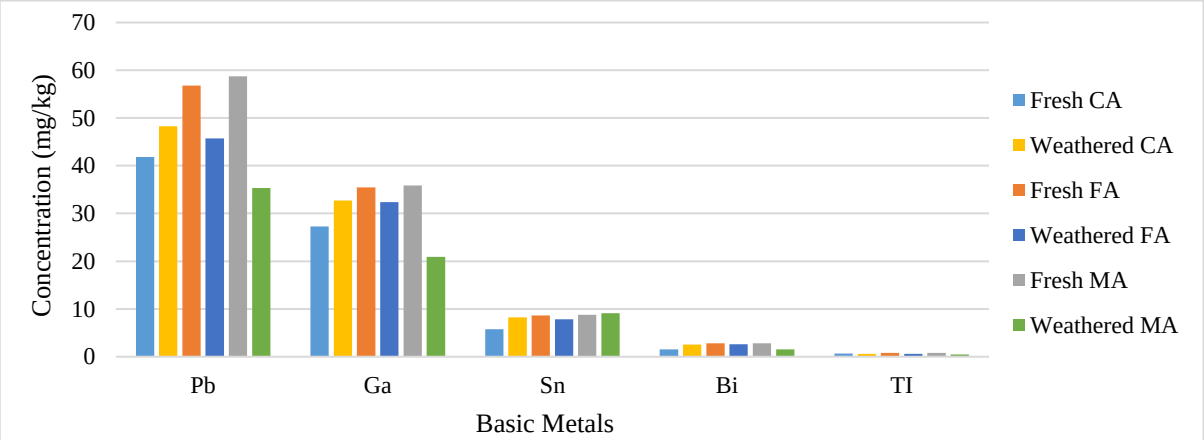

Figure 4-19: Concentrations of Basic Metals

As seen in Figure 4.18 and 4.19, Sn, TI, and Bi have very low leachability and total concentrations. There are also minimal changes between the states and there is no apparent relationship between total concentration and leachability. The correlation coefficients of Sn, TI, Pb, and Bi were 0 for all ash states and types. However, statistical analysis of the Bi concentration in the various ashes showed a difference between the type of the ashes [$F(2, 61) = 5.3548$, $p = 0.0072$]. FA has higher total Bi concentrations than CA which may be due to the relative volatility.

4.2.3.1. Gallium

Statistical analysis of the Ga concentration in the various ashes showed a difference in weathered MA [$F(2, 55) = 4.844$, $p = 0.0115$]. Weathered MA contained a much lower total Ga concentration than the other ashes and had the greatest concentration decrease after weathering (Figure 4.19). Gallium had a higher leachability in comparison to the other basic metals. From the correlation coefficients, it can be seen that fresh CA ($r = 0.84$, $r_s = 0.79$),

weathered FA (r = 0.50, r_s = 0.50), weathered CA (r = 0.83, r_s = 0.70) and weathered MA (r = 0.72, r_s = 0.60) all show a linear relationship whereby higher concentrations lead to higher leachability. It can thus be said that Ga is poorly bound to the ash particles as is easily released depending on the availability following weathering.

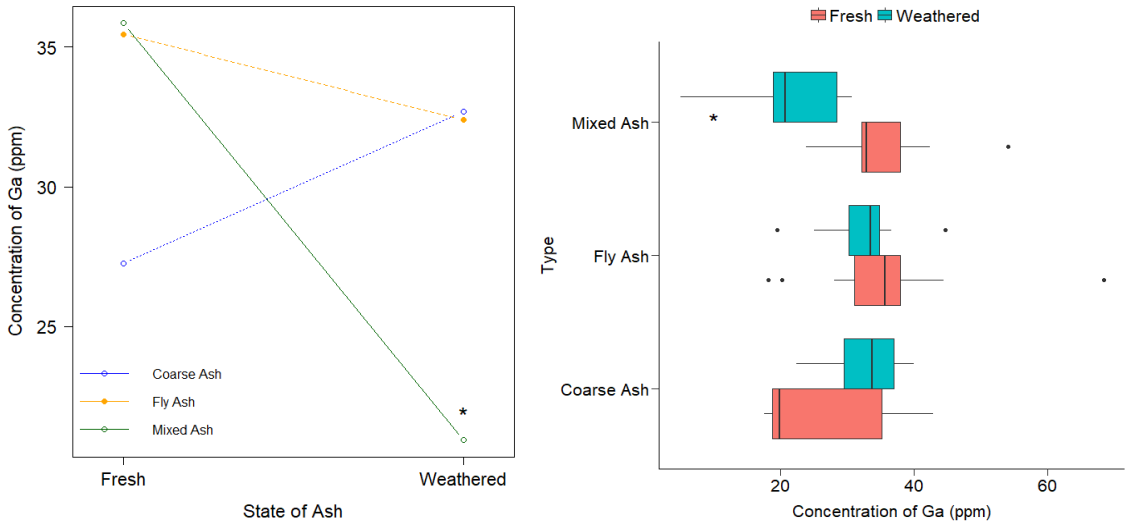

Figure 4-20: Interaction and Bar Plot of Ga Variation between the Different Ash States and Types

4.2.3.2. Lead

There were no observed mass percentage changes in the Pb content in all ash types following weathering. Total concentration limits (TCT0) were exceeded for nearly all ash types except in the case of fresh CA. This is due to the high relative volatility of Pb hence Pb is usually found in higher concentrations in FA as opposed to CA. Although the concentrations were high, leachability was low and below the LCT0 limit of 0.01 mg/kg. A fairly linear relationship can be seen between the concentration and leachability of Pb with regards to weathered CA (Figure 4.21). Due to the toxic nature of Pb, care needs to be taken when using these ashes however in the case of the ashes examined in this study, the percentage leached out was low even though the total concentration in the ash was high.

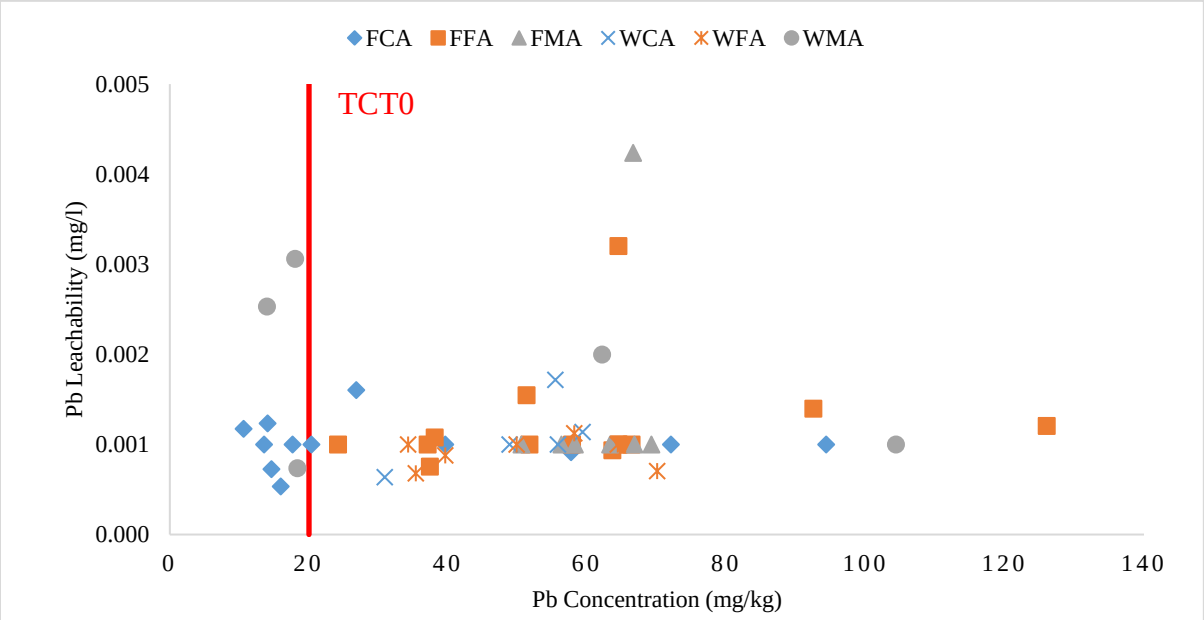

Figure 4-21: Relationship Between Total Pb and the Leachable Fraction

4.2.4. Alkali Metals

Alkali metals include lithium (Li), rubidium (Rb) and caesium (Cs). Sodium and potassium were discussed under their respective oxides in Section 4.2.1.3. Rubidium and Cs occurrence is negligible due to the low total concentration and leachable fraction observed. From the correlation coefficients, the release of Rb follows a linear relationship with the concentration in the case of weathered FA ($r = 0.57$, $r_s = 0.82$) and CA ($r = 0.54$, $r_s = 0.70$). This is due to Rb being trapped in the glass matrix of the ashes and thus the release only occurs upon weathering. Similarly, Cs follows the same relationship with regards to weathered FA ($r = 0.57$, $r_s = 0.61$) and weathered CA ($r = 0.92$, $r_s = 0.71$). Such a slow dissolution rate of these elements results in the low extractable yields in the range of 0.02 mg/kg which is similar to the results in this study (Moreno et al., 2005). The percentage leached for each alkali metal is shown in Table 4.8.

Table 4-8: Total Percentage of Alkali Metals Leached out from CCPs

Element	Li (%)	Rb (%)	Cs (%)
Fresh FA	1,83	2,05	0,008
Fresh CA	1,11	2,56	0,000
Fresh MA	1,25	1,25	0,000
Weathered FA	7,20	5,49	0,007
Weathered CA	1,03	2,57	0,006
Weathered MA	0,32	1,78	0,011

4.2.4.1. Lithium

Lithium can be found in high proportion in CCPs and is used as a potential source for Li production. Approximately 79 – 94% of Li is found in the glass phase with the remaining percentages in mullite or quartz phases (Hu et al., 2018). Statistical analysis of the Li concentration found a significant difference in the state of the ashes for CA and FA. According to Figure 4.22, both CA and FA showed higher leachability and concentration in the weathered state [$F(1, 55) = 5.5794$, $p = 0.0217$]. This confirms that Li is trapped in the glassy matrix of the ash particles and release only occurs once this matrix has been broken down. This is confirmed by the correlation coefficients in the weathered state for MA ($r = 0.75$, $r_s = 0.90$) where a linear relationship between concentration and leachability is observed.

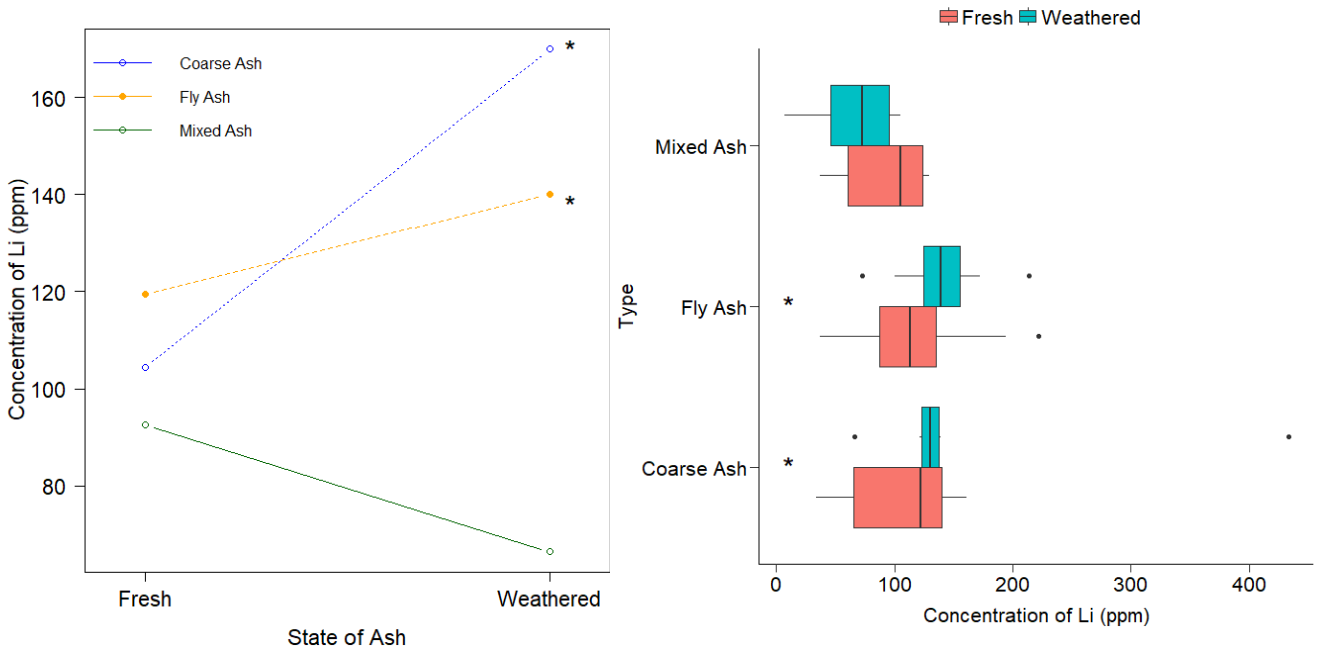

Figure 4-22: Interaction and Bar Plot of Li Variation Between the Different Ash States and Types

4.2.5. Alkali Earth Metals

Alkali earth metals are beryllium (Be), strontium (Sr) and barium (Ba). Calcium and magnesium were discussed above in Section 4.2.2 and 4.2.6, respectively. The variation in the leachability of alkali earth metals is shown in Figure 4.23 and the percentage leached out is shown in Table 4.9.

Table 4-9: Total Percentage of Alkali Earth Metals Leached out from CCPs

Element	Be (%)	Sr (%)	Ba (%)
Fresh FA	0,017	3,79	1,44
Fresh CA	0,019	0,69	0,26
Fresh MA	0,018	1,00	0,30
Weathered FA	0,017	0,89	0,20
Weathered CA	0,016	1,41	0,37
Weathered MA	0,055	0,78	1,78

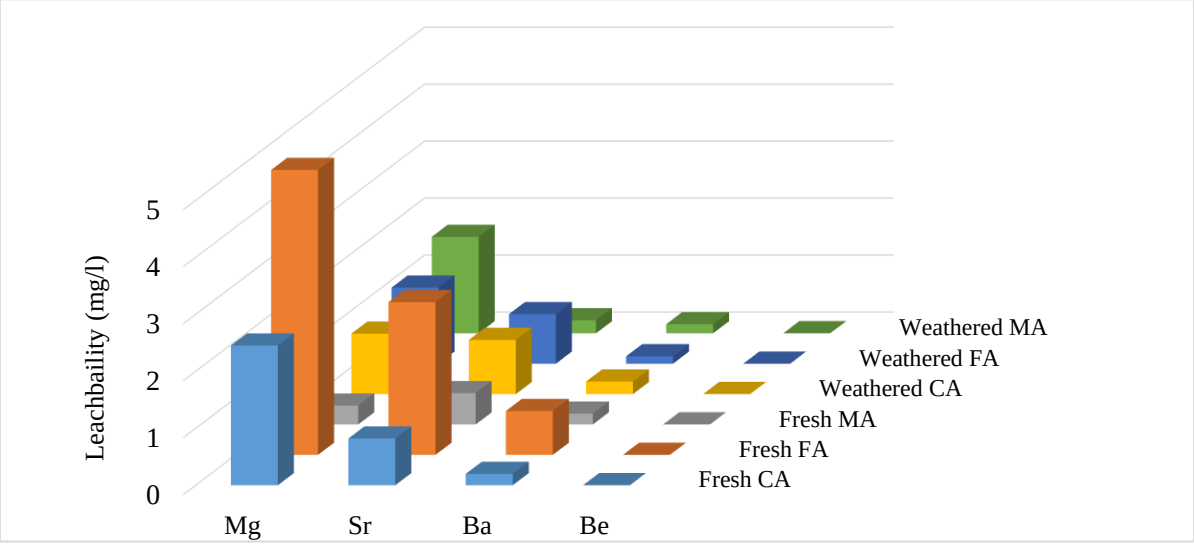

Figure 4-23: Leachability of Alkali Earth Metals

4.2.5.1. Beryllium

No statistical significance was observed in the leachable Be concentration between the different ash samples. Be is insoluble at neutral to alkaline pHs and slightly soluble under acidic conditions (Moreno et al., 2005). This is seen from the very low leachability since the ashes under consideration are alkaline and the minimal percentage leached out into solution.

4.2.5.2. Strontium

Statistical difference in the Sr mass percentage was found [$F(2, 61) = 3.650$, $p = 0.0318$]. Fly ashes had a higher strontium content than mixed ashes. However, this difference is fairly small. The Sr concentrations were found to increase in weathered FA in comparison to the fresh ash. This may be due to the resultant pH decrease as fresh FA weathers. Lower pHs do not favour Sr-rich mineral phases (Gitari et al., 2009). The leachability of Sr increases as the concentration increased for fresh CA ($r = 0.59$, $r_s = 0.75$) and fresh MA ($r = 0.81$, $r_s = 0.93$). This is indicative that Sr is most likely not encapsulated in the glassy matrix of the ashes.

4.2.5.3. Barium

No significant statistical differences were found upon analysis of the Ba content in the various ashes. However, both the total concentration and leachable fraction exceeded TCT0 and LCT0 as shown in Figure 4.24. Ba has a negligible mass percentage variation upon weathering. There is also no observable trend between the total concentration and the leachable fraction of barium coupled with the low percentage leached out into the solution.

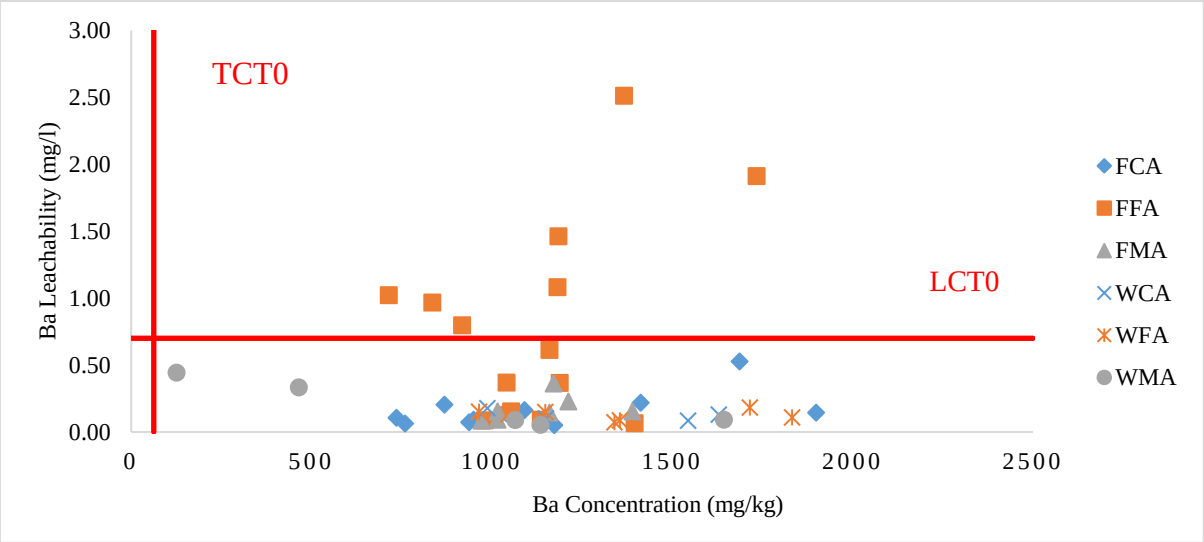

Figure 4-24: Relationship Between Total Ba and the Leachable Fraction

4.2.6. Transition Metals

Transition metals all occur in varying proportions in the CCPs. The limits for disposal are given according to SANS10234. Transition metals analysed were scandium (Sc), vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), yttrium (Y), zirconium (Zr), niobium (Nb), silver (Ag), cadmium (Cd), hafnium (Hf), tantalum (Ta), tungsten (W), iridium (Ir), platinum (Pt), gold (Au) and mercury (Hg).

From the analysis of the correlation coefficients for each transition metal, it is evident that the weathered ashes show more of a relationship between the leachable fraction and the total concentration than the fresh ashes for –

- Zn in weathered CA ($r = 0.83$, $r_s = 0.80$)
- Hg in weathered CA ($r = 0.81$, $r_s = 0.60$) and weathered MA ($r = 0.87$, $r_s = 0.70$)
- W in weathered CA ($r = 0.83$, $r_s = 0.70$) and weathered MA ($r = 0.80$, $r_s = 0.60$)

Conversely, fresh ashes show a positive relationship between leachability and concentration for –

- Sc in fresh FA ($r = 0.73$, $r_s = 0.71$)
- V in fresh CA ($r = 0.86$, $r_s = 0.90$)
- Ni in fresh MA ($r = 0.75$, $r_s = 0.64$) and fresh FA ($r = 0.51$, $r_s = 0.50$)
- Cd in fresh CA ($r = 0.82$, $r_s = 0.68$)

This could further indicate that some of these transition metals are encapsulated in the glassy ash matrix whereas others are associated with the less soluble internal matrix of the ash particles. There was no correlation between the two parameters for Cr, Co, Cu, Y, Zr, Nb, Ag, Ta, Ir, Pt, and Hf.

The change in leachability between the fresh and weathered state for transition metals was very low (< 0.1 mg/l), thus these changes were considered negligible and not a cause of concern with regards to the release of these transition metals to the environment. The transition metals which were analysed with respect to the TCT and LCT limits and the results of the metal which exceeded the limits are presented in Table 4.10 and 4.11. Metals that exceeded the LCT limits were Cr and V whereas metals that exceeded the TCT limits were Cu and V.

The leachable total Cr concentrations exceeded the LCT0 limits for all ashes except fresh CA. The leachable and total concentration of V exceeded the LCT0 limits for weathered CA and TCT0 limits for weathered FA. The total Cu concentrations exceeded the TCT0 limits in the case of all ashes. Hence, the FA, CA and MA under consideration can be classified as a Type 3 waste for total and leachable concentrations according to the methodology prescribed in GN R. 635.

Table 4-10: Metals Which Exceeded TCT Limits

Cr				
	Concentration (mg/kg)	TCT0 (mg/kg)	TCT1 (mg/kg)	TCT2 (mg/kg)
Fresh FA	196,90	46000	800000	N/A
Fresh CA	175,63			
Fresh MA	204,54			
Weathered FA	152,07			
Weathered CA	194,87			
Weathered MA	175,97			
V				
Fresh FA	133,51	150	2680	10720
Fresh CA	111,45			
Fresh MA	131,35			
Weathered FA	152,56			

Weathered CA	123,26			
Weathered MA	80,79			
Cu				
Fresh FA	47,33	16	19500	78000
Fresh CA	42,16			
Fresh MA	54,80			
Weathered FA	43,92			
Weathered CA	41,13			
Weathered MA	41,19			

Table 4-11: Metals Which Exceeded LCT Limits

Cr				
	Leach (mg/l)	LCT0 (mg/l)	LCT1 (mg/l)	LCT2 (mg/l)
Fresh FA	0,137	0,05	2,5	5
Fresh CA	0,029			
Fresh MA	0,138			
Weathered FA	0,276			
Weathered CA	0,087			
Weathered MA	0,055			
V				
Fresh FA	0,034	0,2	10	20
Fresh CA	0,024			
Fresh MA	0,047			
Weathered FA	0,068			
Weathered CA	0,699			
Weathered MA	0,029			
Cu				
Fresh FA	0,003	2	100	200
Fresh CA	0,002			
Fresh MA	0,004			
Weathered FA	0,002			
Weathered CA	0,001			
Weathered MA	0,005			

Furthermore, the transition metals were analysed with respect to the percentage leached out from the ashes. The total concentration (mg/kg) was compared to that of the leachable concentration (mg/kg) to determine the percentage of the total concentration which leached out into the solution. The results are shown in Table 4.12. It is clear from the table that weathered ashes showed a higher percentage leached for Sc, V, Cr, Co, Ni, Cu, Hg and Y whereas the fresh ashes showed a higher percentage leached for Zn, Nb, Ag, Hf, Ta, W, Ir, and Pt. This indicates that the latter elements may be more associated with the surface of the ashes and thus are more easily released in relation to the other transition metals.

Additionally, due to the relative volatility of the elements, a higher percentage leached can be seen in FA for Cr, Cu, and Ir. With regards to the Cr leached, this is noticeable for the weathered FA, but the weather CA and MA are quite similar. The Cu leached is only high for the fresh FA compared to the other fresh ashes. However, the weathered MA has a higher percentage leached than any of the other ashes. The Ir leach in the fresh FA is higher than others, but although the weathered FA is higher than the other weathered ash types, it is lower than the Fresh MA. These observations are likely due to the coal combustion chamber temperatures, are more likely to be trapped with the FA. Higher percentages leached out for CA can be seen for Zn (for fresh CA and closely followed by weathered MA), V (for weathered CA only), and W (for fresh CA and the weathered CA and FA).

Table 4-12: Percentage of Transition Metals Leached Out into Solution

Element	**Sc (%)**	**V (%)**	**Cr (%)**	**Co (%)**	**Ni (%)**	**Cu (%)**
Fresh FA	0,55	0,42	1,35	0,18	0,37	0,16
Fresh CA	0,83	0,38	0,35	0,19	0,12	0,13
Fresh MA	1,05	0,72	1,31	0,15	0,13	0,14
Weathered FA	0,56	1,15	3,08	1,00	0,09	0,11
Weathered CA	0,31	10,27	0,89	0,16	0,10	0,07
Weathered MA	1,59	0,66	0,57	0,28	0,59	0,33
Element	**Zn (%)**	**Y (%)**	**Zr (%)**	**Nb (%)**	**Ag (%)**	**Cd (%)**
Fresh FA	0,42	0,52	0,01	0,06	16,26	0,00
Fresh CA	3,18	0,53	0,01	0,06	12,85	0,00
Fresh MA	0,63	0,37	0,01	0,07	1,00	0,00
Weathered FA	0,73	0,35	0,00	0,06	11,41	0,00
Weathered CA	0,23	1,46	0,00	0,05	8,51	0,00
Weathered MA	3,00	1,55	0,01	0,04	0,00	0,00
Element	**Hf (%)**	**Ta (%)**	**W (%)**	**Ir (%)**	**Pt (%)**	**Hg (%)**
Fresh FA	0,19	0,86	4,31	103,64	47,49	20,23
Fresh CA	0,25	0,84	8,46	63,26	44,90	4,90
Fresh MA	0,30	1,01	6,80	75,98	59,71	3,31
Weathered FA	0,27	0,76	8,00	67,53	53,75	8,12
Weathered CA	0,22	0,62	8,01	61,06	41,88	14,00
Weathered MA	0,20	0,57	4,14	63,08	38,35	35,25

The transition metals Cr, Cu, Ni, V, Zn, and Zr were analysed in terms of mass percentages, total elemental concentration, and the leachable fraction. However, the total elemental mass percentages of these elements were less than 0.01% of the total ash composition and thus considered negligible. Changes in concentration following weathering are shown in Figure 4.25 below.

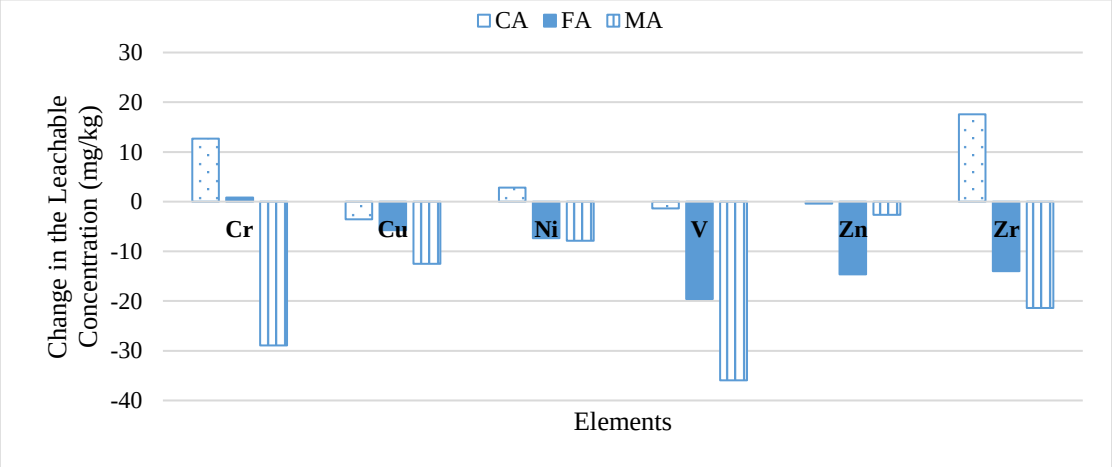

Figure 4-25: Change in the Total Leachable Concentration of Transition Metals (Cr, Cu, Ni, V, Zn, Zr)

Most metals are more susceptible to leaching under acidic conditions thus the low leachability for the transition metals is observed. Chromium exists in two oxidation forms, namely Cr(III) and Cr(VI). These different oxidation states pose different environmental and health risks and thus need to be monitored. Cr(VI) occurs as dichromate and chromates and is considered carcinogenic and highly soluble. Cr(III) poses a lesser concern and is less soluble (Izquierdo and Querol, 2012). Chromate is the soluble form in alkaline ashes which is what accounts for the percentage leached into solution. The leachable Cr fraction increased in CA and FA but decreases in MA. Copper is most likely leachable in acidic environments. Copper removal is less than 0.1% by water leaching of alkaline ashes (Moreno et al., 2005). The change in concentration for the other transition metals is shown below in Figures 4.26 and 4.27, respectively.

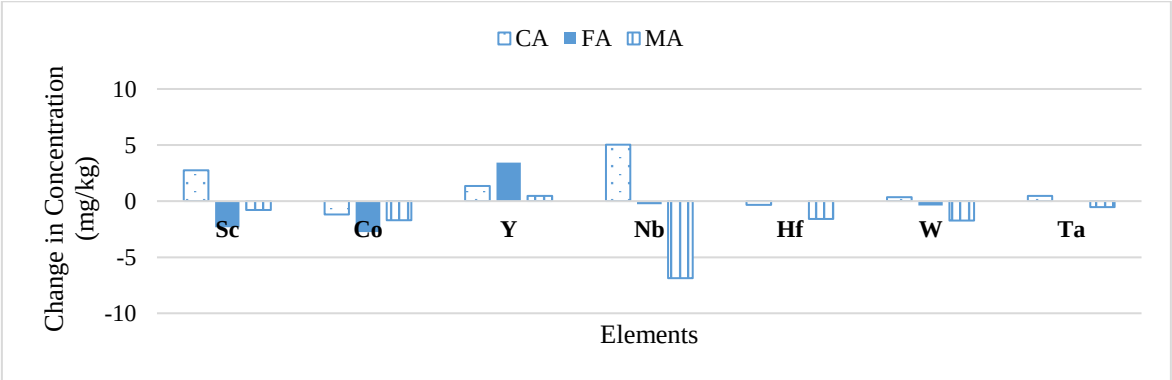

Figure 4-26: Change in Concentration of Transition Metals

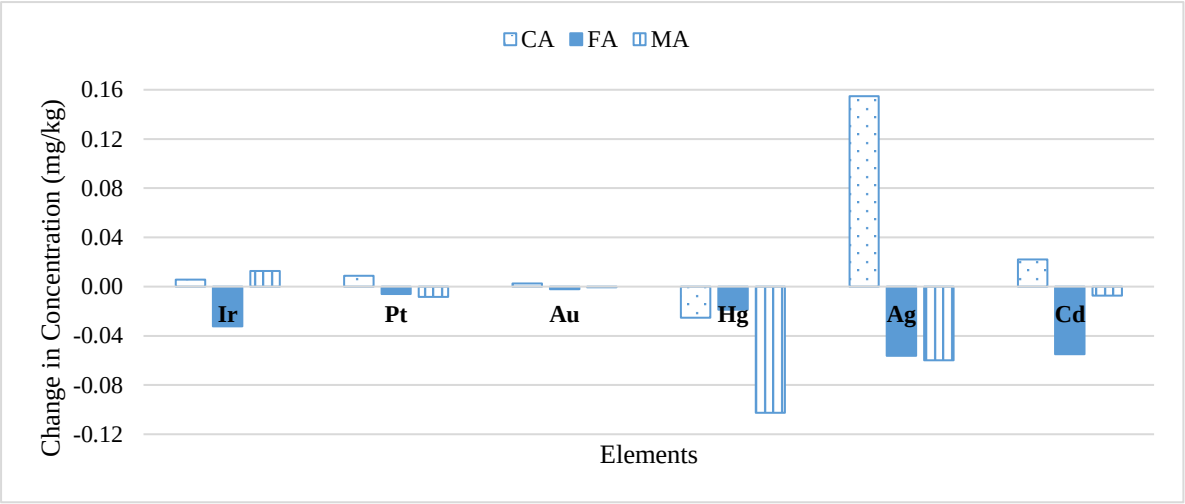

Figure 4-28: Change in Concentration of Transition Metals

Upon analysis of the remaining transition metals, statistical differences were only found for the leachable concentration of Nb and Ta. The concentration of Nb differed between the type of ashes [F(2, 55) = 4.316, p = 0.0182] with MA and FA having a large difference whereby the concentration in the MA decreased after weathering. Similar finding were obtained upon analysis of the Ta concentration [F(2, 55) = 3.6568, p = 0.0323]. It can be seen from Figure 4.28 that the CCPs have similar changes in both these metals hence the behaviour of these transition metals is similar. It can also be seen that FA and MA have lower concentrations in the weathered state.

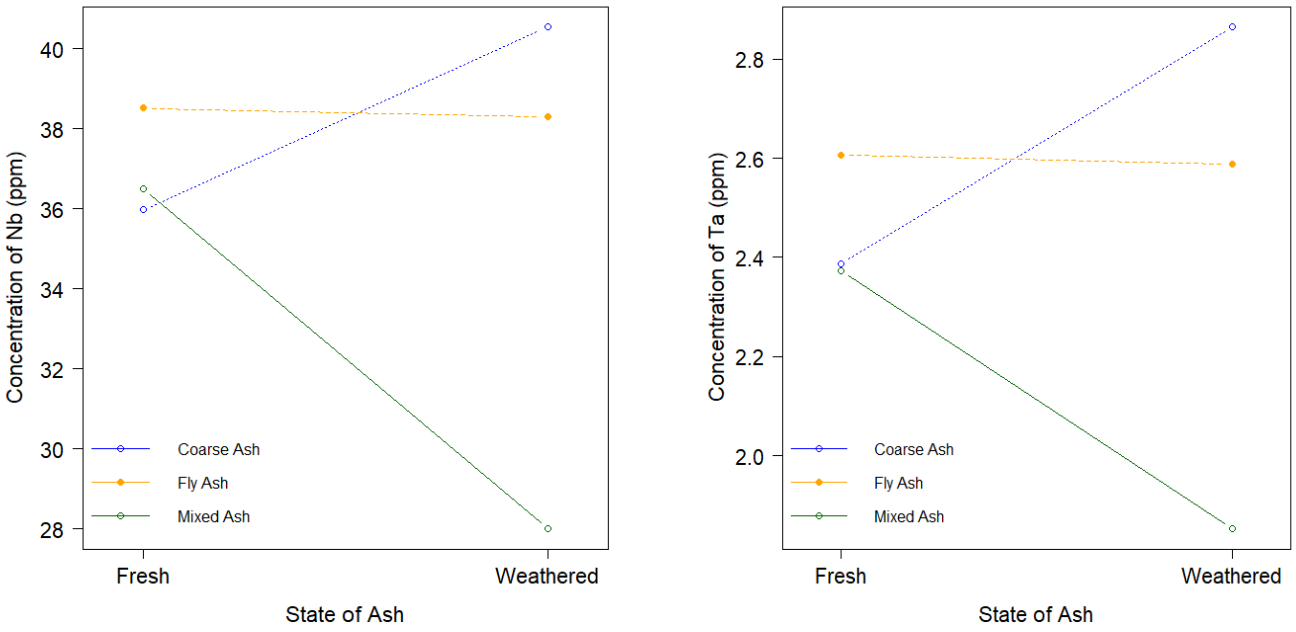

Figure 4-27: Interaction and Bar Plot of Nb and Ta Variation Between the Different Ash States and Types

Backfilling is advantageous as the risk of toxic metal leaching is reduced. A detailed review of the leaching behaviour of FA was done by Izquierdo and Querol (2012). They found that metals and a large number of other elements are tightly bound to the FA particles and thus will not easily be leached, regardless of the nature of the FA. Wang et al. (2016) found that during the cement-making process, cement addition has a positive effect on the immobilization of trace metals. Madzivire et al. (2017) focused on the risk of metal leaching following the use of CFA as a backfill material and found that backfilling with FA can neutralize and capture 50 – 95% of the toxic metals and other contaminants, such as Fe, Al, Zn, Cu, Co, and Mn. It must be noted that these removed contaminants can be remobilized when the backfill material is exposed to fresh AMD. The trace element mobility is largely dependent on the pH.

4.2.7. Loss on Ignition (LOI)

The LOI, which is a measurement of the unburnt carbon content in the ash is critical in concrete applications. A maximum allowable percentage of 12% is recommended for class F ashes and 6% for class C ashes (Thomas, 2007). It is advisable in both concrete and CPB applications that ashes should contain a low and consistent LOI as this is important in predicting product quality.

Statistical analysis of the LOI content in the various ashes revealed a significant difference between the state of the ashes [$F(2, 61) = 4.145$, $p = 0.046$]. Weathered ashes have a higher LOI than fresh ash. There is an approximate increase of 2.11 % in the LOI between the fresh and weathered ash state. The major difference between the fresh and weathered states could be due to the hydrated water and carbon dioxide loss from the secondary minerals formed in the weathered ash (Yeheyis et al., 2009). These differences arise due to the different coal sources and the different combustion temperatures at the coal power stations.

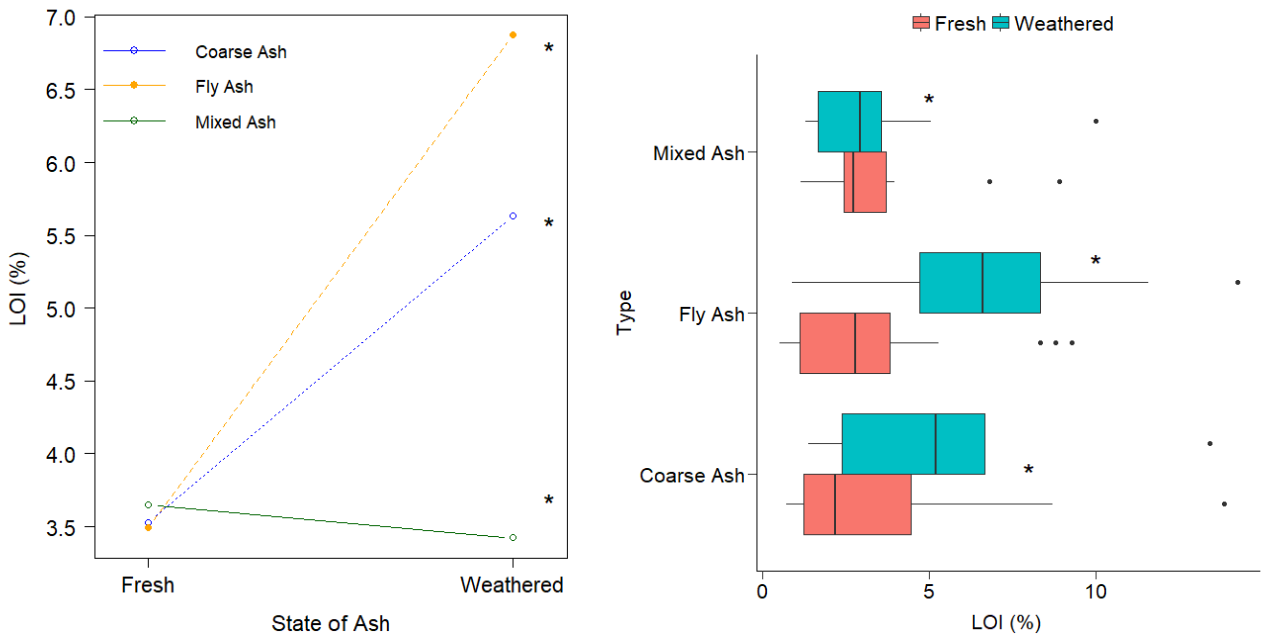

Figure 4-29: Interaction and Bar Plot of LOI Variation Between the Different Ash States and Types

From Figure 4.29, it can be seen that fresh ashes are most suited to CPB applications. The most detrimental effect of high LOI content is the resulting high water demand. A high water demand would result in a higher cost for backfilling operations which is undesirable. Furthermore, this would reduce the compressive strength of the CPB and increase the porosity of which all would have adverse structural applications.

4.2.8. pH

The prevailing pH is an extremely important and necessary parameter to consider in both the CCPs and the CPB. It is the major variable that controls the leaching of potential groundwater contaminants and is largely dependent on the source of the coal. From Figure 4.30, it can be seen that FA has alkaline pHs. According to SANS10234, a pH >11.5 is considered corrosive to the skin and is thus classified as a hazardous material. There were significant statistical differences found with regards to the pH between the type as well as the state of the ashes.

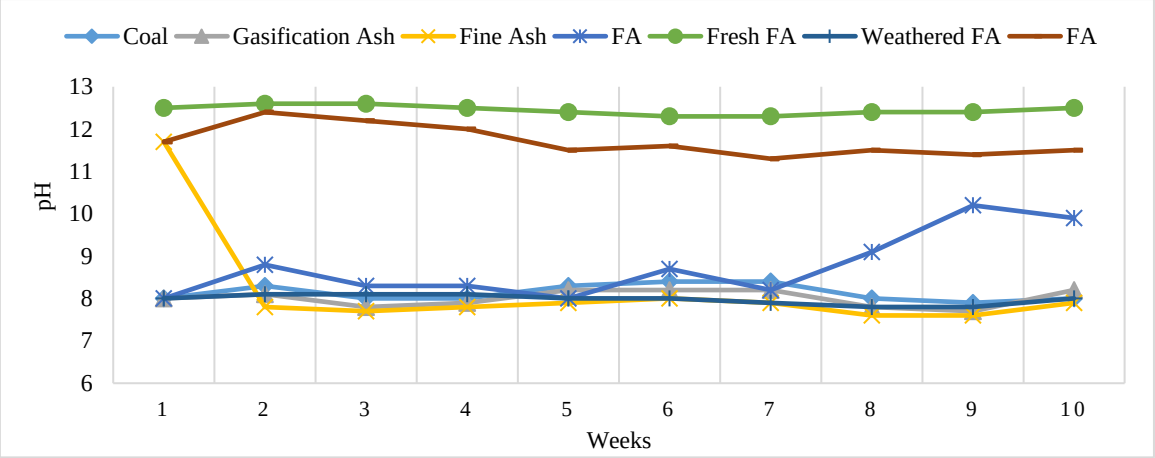

Figure 4-30: Humidity Cell Change in pH

4.2.8.1. Type

There was a significant difference found between the type of ashes [F(2, 59) = 7.095, p = 0.0017]. FA had a more alkaline pH than that of MA and CA (with a difference of 1.17 and 0.76, respectively). This can be seen from Figure 4.30 and Figure 4.31 in which fresh FA had the most alkaline pH in relation to the other ashes. Fresh FA and weathered MA had the greatest variation in pH.

4.2.8.2. State

There was a significant difference found between the state of the ashes [F(2, 59) = 12.549, p = 0.00078]. Fresh ashes have a higher pH than weathered ashes. There is a mean decrease in pH from 11.36 to 10.42. This occurs in both MA and FA. Similar findings were obtained by Eze et al. (2013) and Gitari et al. (2009). CA has a minimal pH change.

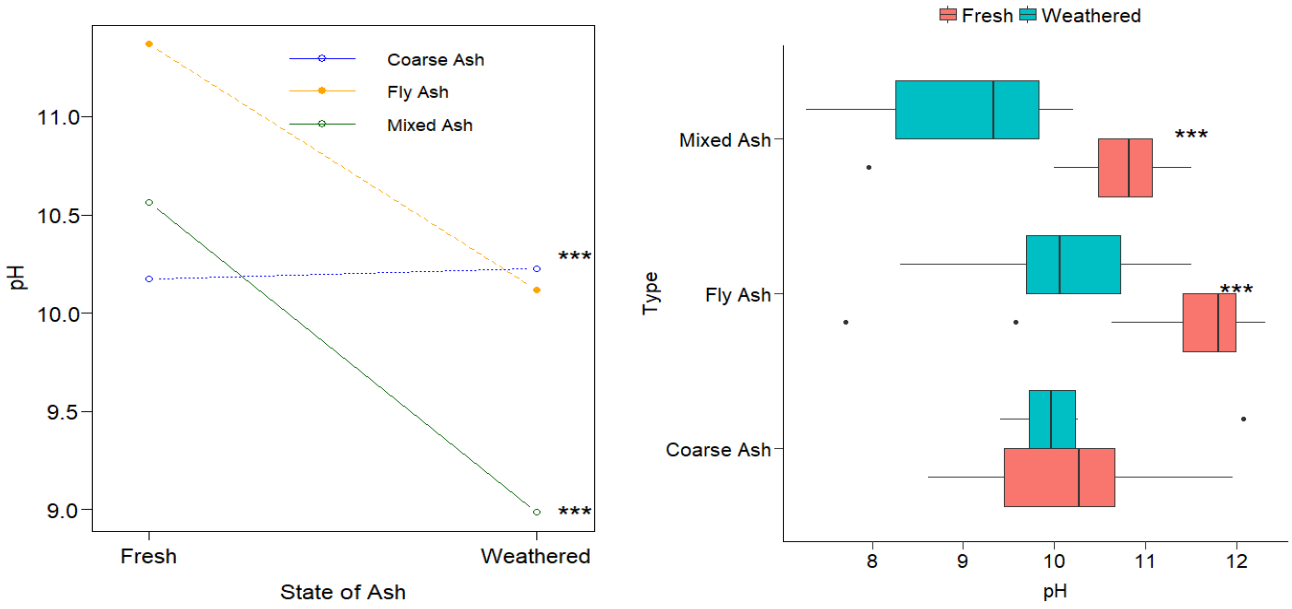

Figure 4-31: Interaction and Bar Plots showing pH Variation

From Figure 4.31, the pH decreases as the ash weathers in the case of FA and MA. The pH remains fairly constant in CA. The greatest pH decrease was by 1.58 units as shown in the case of MA. This phenomenon is experienced because MA also had the greatest decrease in the alkali content which is a major contributor to the pH. The ashes such as FA and MA still remain alkaline due to the presence of MgO and CaO increasing as these ashes weather. This is especially true due to the importance of carbonation reactions whereby on weathering the CO2 in the atmosphere reacts with the Ca hydroxides (which controls the alkalinity) and through the formation of calcium carbonates, the pH of the ash will typically decrease. Si does play a role in maintaining the alkali status of even weathered ash. It has been noted that in practical applications, it is difficult to vegetate fresh ash and once an ash dump has stood for several years, the natural process of vegetation starts as a result of the more favourable pH conditions for plant growth.

CA has an increase in CaO but a decrease in MgO, thus overall there is a negligible pH change. The pH of the solution is very important as it determines the surface charge of the coal ash, the degree of ionization and speciation of the elements in solution. This is important as the interactions between the charged ions in solution, as well as the surface of the ash particles, contribute to the release or adsorption of certain soluble solids such as toxic metals.

The high pH observed in the ashes above is due to the dissolution and hydrolysis of alkali earth and alkali earth metal oxides such as CaO, MgO and Na_2O_{eq}. Once these oxides have come into contact with water, they contribute greatly towards the alkalinity (Choi et al., 2002). Consequently, fresh FA had the highest CaO content thus confirming this may be the cause of the alkaline pH. The weathered ashes show a decrease in pH indicating that significant weathering has taken place as well as the loss of alkalinity. This decrease in pH is due to the conversion of calcium oxide to calcium carbonate following a reaction with carbon dioxide and water. It may also be attributed to contact with brine or atmospheric oxygen which ultimately leads to the dissolution of the alkaline earth metal oxides and leaching of calcium oxide. This could be a concern because as the ashes acidify, metal mobility can be expected. However, very low pHs favour metal mobility whereas the ashes under concern are alkaline.

4.2.8.3. pH Flowchart

The flowchart shown in Figure 4.32 represents general guidelines to be used when considering the use of CCPs with varying pHs. The following outlines the decision tree in Figure 4.32 –

- Low pH range (< 6) –

  Increased leaching is observed for magnesium and calcium ions at low pHs (Hosseini et al., 2011). This may be due to the competitive release of calcium ions (Ca^{+}) with the hydrogen ions (H^{+}) in solution, thus leading to the release of more calcium ions (Gitari et al., 2009). The dissolution of amorphous crystalline Al phases as well as quarts Si (SiO_2) also occur in this region. The solubility of trace metals is high at low pHs.

- Intermediate pH range (6-10) –

  The pH in this region is controlled by the dissolution of aluminosilicates. High Mg leachability is expected due to the dissolution of $Mg(OH)_2$ which is formed at higher pHs. Possible leaching of Al and Si could occur due to the amorphous $Al(OH)_3$ phase and $CaAl_2Si_4O_{12}.2H_2$, respectively. The lowest leaching of cations such as Ni, Cu, Zn, Cd, and Pb occurs in this region. Potential higher leaching of As could be observed in this region due to As being an oxyanionic species (Tiruta-Barna et al., 2006).

- High pH range (10-13) –

  Limited Mg solubility is due to the formation of $Mg(OH)_2$ which is stable at high pHs. Numerous studies have shown that at high pHs, the surface of the ashes becomes negative thus leading to the adsorption of the positively charged metal ions such as Pb, Ni, and Cu from solution (Cho et al., 2005; Steenari et al., 1999). Highly alkaline pH facilitates this uptake. However, ashes with pHs greater than 11.5 are considered hazardous.

  The release of inorganic soluble salts such as Na, K, Cl, and Br is independent of pH.

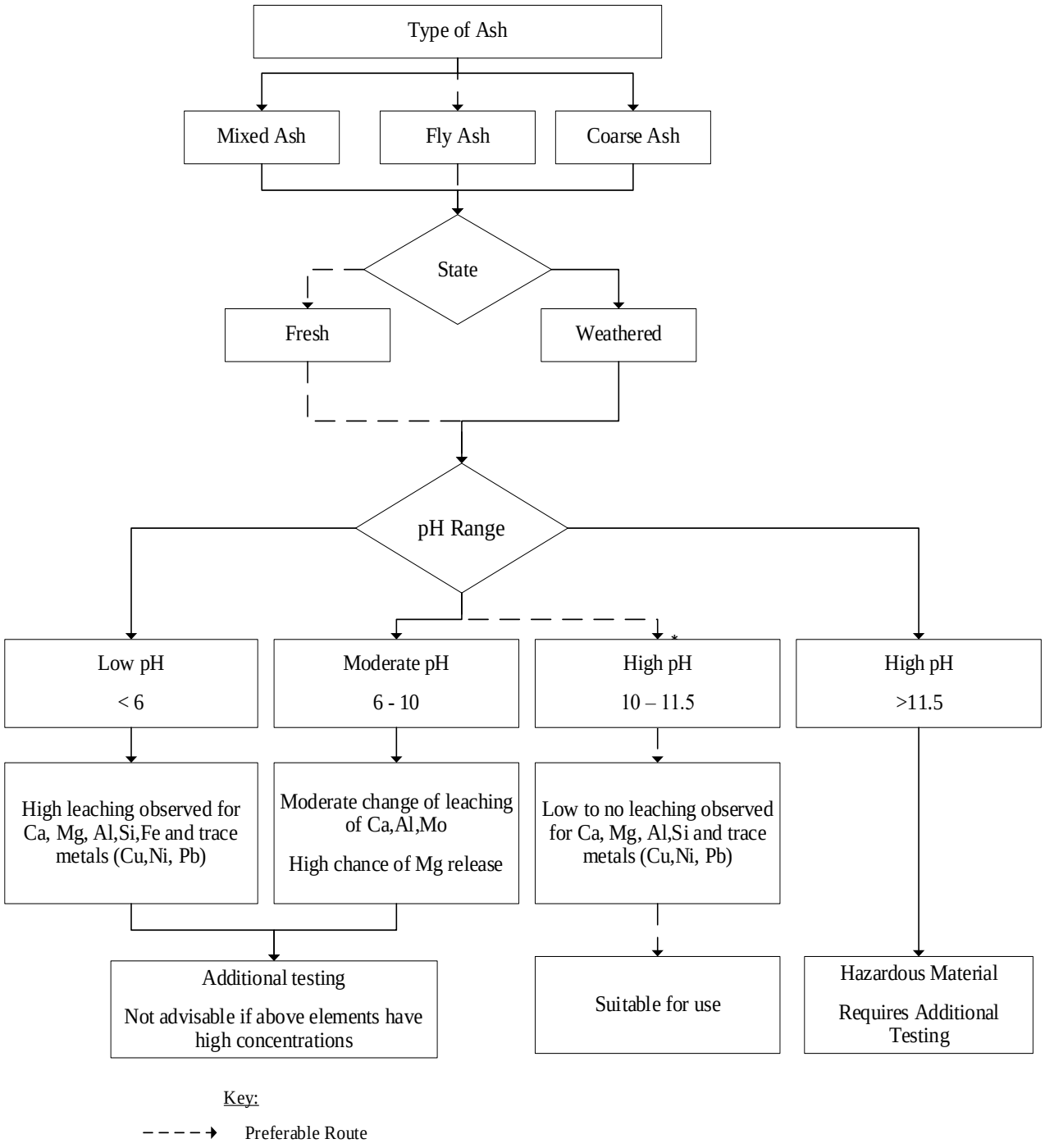

Figure 4-32: pH Decision Flowchart

4.2.9. Total Dissolved Solids (TDS)

The total dissolved solids (TDS) provides an indication of the release and entrapment of various elements during weathering (Eze et al., 2013). TDS refers to the TDS in the ash leachate. Statistical analysis showed that the TDS of ash leachate differed between the different ash type [F(2, 46) = 10.439, p = 0.00018]. There was a large difference in the ash leachate TDS between FA and the other ashes with FA having the highest TDS in relation to CA and MA. FA also showed the greatest decrease in TDS following weathering.

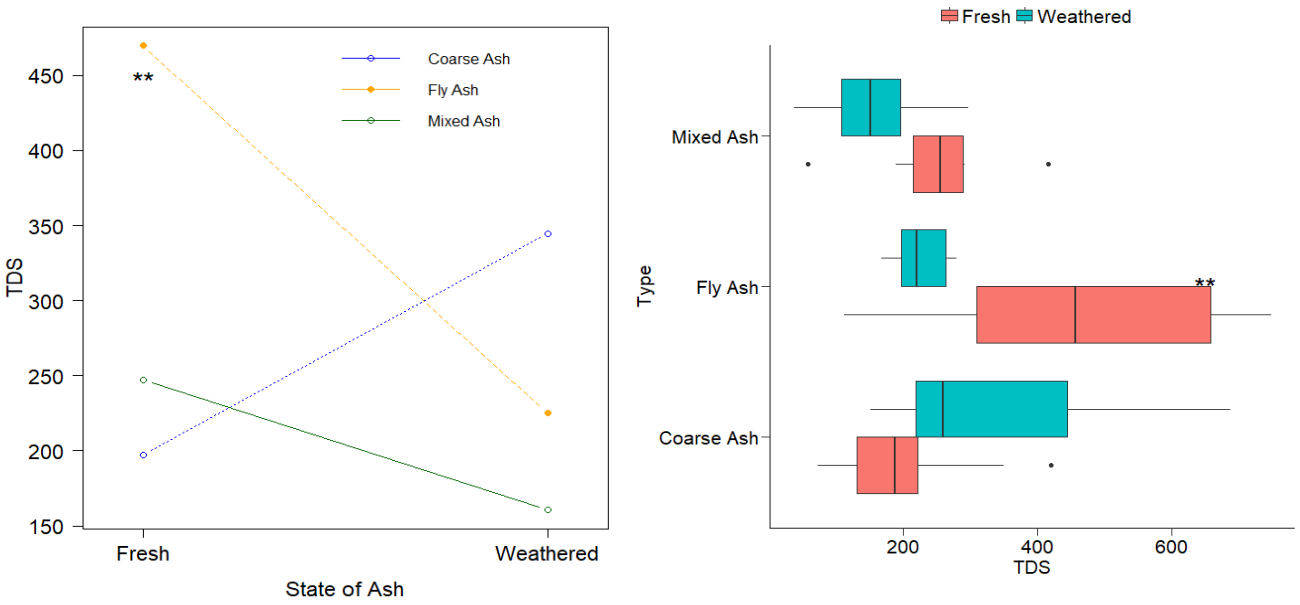

Figure 4-33: Interaction and Bar Plot of TDS

From Figure 4.33, the TDS decreases as chemical weathering progresses. This decrease shows that leaching has occurred and that these ashes have poor salt sinking capabilities. Similarly, Figure 4.34 shows that the ash leachate TDS progressively decreases until a plateau is reached at approximately 7 weeks.

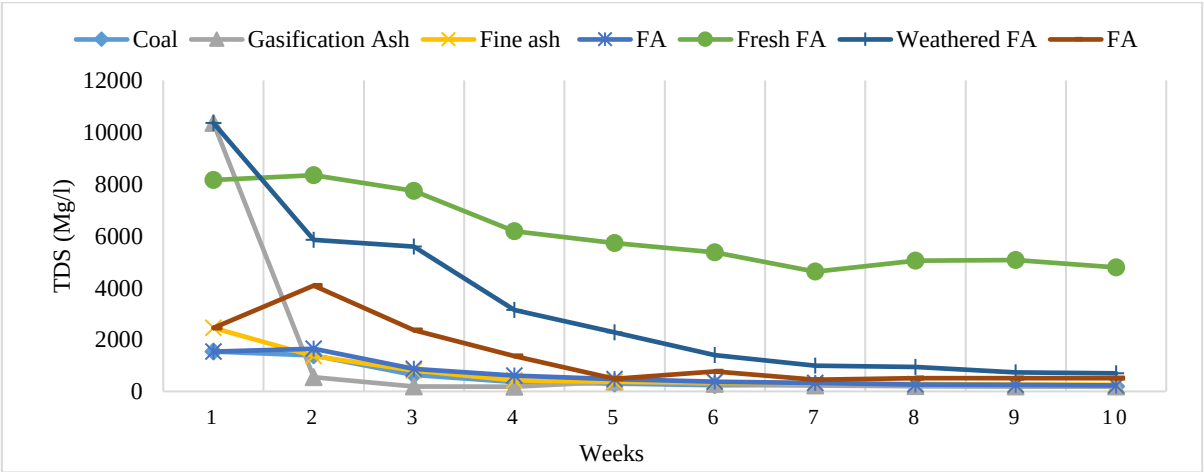

Figure 4-34: Total Dissolved Solids change following Weathering in Humidity Cell Test

4.2.10. Electrical Conductivity

The electrical conductivity (EC) is a measure of the quantity of ions present. The change in EC is shown below in Figure 4.35. The change followed a similar trend to that of the TDS. A high initial EC indicates that the ashes have high contents of soluble ion species and over time this decreases due to leaching and loss of ionic species (Bhattacharyya et al., 2009).

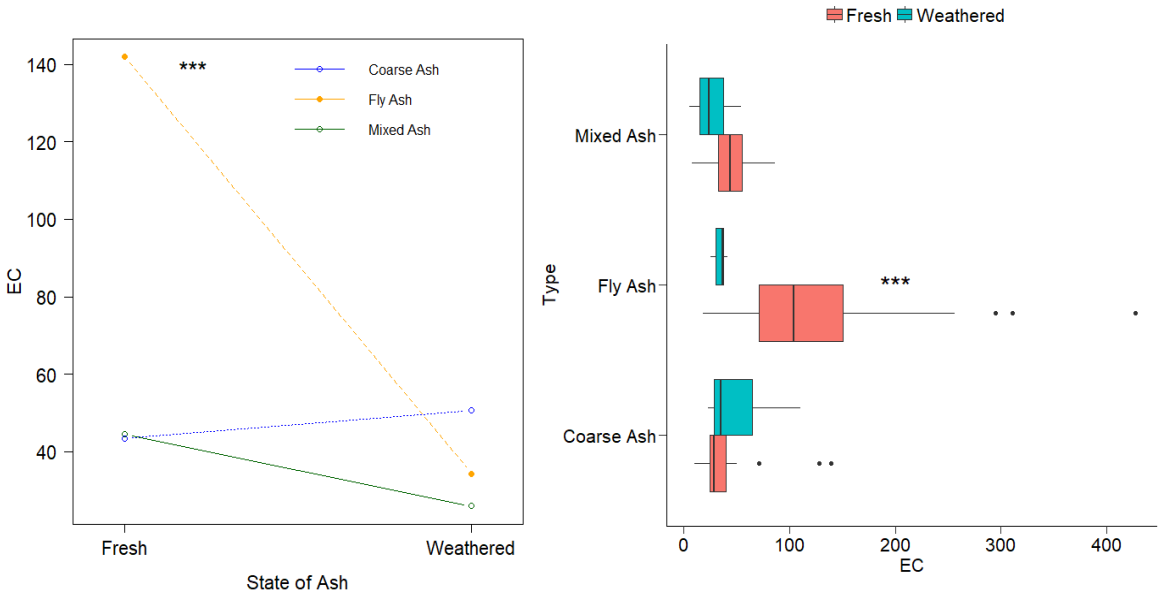

Figure 4-35: Interaction and Bar Plot of EC

Statistical analysis showed that the EC had a significant difference between the different ash types [$F(2, 61) = 12.75$, $p = 2.36\times10^{-5}$]. There was a similar difference as that with TDS as FA has the greatest content and decrease in the leachate EC after weathering in comparison to the other ashes. This is expected as there is a correlation between EC and TDS specifically within the neutral pH range. The high EC observed in the leachate of the ashes above signifies the release of more soluble ion species from these ashes into the solution while the lower values signify that smaller amounts of ions are released into solution. The decrease in all ash types indicates a loss of ionic species following weathering. This may be a result of leaching.

Similarly, to the decrease in TDS and EC, the fluoride concentration decreased indicating surface wash of and removal of the more ionisable species. This is shown in Figure 4.37.

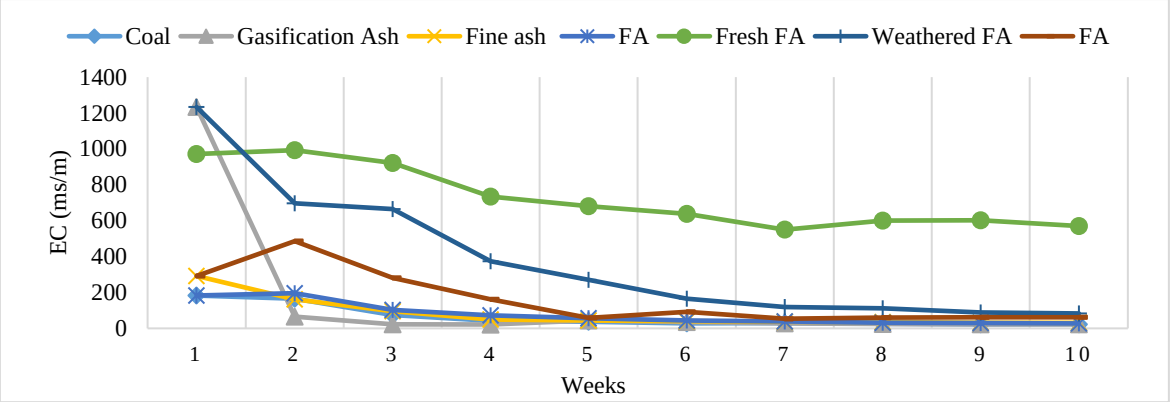

Figure 4-36: Electrical Conductivity change following Weathering in Humidity Cell Test

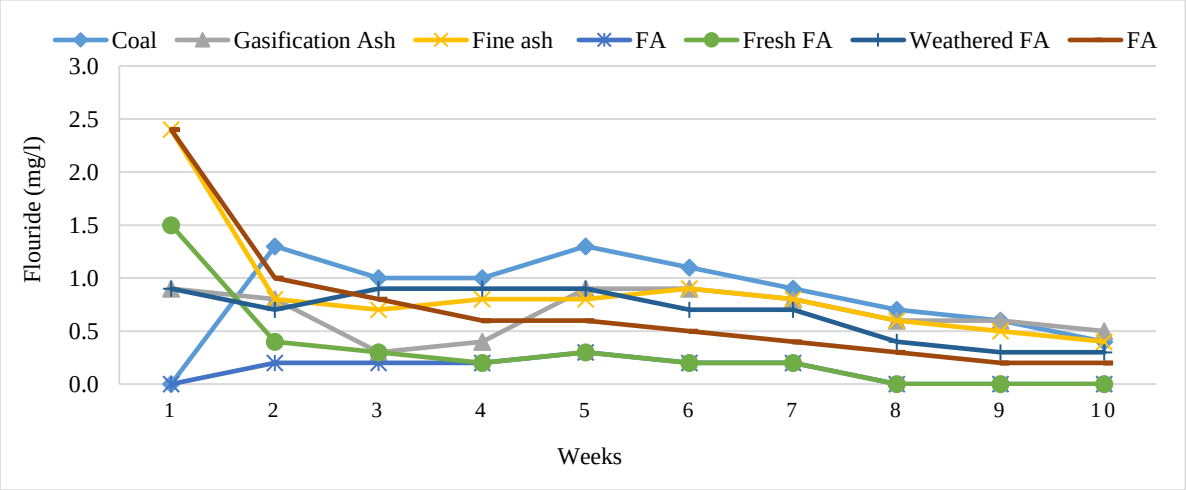

Figure 4-37: Fluoride change following Weathering in Humidity Cell Test

4.2.11. Discussion and Conclusion

Following the statistical analysis, it can be said that the finer FA and MA particles (which contain a significant amount of FA) are richer in the glassy phase and are more reactive than the CA particles, which are richer in unburnt carbon (Chancey et al., 2010). This may be why the CA appears to have higher total concentrations in comparison to FA and MA following weathering as the latter ashes are more reactive. Alternatively, this higher total concentration in the weathered phase may be due to the rapid loss of major compounds such as Si and Ca, thus making it appear as if the total element concentration increased in the weathered state. Furthermore, it can be deduced that a large amount of metals and elements are locked within the glassy matrix of the ashes and are only released upon long term chemical weathering (Gitari et al., 2009). This is seen in the case of As, Sb, Ge, Rb, Ce, and Li. This is also seen in the release of Si, Fe, and K whereby a relationship of a higher leachable fraction was observed as the total concentration increased. This was only the case

in the weathered ashes. Generally, a relatively small difference is found regarding element mobility between fresh and weathered ashes. This suggests that equilibrium has been reached between the ash particles and the surrounding water and once the readily available and easily leached elements are removed, the system remains stable with time (Ward et al., 2009). This provides positive results for the use of these ashes in the CPB as element release is low.

In some instances, the elemental release is independent of the state and type of ash. This is observed in the results of Sn, Te, TI, Pb, Bi and Be. On the other hand, elements that were located on the more soluble internal fraction of the ashes include B, Ga, and Sr. These elements are more easily released in fresh ashes in comparison to the weathered ashes. Overall, it has been stated that pH is the ultimate controlling factor determining elemental and metal release with acidic conditions favouring high metal mobility. Since the ashes under consideration were alkaline, a low mobility is seen. Recommendations going further would be to examine the release in acidic conditions using the acid neutralization capacity tests.

Based on the literature review conducted, the following summarises the important compounds and elements which may have an effect on backfilling as well as proposed guidelines on the type of CCPs to be used –

- Class F ashes
- Silicon dioxide: SiO_2 should be greater than 51%
- Calcium oxide: CaO should be limited to less than 10%
- Alkalis (Sodium and potassium oxide): Na_2O_{eq} <1.5% and the alkalis present in concrete need to be <0.6%
- Magnesium oxide: MgO <5%
- Transition metals: Should be limited below TCT0 and LCT0 set out by SANS10234
- LOI: Should be below 6%.

The typical elemental concentration range and the leachability ranges for each element in the CCPs analysed are summarized in Table 4.13 and Table 4.14, respectively.

Table 4-13: Total Element Concentration Ranges in CCPs

Range of Total Concentration (mg/kg)	Element
<0.001	Au
<0.01	Cd, Ir, Pt
<0.1	Hg, Ho, Te, TI
<1	Ag, Sb, Se
<10	As, Be, Bi, Cs, Ge, La, Mo, Nd, Rb, Sc, Sn, Ta, Th, U, W, Y
<30	Co, Hf, Ce, Ga
<50	Nb, Cu, Pb, Zn
<100	B, Li, V
<200	Cr
<400	Mn, Zr
<1200	Ba, Sr

Table 4-14: Element Leachable Fraction Ranges in CCPs

Range of Leachable Fraction (mg/l)	Element
~0.00001	Au, Be, Bi, Hf, Ho, Ir, Nb, Pt, Ta, Te, Th, TI, U, Y
~0.0001	Ag, Cd, Nd
~0.001	Ce, Co, Cs, Hg, Ni, Pb, Sb, Sc, Sn, Zr
~0.01	As, Cu, Ga, Ge, Mn, Zn
~0.1	Rb, W
~5	Cr, Mo, Y
~10	B, Ba, Li, Sr

4.3. Experimental Analysis Results

The following section is presented as a paper that has been sent for submission to The International Journal of Technological Innovation, Entrepreneurship, and Technology Management. The paper presented is entitled "Structural and Environmental Properties of Coal Combustion Products in Cemented Paste Backfill Applications". I request the reader's indulgence and understanding when reading this chapter as there are some areas that have a certain degree of overlap with previous sections. These include the background and literature review as well as the methodology section (Section 3.3) which outlines the experimental procedure as well as the accompanying figures and tables. Additionally, there are some areas that reiterate the findings stated elsewhere in this thesis.

The experimental methodology and analysis presented in this section were formulated based on the results of the previous section (Section 4.2). The previous section provided various guidelines to be followed when using CCPs in CPB applications and this chapter aimed to test the practicality of these guidelines. Chapter 5 will provide a detailed comparison of the theoretical and practical implications of using CCPs in the CPB by comparing the guidelines in Section 4.2 to the results found in Section 4.3. Furthermore, based on the finding of the previous chapter whereby metal mobility was largely dependent on pH, this chapter aimed to further examine this relationship.

4.3.1. Abstract

In this study, the environmental and structural properties of fly ash (FA), coarse ash (CA) and brine used in cemented paste backfill (CPB) mixtures were investigated. Varying mass percentages of FA and CA (68%), brine (32%) and a hydraulic binder (5%) were used to construct a CPB whereby the net environmental benefit (NEB) was investigated. The NEB was used to examine the environmental impact on the groundwater and surrounding environment of the current surface ash disposal methods of FA, CA, and brine in comparison to that of a CPB operation. The aim was to assess the current environmental concerns associated with backfilling mine voids with these wastes whilst ensuring the structural properties of the CPB were met. The unconfined compressive strength (UCS) showed that CPB mixtures containing greater proportions of FA met the required strength limits, however, particle size and loss on ignition (LOI) determined the extent to which reaction hydration products were produced and subsequent strength development. This study further

investigated the leaching behaviour of toxins such as Pb, As, Cr and Ni as well as other ionic species associated with soluble salts such as Ca, Na, Mg, K, Fe, Al, B, and Ba. Leaching tests were conducted on different CPB mixtures under alkaline and acidic conditions in order to assess the effect of pH on the leachability. Results showed that leaching increased linearly as the pH of the leachant decreased for Ca, Mg and B. Leaching is found to be independent of solution pH for Na, K, and Ba. Cr and Pb exhibited amphoteric behaviour with higher solubility observed at the extreme ends of the pH range. Results from the tank leach test (TLT) used to simulate flooding showed that the concentrations of soluble salts in the leachate were in the order of Na > Ca > K > Mg. A large fraction of these soluble salts is available as the salts are deposited on the surface of the monoliths and thus a high release was observed initially upon contact with water. Results showed that the CPB posed a significantly lower environmental risk in comparison to surface ash disposal. The leachates contained a lower amount of soluble salts and toxic trace metals in comparison to the weathering cell tests. This indicates that these elements are encapsulated within the CPB. Particle size and exposed surface area have the greatest effect on the leaching behaviour. The addition of small proportions of CA reduces leachability as a lower elemental release is seen for Na, Mg, K, and Ba in comparison to the CPB containing only FA. By physically and chemically altering the FA, CA and brine interaction a more environmentally suitable option exists for the co-disposal of these wastes through the development of a CPB. The graphical abstract is shown in Figure 4.38.

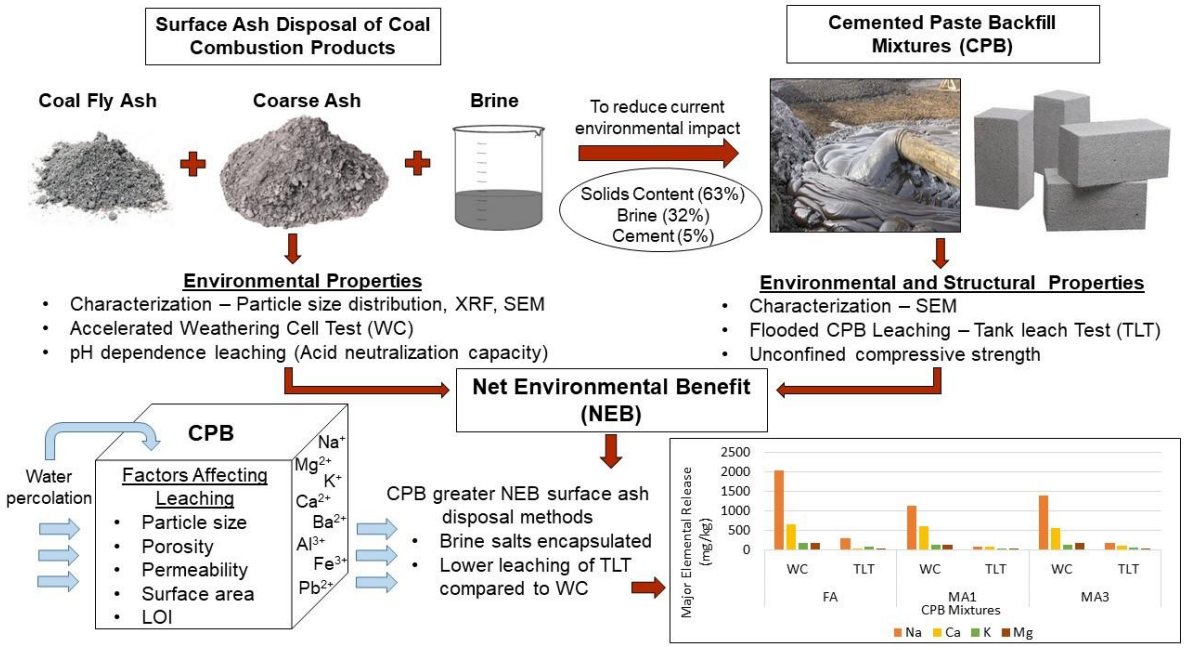

Figure 4-38: Graphical Abstract

4.3.2. Introduction

Large scale coal-based power generation began in the early 1920s resulting in the global production of millions of tons of coal combustion products (CCPs) such as fly ash (FA) and coarse ash (CA) along with other by-products such as boiler slag and flue gas (Ahmaruzzaman, 2010). Worldwide coal FA production is estimated at 300 million tons per annum whereas, in South Africa alone, an excess of 25 million tons of FA is produced annually with only 5% being productively used in the cement industry (Petrik et al., 2005). The large majority of ash is often placed temporarily in stockpiles or dumped in landfill sites, ash dams or lagoons and left to undergo chemical weathering (Gitari et al., 2009). Most often FA and CA are dumped together in varying proportions which is termed mixed ash (MA). This creates vast amounts of ash dams which cause numerous short and long term environmental problems such as the risk of toxic trace metal leaching which can contaminate the surrounding soil, groundwater and surface water (Dutta et al., 2009; Izquierdo and Querol, 2012).

Mining operations also produce other wastes such as brine. Brine is water or liquor with over 2% salinity containing predominately inorganic dissolved salts such as Na, Mg, Cl, K, SO_4 and other trace metals such as Pb, Cu, and Cr (Fatoba et al., 2015). Brine is formed from coal utilizing technologies such as gasification and combustion processes which create large amounts of wastewater that require further treatment. In an attempt to treat, recover and reuse this water, wastewater treatment methods produce a stream highly concentrated with salts. It is estimated that for every $1m^3$ of desalinated water, an equivalent amount of brine is produced (Petrik et al., 2015). This brine is often co-disposed with FA and CA. The need for brine usage is also becoming increasingly prevalent as the minimization of industrial wastewater, through its treatment, reuse, or safe re-entry into the surrounding environment is a critical part of water management and integral in tackling water scarcity issues. The co-disposal of brine and ash can negatively impact the environment as both these wastes contain significant amounts of salts and toxic elements which have the potential to leach into the surrounding environment. The risk is greater whereby the infiltration of rain water into the ash dumps creates an environment favourable for leaching (Nyale et al., 2014). As a result, effective waste management plans which are environmentally sustainable are required for FA, CA and brine disposal to prevent the number of already existing ash dams

from increasing as well as minimizing the growing environmental concern associated with these wastes.

Cemented paste backfilling is found to be one such method to combat the environmental problems posed by CCPs and brine. Backfilling is defined as the process whereby mine tailings and other mine wastes are placed or reinserted into the void openings of underground mines (Rong et al., 2017). The CPB is comprised of a mixture of mine tailings or coal gangue, hydraulic binders (4-7%) such as ordinary Portland cement (OPC) and water (25%), which may consist of mine processed water or brine. Mine backfilling is advantageous in industry as it has the potential to reduce the current environmental impact of the existing mine sites (Ke et al., 2015). This is done through minimizing water leaching into the mine voids thus preventing further generation of acid mine drainage (AMD) (Murarka and Erickson, 2006). Furthermore, it is an effective way to process and dispose of mining waste such as CCPs and brine.

The paste backfilling operation is further justified if a net environmental benefit (NEB) is achieved. The NEB is defined as the difference between the environmental risks of the current utilization of the CCPs and mine disposal processes in comparison to the environmental risks of the CCPs when implemented in a backfilling operation. Hence, the total environmental risk of the backfilling operation needs to be less than that of a surface ash disposal facility in order for a NEB to be achieved. The concept of a NEB is further investigated in this study to prove the benefits of backfilling in comparison to ash surface disposal. This will be done through leaching tests on the CCPs prior to implementation as well as the constructed CPB to critically examine differences in the environmental impact.

There are various interactions that occur between the CPB and the surrounding water system and leaching occurs as a result of precipitation/dissolution, complex formation, adsorption/desorption, and redox reactions. These are all factors which control the mobilization of major and minor elements in the solution. Additionally, the physical factors of the ashes such as the size, shape, porosity, origin, combustion temperature and mineral phases are equally important in predicting the leachability (Quina et al., 2009). It has been identified that the major leaching processes that occur which influence element mobility are neutralization and chemical weathering (Gitari et al., 2009; Krebs et al., 1988). Element mobility is also largely dependent on pH (Dutta et al., 2009). The addition of hydraulic binders such as OPC to the CPB is said to increase the strength, durability, and the overall

acid neutralization potential. Studies conducted by Benzaazoua et al. (2004) have shown that cementation can enhance contaminant stabilization within the matrix of the CPB. Solidification of the CPB reduces permeability thus minimising the production of secondary minerals and resultant leachability (Paria and Yuet, 2006). These metals become encapsulated in the solidified CPB due to the hydration and calcination reaction products. A few researchers investigated the environmental impacts of the CPB when placed in underground mine voids. These studies examined the metal release, neutralization capacity, the effect of different binder types and ash content (Hamberg et al., 2018; Jiao et al., 2011; Qi et al., 2015; Tikou and Benzaazoua, 2007). Other studies focused on the physical and chemical properties of the mine tailings and ash in relation to the CPB performance properties (Belem et al., 2002; Fall et al., 2005; Kesimal et al., 2004b). Other studies found that the addition of FA to the CPB could lower the leachability of some elements in comparison to the cement only backfills (Kadir et al., 2016; Kamali et al., 2008; Yao and Sun, 2012). The disposal of CCP's in CPB could have adverse effects on the receiving environment if the pH is not closely monitored as pH is the greatest controlling factor of element mobility. Despite the unique findings from these studies, there are still significant uncertainties concerning the environmental impacts of the CPB with regards to the use of FA, CA, and brine. Limited research exists which examines both the conditions prior to and following CPB implementation as well as the use of a combination of FA and CA coupled with brine. This study aims to close this research gap and potentially minimize the current environmental impact of FA, CA and brine whilst minimizing binder content and maximizing the amount of ash used.

As a result, the leaching and acid neutralization tests implemented in this study will aim to simulate actual environmental conditions in order to determine the reactivity and leaching characteristics of the ashes prior to use, after the construction of the CPB as well as when exposed to different pHs. The tank leach test (TLT) is suitable for examining the response of the CPB to flooded conditions whereas accelerated ash weathering is used to simulate the elemental release of the current ash disposal methods. Comparison between the two leaching methods will determine if FA and CA co-disposed of with brine are capable of trapping and encapsulating the metal species and soluble salts over time. Structural properties such as the unconfined compressive strength (UCS) are evaluated in order to determine the suitability and properties of the different CPB mixtures.

4.3.3. Materials and Methods

4.3.3.1. Coal Combustion Products

The CCPs utilized in this study were fly ash (FA), coarse ash (CA), DuraPozz and PozzFill. DuraPozz is a classified FA which is characterized by its very fine particle size. PozzFill is an unclassified ash product produced from pulverized fuel ash. PozzFill and DuraPozz were obtained from Lafarge in South Africa and were used in strength determination. PozzFill and DuraPozz contain a unique particle size distribution and chemical composition which enables these ashes to significantly improve the structural properties of cement or the CPB when added to a concrete mix in conjunction with a cementitious binder. Two FA and CA ash samples produced from two different coal-fired power utilities operated in South Africa were used. The ashes were kept in sealed plastic containers to prevent the ingress of air and stored at room temperature until needed. The particle size distribution (PSD) of all the ashes were determined using a Malvern particle size analyzer 2000. LOI determination was done by placing the ashes in a furnace at 950°C for two hours and measuring the mass loss upon ignition. The bulk ash was analysed using X-ray fluorescence (XRF) using a Philips 2404 Wavelength Dispersive spectrometer fitted with an Rh tube. The morphology of the ash samples and the CPB mixtures were determined using scanning electron microscopy (SEM). The energy dispersion spectroscopy (EDS) analysis was done on some spots for qualitative elemental composition.

4.3.3.2. Brine

Brine was synthetically produced in order to simulate the actual brine compositions produced from a typical reverse osmosis desalination plant. The brine was synthesized with high concentrations of the major species such as Na, Cl, and SO_4 with smaller proportions of Ca and Mg. An average of typical brine compositions was used to prepare the brine which was then characterized using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The ICP-OES was conducted using a Spectro Arcos whereas the ICP-MS was conducted using a PerkinElmer NexION300X. The brine was stored in a sealed plastic container at ambient temperature until further use.

4.3.3.3. Cemented Paste Backfill Sample Preparation

The desire solids content of 68% and liquid content of 32% was chosen based on a study conducted by Mahlaba and Pretorius (2006). The study found this to be the most suitable mix design of those investigated and, in this range, the CPB remains a non-segregating paste regardless of the brine composition. The materials used to construct the CPB include FA, CA, brine and ordinary Portland cement (OPC). Table 4.15 shows the mix design and relative weight dosages as approximate mass percentages. A water to cement ratio (w/cm) of 0.5 was maintained for all mix designs. All mix designs were created from a single batch for consistency. Samples 7 and 8 were constructed for unconfined compressive strength (UCS) testing only.

Table 4-15: Paste Backfill Mix Design

#	Sample Name	OPC (%)	Fly ash (%)	Coarse Ash (%)	Solids content (%)	Brine (%)
1	FA	5	63	0	68	32
2	MA1	5	31.5	31.5	68	32
3	MA2	5	42	21	68	32
4	MA3	5	21	42	68	32
5	MA4	5	50	13	68	32
6	CA	5	0	63	68	32
7	PozzFill	5	63	0	68	32
8	DuraPozz	5	63	0	68	32

The solids (FA, CA and OPC) were first mixed to ensure a homogeneous uniform powder was attained. This is because the setting of cement is fairly prompt. The brine was then added to the solids and mixed until a non-segregating paste was formed. After the desired paste consistency was reached, the paste was manually poured into moulds. After filling the moulds, the mixture was placed on a vibrating table to remove any air bubbles.

4.3.3.4. Unconfined Compressive Strength (UCS)

The CPB paste was poured into cube moulds of 100 mm x 100 mm x 100 mm. After demoulding the monoliths, the samples were allowed to cure for 14, 28 and 52 days in a water bath maintained at 25°C. Following the curing of the CPB at the specified time period,

the mechanical property of the CPB was evaluated using the unconfined compressive strength testing (UCS). The UCS was done using a mechanical cube press foot test with a loading rate of 10kN/min. This was in accordance with the American Society for Testing and Materials (ASTM), ASTM C109/ C109M-16a standard method of testing. To ensure the validity of the measurement, each test was performed in triplicate and an average result recorded.

4.3.3.5. Leaching Tests

The leaching tests presented in this paper evaluate the behaviour of major and minor species such as Na, Mg, K, Fe, B, Al, Ca, Cr, Ni, As, Ba and Pb in CPB equilibrium as well as dynamic conditions (mass transfer based leaching tests). These tests were selected in order to simulate actual scenarios that would provide realistic leachable estimates on the long term ash matrix interaction. This would allow a critical comparison of the environmental impact of both utilization methods in order to determine if the CPB has a NEB. This will provide further information about the chemical stability of the compounds in the ashes in relation to the CPB. According to Hyks et al. (2009), the elemental release will be mainly availability controlled, solubility controlled or complexation/sorption controlled.

4.3.3.5.1. Tank Leaching Test

The semi-dynamic tank leaching test (TLT) was conducted to simulate flooded CPB mixtures. This test was conducted in accordance with the USP EPA Method 1315. This method evaluates the continuous leaching of a water saturated monolithic material by the use of an eluent filled tank that is periodically renewed with a leaching solution such as deionized water. Both the monolith and vessel dimensions are specified so that a specific liquid to area (L/A) ratio of 10 can be maintained (10 cm^3 solution/cm^2 of exposed solid). Monoliths were cast in cylindrical moulds with a height of 6cm and diameter of 6.5cm. Samples were placed on plastic support to ensure the leaching of the monolith on all faces (at least 2 cm on each side). Duplicates were used for each CPB mixture so a total of 8 monoliths were leached under the same conditions (FA, MA1, MA3, and MA4). The leaching solution was renewed at nine predetermined intervals of 2h, 1 day, 2 days, 7 days, 14 days, 28 days, 42 days, 49 days and 63 days from the start of the test. Prior to sample collection, the leachate was stirred manually. The pH, EC, and TDS were measured for each renewal interval and samples were collected, filtered (< 0.45 µm) and acidified for elemental

composition analysis by flame Atomic Adsorption Spectroscopy (AAS) analysis. The elemental mass transfer from the CPB was calculated using Eq. 4.2 –

$$M_{ti} = \frac{C_i \times V_i}{A} \quad \text{(Eq. 4.2)}$$

Where M_{ti} is the elemental mass released during the leaching interval *i* (mg/m^2), C_i is the elemental concentration in the leachate during interval *i* (mg/l), V_i is the leachate volume (L) and A is the surface area exposed to the leachate (m^2).

4.3.3.5.2. Weathering Cell Test

The weathering cell test is conducted to simulate the accelerate weathering of the CCPs. This test is a simplified version of the commonly used humidity cell test specified by ASTM D5744-96. This test aims to accelerate the weathering process of the CPB in order to evaluate the reactivity and long term environmental performance. Cruz et al. (2001) proposed this adapted test method as it requires less material. Approximately 70 g of the crushed CPB mixture is placed on a filter paper in a Büchner-type funnel and exposed to weekly leaching cycles. These cycles include of one day leaching, three days of ambient air exposure, another day of leaching and lastly two days of air exposure. Leaching was performed by immersing the crushed sample in 50 ml of deionized water and stirring for 2 hours. The leachates were removed by vacuum filtration and tested for pH, EC, and TDS. Samples were then acidified and stored for AAS analysis. Each crushed CPB sample was duplicated so that a total of 10 CPB weathering tests were conducted (FA, MA1, MA2, MA3, and CA). Approximately 10 cycles were performed to reach a pseudo steady state. Results are presented as the leached concentration per mass of solid material (mg/kg) as shown in Eq. 4.3.

$$C_c = \frac{\sum(C_i \times V_i)}{S} \quad \text{(Eq. 4.3)}$$

Where C_c is the cumulative leached amount (mg/kg), C_i is the elemental concentration in the leachate during interval *i* (mg/l), V_i is the leachate volume (L) and S is the sample weight (kg). The TLT and weathering cell tests can be effectively compared by using the liquid to solid (L/S) ratio (Volume of liquid in contact with a dry solid material). The leachate concentrations (mg/l) are multiplied with the defined L/S or L/A ratio of the test which

results in the mass released per a kilogram of solid (mg/kg). This ensures proper comparison of results obtained for the same material during different leaching experiments.

4.3.3.5.3. Acid Neutralizing Capacity (ANC)

The acid neutralization capacity (ANC) is an important parameter used to estimate the buffering capacity of the CCPs and CPB mixtures as it provides information on further utilization of FA and CA. This can be used to predict the long-term behaviour of the CPB mixtures since precipitation/dissolution of metals is directly affected by the buffering capacity. The ANC of the CCPs can be used to predicate the reactivity with acids and to determine the leaching characteristics as a result of changes in pH (Yan et al., 2000). Since leachability is pH-dependent, the ANC will provide an indication of the leaching resistance of the CPB mixtures as the ability to neutralize acids will allow prediction of which species are able to accept and neutralize protons.

This method is divided into two stages as set out by the European standard method prEN14429. Firstly, a preliminary test to evaluate the acid consumption was performed to determine the amount of acid addition required to attain nine different endpoint pH values. These pH values range between 3 and 11 as a pH of 11 is typically that of the natural FA and CA. In this pH range, most of the cementitious phases are dissolved (Coussy et al., 2011). The test was carried out by placing 15 g of each crushed CPB sample in rinsed polyethylene bottles with 135 ml of deionized water to attain a L/S of 9. After stirring for a period of 1h, pre-determined amounts of 2.5 M nitric acid (HNO_3) were added to each bottle and stirred. The pH was measured and adjusted with more HNO_3 if necessary to attain the desired endpoint pH. A final L/S ratio of 10 was reached following acid addition. The total amount of HNO_3 added to attain the required pHs was recorded and used to construct a titration curve. The main ANC test was carried out using the titration curve to prepare 150ml acid solutions of different pHs. The test involved using nine batches of each sample containing 15 g of ground CPB samples placed in 250 ml polyethylene bottles. Each bottle was filled with 150 ml of nitric acid solution to attain a pH between 3 and 11 and stirred for a period of 8 days in order to reach equilibrium. A L/S ratio of 10 was maintained. The pH, EC, and TDS of the leachates were measured followed by ICP-MS and ICP-OES analysis after filtration using a 0.45 µm pore membrane filter and acidification. The ANC test was

conducted in duplicate thus a total of 18 ANC tests were conducted for five different CPB samples (FA, MA1, MA2, MA3, and CA).

4.3.4. Results and Discussion

The results of the characterization of the CCPs and brine are presented first followed by the UCS of the CPB as the mineralogy is used to examine the structural behaviour. The dynamic test results of the TLT and weathering cell test is presented followed by a comparison of the two test methods. The ANC test results are then presented which further elaborates on compound stability.

4.3.4.1. Chemical and Physical Characterization of CCPs and Brine

The characterization of CCPs and the brine is especially important as the chemical and physical properties have an effect on the environmental and structural suitability when implemented in backfill applications. The compositions of the synthetic and real brine on which it was modelled are given Table 4.16.

Table 4-16: Brine Compositions

Composition (mg/l)	This Study	(Fatoba et al., 2015)	(Muriithi et al., 2014)	(Sonqishe, 2008)	(Fatoba, 2010)
Na	2988	4475	3355	4719	4805
Mg	108	75.4	112	198	163
K	8.68	56.4	78.8	115	106
Fe	7.01	0.043	0.068	3.3	0.24
B	0.81	1.39	0.154	1.6	2.24
Al	1.47	0.016	0.023	2.8	0.045
Ca	105	101	210	112	107
Cr	0.009	0.0063	0.023	0.4	0.014
Ni	0.011	0.057	2.5	0.4	0.12
As	0.013	0.0036	0.076	BDL	0.0068
Ba	0.090	0.029	0.15	0.1	0.057
Pb	0.007	0.0009	1.6	0.1	0.0039
pH	11.83	7.75	8.48	7.8	7.75
EC (mS/cm)	12.39	16.69	-	15.83	17.19
TDS (g/l)	6.07	8.35	-	7.92	5.40

The chemical composition of the CCPs obtained from XRF analysis is given in Table 4.17. All ashes contained high concentrations of major oxides such as SiO_2, Al_2O_3, Fe_2O_3, and CaO. The concentration of these constituents varied between FA and CA with FA having a higher concentration of all major oxides. This is an important contributor to the alkalinity of the ash. All CCPs were classified as Class F ashes according to the ASTM C618 standard classification. Due to the high LOI of FA1 and CA1 ashes, these ashes were not analysed in further tests. A high LOI is found to reduce the effectiveness of the CPB as this increases the water demand and reduces workability (Abubakar and Baharudin, 2012; Wang et al., 2009). Workability tests, which include the slump and bleed test showed that these ashes exhibited poor workability and thus were not used in further analysis as these were undesirable characteristics of the CPB. FA and CA were used to construct the CPB mixtures discussed further in this study.

Table 4-17: Chemical Composition of CCPs

	FA	FA1	CA	CA1	PozzFill	DuraPozz
SiO_2	59,44	34,41	41,34	42,4	55,26	55,22
Al_2O_3	26,66	17,51	16,51	17,73	31,91	31,86
Fe_2O_3	7,35	2,09	5,96	4,28	3,86	3,27
MnO	0,09	0,02	0,07	0,04	0,04	0,04
MgO	0,85	0,67	0,48	0,93	1,13	1,12
CaO	2,79	2,56	1,58	4,00	4,34	3,88
Na_2O	0,06	0,07	0,07	0,08	0,2	0,27
K_2O	0,78	0,3	0,49	0,34	0,65	0,73
TiO_2	1,24	1,01	0,75	1,06	1,62	1,66
P_2O_5	0,39	0,23	0,16	0,32	0,40	0,42
Cr_2O_3	0,02	0,03	0,01	0,06	0,05	0,05
NiO	0,01	0,01	0,00	0,01	0,01	0,01
LOI	0,37	42,00	33,00	28,00	0,54	1,23

Particle size distribution (PSD) of the ashes was done on FA, CA, DuraPozz, and PozzFill. The cumulative PSD curve of the ashes is presented in Figure 4.39. It is well documented that the abundance of particles <20 µm must exceed 15% in order for a stable paste to be formed (Jewell and Fourie, 2006). Figure 4.39 shows that FA has 27%, PozzFill has 59% and DuraPozz has 16% and CA has 0% above the minimum required particle size. The particle size distribution is an important property of ashes with smaller particle sizes having

a greater surface area. Size distribution ultimately determines the interaction of the ash with different leaching solutions, since it affects the mobilization of any trace elements which are deposited on the surface of the particles.

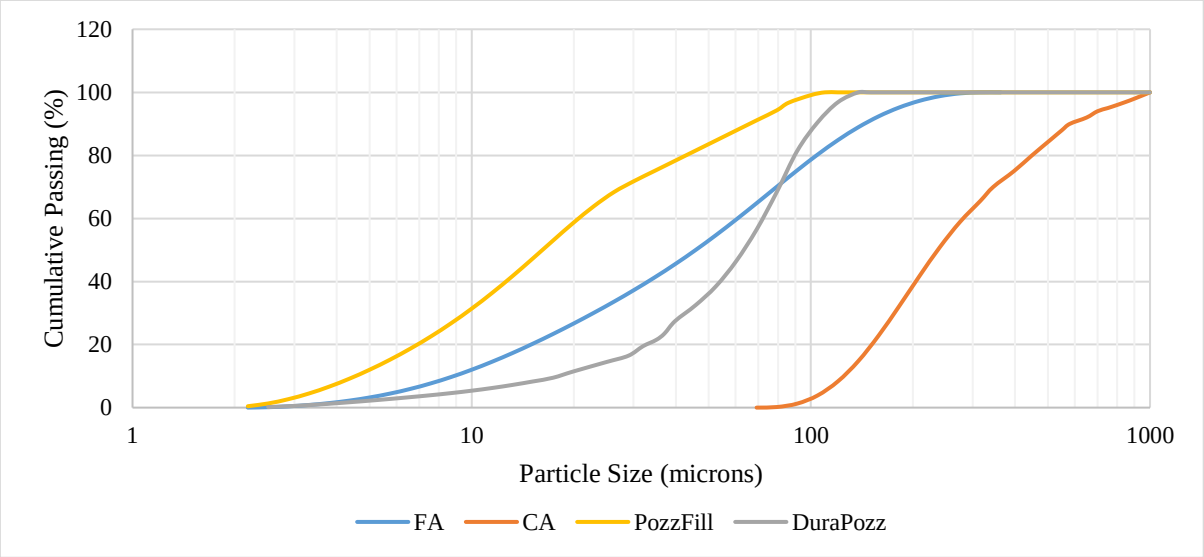

Figure 4-39: Cumulative Particle Size Distribution of CCPs

SEM analysis showed that FA typically consists of smooth, spherical shaped particles as can be seen in Figure 4.40A. However, some irregularly shaped particles, cenospheres, and agglomerates can also be seen. This is a result of high combustion temperatures. Figure 4.40B shows that the CA is characterized by a larger irregular particle size. EDS analysis showed that the FA and CA ashes to be rich in oxygen, Si and Al. EDS spot analysis on the CPB samples (C, D, and E) showed high concentrations of Ca, Mg and Si which is indicative of Ca–Mg-rich or Ca–S-rich phases and the presence of ettringite and the calcium-silicate-hydrate (CSH) gel structures.

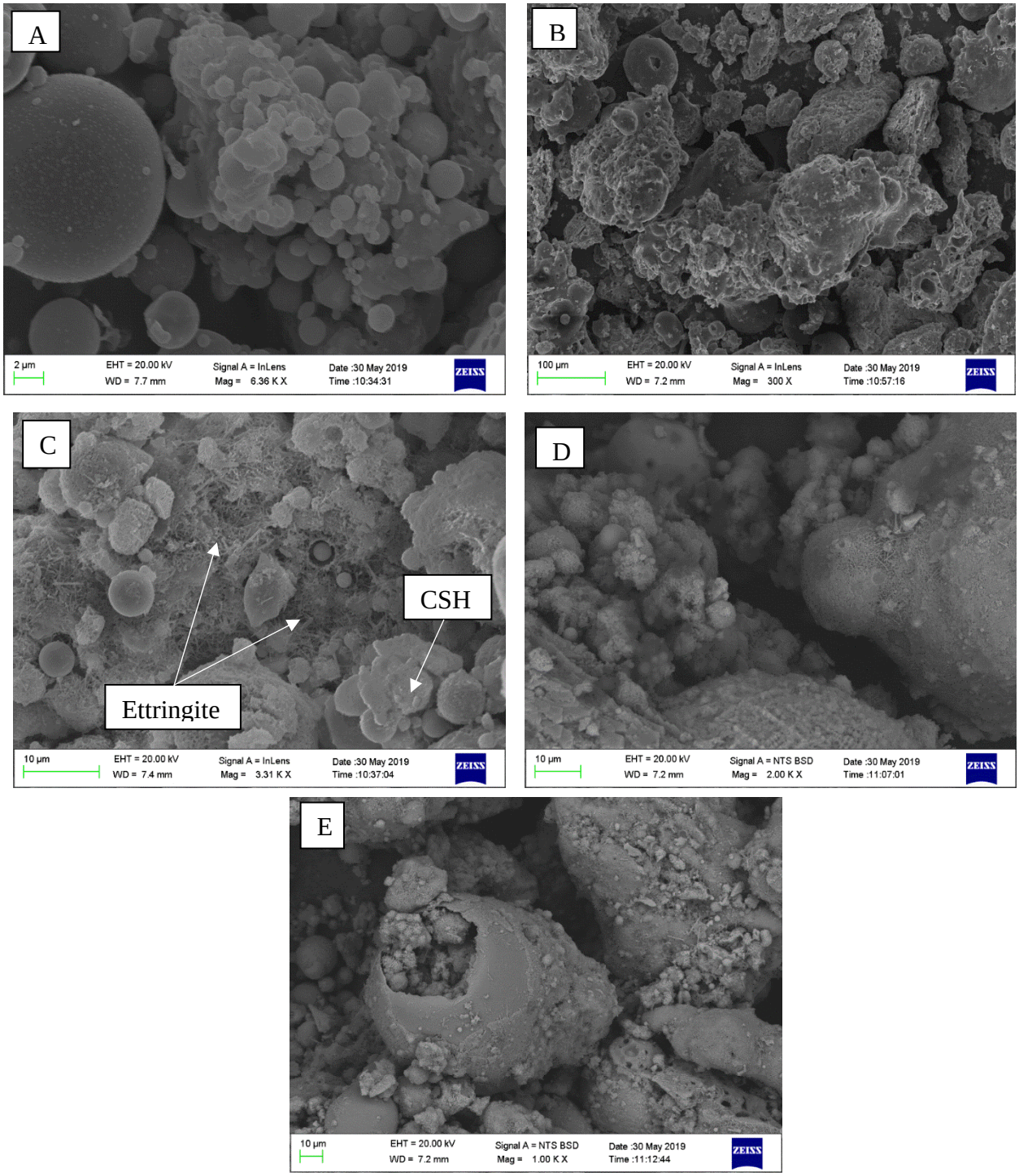

Figure 4-40: SEM Micrograph of FA (A), CA (B), FA at 28 Days (C), MA1 at 28 Days (D) and MA3 at 28 Days (E)

4.3.4.2. Mechanical Behavior

The UCS increased for all CPB mixtures as the curing time increased as shown in Figure 4.41. Typically, a 28 day UCS of 0.5 – 2 Mpa of the CPB is required in order to ensure slope and ground stability (Brackebusch, 1995; Peyronnard and Benzaazoua, 2012). PozzFill, DuraPozz, and FA all met the required minimum UCS after 28 days with values of 2.17 MPA, 0.94 MPa, and 0.73 MPa, respectively. Mixed ashes (MA1 and MA3) containing varying proportions of CA did not meet this requirement due to the larger particle size and high LOI of the ash. Abdulmatin et al. (2018) found that unmodified CA is not suitable as a pozzolan and should undergo particle size reduction in order to improve the pozzolanic activity. The pozzolanic reactivity of the ash could increase by 27% upon particle size reduction (Cheriaf et al., 1999). For CA to be effectively utilized as a pozzolan, at least 25% of the particles should be able to be retained on a No. 325 sieve (45 μm) according to the ASTM C618 FA Class F requirements. PozzFill showed the greatest strength development reaching a UCS of 2.64 MPa due to the fine particle size. This result is expected as finer particles, which are richer in the glassy phase are more reactive than coarser particles which are rich in unburnt carbon (Chancey et al., 2010; Mahlaba et al., 2011). This is further confirmed by the SEM analysis which shows Figure 4.40C having an abundance of reaction products as shown by the formation of ettringite crystals and the CSH structure. The strength of the CPB is predominately due to the abundance of the CSH gel being (Peyronnard and Benzaazoua, 2012). Figure 4.40D shows a lesser amount of reaction products deposited on the surface of the FA particles as the amount of FA is lowered whereas Figure 4.40E lacks the presence of these reaction products. Thus, strength development is decreased as the FA content decreases due to a lack of pozzolanic activity and the formation of reaction products. These reaction products fill the porous areas inside the mixture which leads to a stronger aggregate of particles and a denser CPB.

Strength development is largely dependent on the PSD of the ashes with larger particles containing a high amount of unburnt carbon having an adverse effect on strength development. Poor strength development could arise upon setting as the larger coarse particles separate from the finer FA particles and this forms a non-uniform CPB (Ercikdi et al., 2017). Studies by Hamberg et al. (2015) showed that mine operators could require a minimum UCS of as low as 200 kPa for CPB applications, in which case all the CPB

mixtures would be suitable for use. However, this minimum strength requirement is based on site-specific requirements.

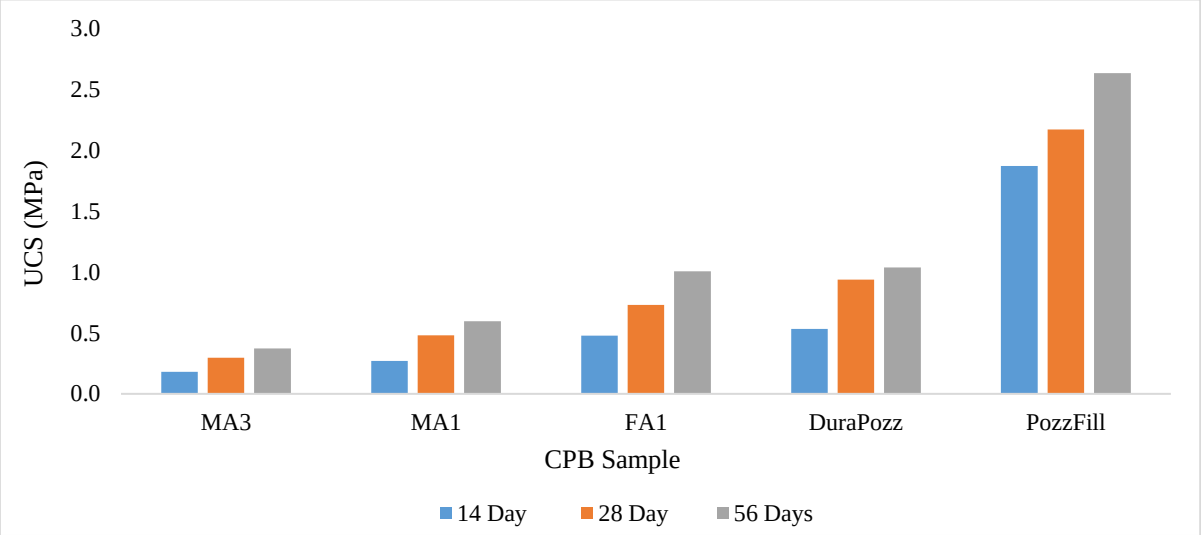

Figure 4-41: UCS of CPB Samples at Various Curing Times

Figure 4.41 shows that the UCS increased for all CPB mixtures as the curing time increased. This is an important observation as some studies reported that the UCS decreases after 28 days when brines are used (Saw and Villaescusa, 2011). This difference in observation is unique to the brine and ash used in this study and similar results were obtained by Mahlaba et al. (2011).

Strength development is initially delayed as the increase in strength between days 14 and 28 is much smaller than the strength development between days 28 and 56. Strength development is a result of the pozzolanic activity of the ashes. The delay in hydration of the CPB and slow pozzolanic reactivity during the early curing period may be the possible reason for the poor strength development as the expected secondary minerals have not formed. DuraPozz and FA both had a similar particle size and thus similar UCS values. Particle size is the major contributor to strength development and the extent to which the ashes display pozzolanic activity. Finer particles are able to react more easily with $Ca(OH)_2$, have a greater amount of reaction products and exhibit a greater mineralogical transformation.

Table 4.18 shows the 28 day UCS values of different CPB mixtures. The values obtained in this study are comparable to those obtained in other studies. The strength development is based on particle size, LOI, binder content, ash content, and ash composition. These

properties all have a significant effect on the pozzolanic activity of the ashes and resultant strength development. Since the CPB mixtures showed favourable UCS values, it can also be said that the operational costs of coal mining can be reduced by using brines instead of water (Mahlaba et al., 2011).

Table 4-18: UCS Comparison

Composition	28 Day UCS (MPa)	Reference
PozzFill, OPC, Brine	2.17	This study
DuraPozz, OPC, Brine	0.94	This study
FA, Brine, OPC	0.73	This study
FA; coal gangue; cement; water	7.8	(Qi et al., 2015)
FA; Brine	1.65	(Mahlaba et al., 2011b)
FA; Brine (High salinity)	3.00	(Mahlaba et al., 2011b)
Mine tailings, OPC	1.51	(Li and Fall, 2018)
Mine tailings, OPC	1.82	(Xu et al., 2019)
Mine tailings, OPC	1.5	(Liu et al., 2018)
Gold tailings, FA, OPC	0.2	(Hamberg et al., 2015)

4.3.4.3. Tank Leach Test Results

The elemental release of the TLT experiment showed small deviations in the duplicated samples and thus an averaged value is presented. The purpose of investigating the leaching behaviour of the flooded CPB is to examine the environmental impact as the CPB is typically flooded when mine operations close and the groundwater returns to normal levels. Ideally, the addition of OPC should reduce the porosity and restrict water percolation through the CPB mixtures. As a result, trace metal leaching would be decreased and any leaching would occur predominantly due to surface wash off. During the curing period, the MA2 and CA mixtures disintegrated and thus were not analysed further. This suggests that the cementitious phases in these mixtures dissolved upon water percolation and exhibited poor binding properties. Hamberg et al. (2018) suggested that flooding of CPB should occur rapidly to prevent unsaturated zones from forming which facilitates the oxidation of sulphide materials and increases the mobility of trace metals.

Initially, the pH of all CPB mixtures was alkaline and increased continuously during the first three renewal cycles (Figure 4.42). This is due to the surface wash-off of Ca, Na and K, as these elements are readily available and are easily removed due to the high solubility at alkaline pHs. This is further confirmed by the high release of these elements as seen in Figures 4.44, 4.45 and 4.46. Once these easily soluble species have been removed, a decrease in pH is observed at day 7. Thereafter, a rapid increase in the pH is a result of the dissolution of the aluminosilicate and glass fractions encapsulated further in the CPB. Water percolation occurs slowly as the glass fractions begin dissociating after a period of 7 days.

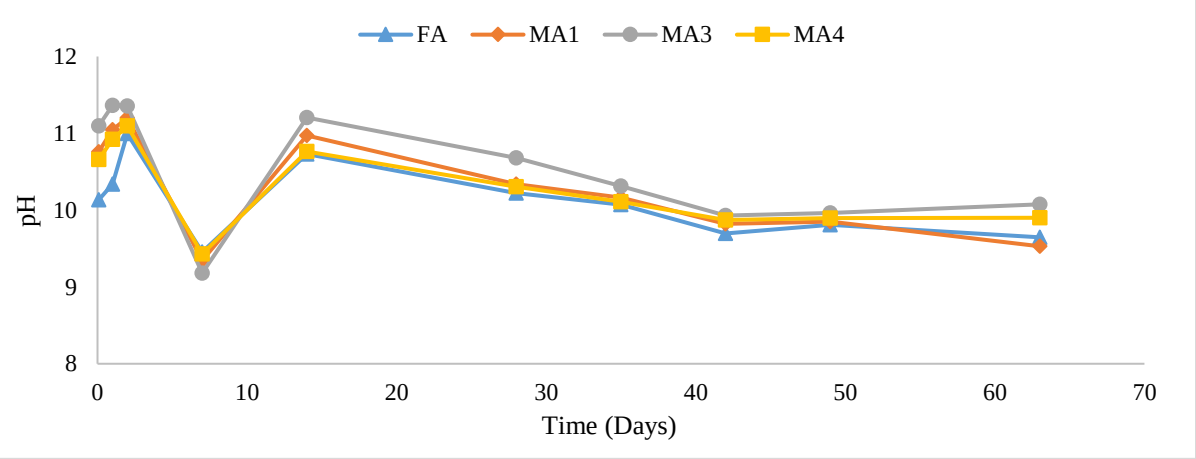

Figure 4-42: pH Evolution during the TLT

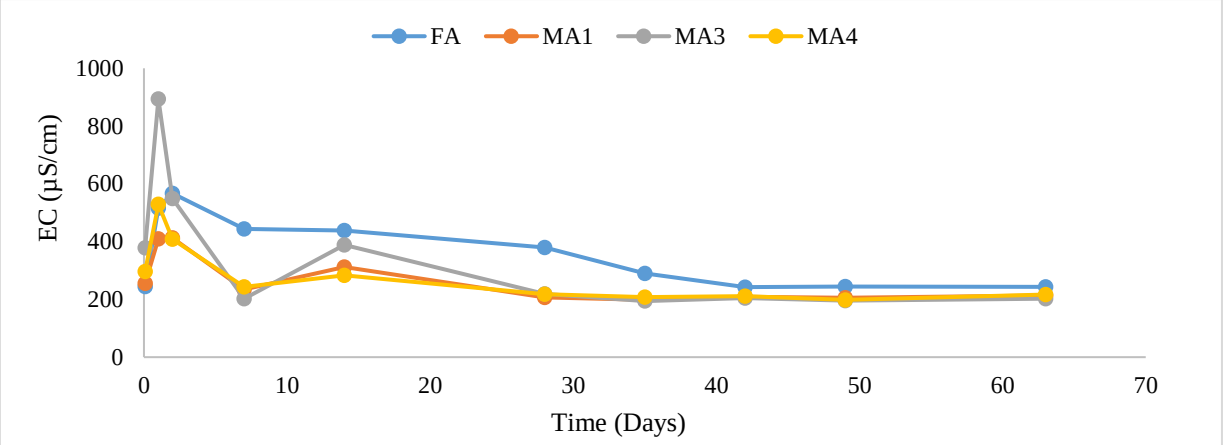

Figure 4-43: EC Evolution during the TLT

This is accompanied by an increase in the elemental release of Ca, Al, K, Mg, Ba, and Fe. The pH then continuously decreases as the number of leachable species decreases. This is confirmed by the EC which follows the same pattern (Figure 4.43). The initial increase in the cumulative release of Ca seen in Figure 4.44 is probably due to the easily soluble fractions deposited on the surface of the monoliths as well as due to the addition of OPC. Thereafter, the continuous increase is due to the dissolution of the cementitious materials formed during curing which would include portlandite, calcium aluminates or the CSH gel (Coussy et al., 2011; Peyronnard et al., 2009). The dissolution of these species is responsible for the alkaline pH throughout the TLT. However, the lower leachable Ca released from the FA mixture is a result of the lower permeability of the CPB. As a result, the dissolution of the glass fraction would be slower and lower elemental release of elements associated with this fraction would be seen.

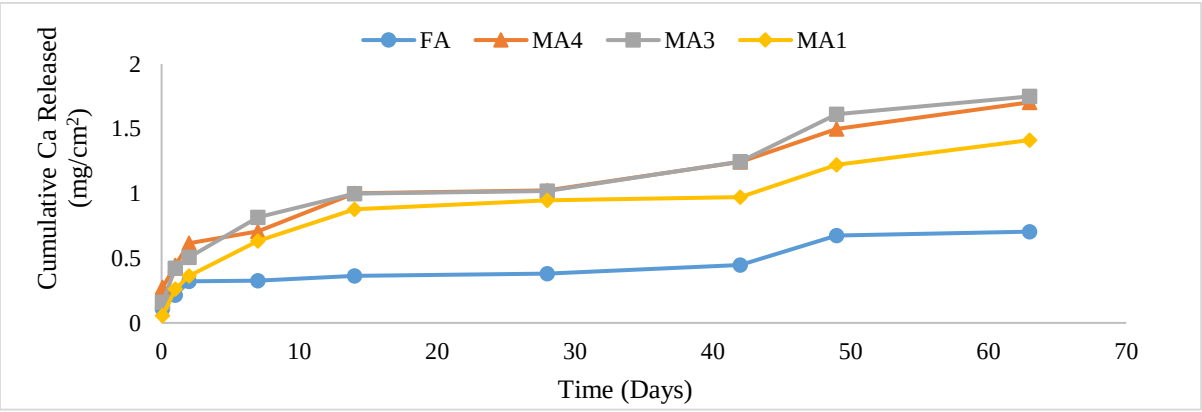

Figure 4-44: Ca Released during the TLT

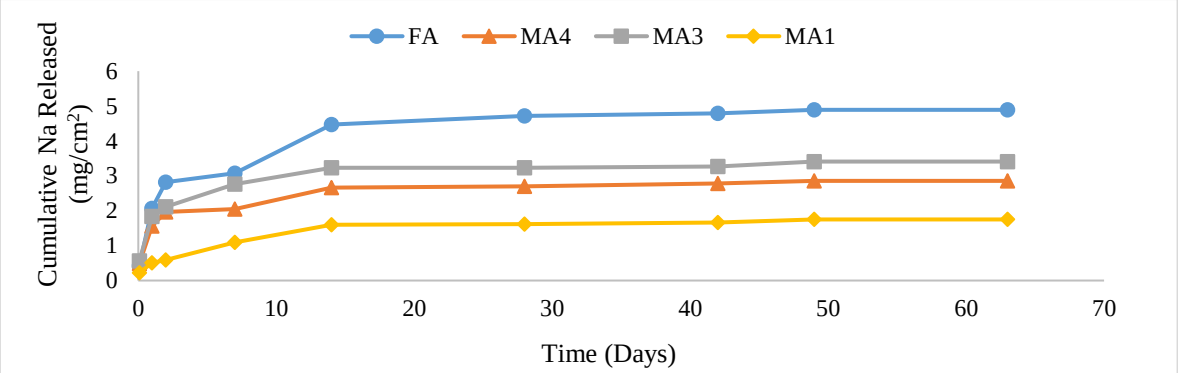

Figure 4-45: Na Released during the TLT

The concentration of Na was significant in the leachate and increased until day 14, thereafter, equilibrium was reached (Figure 4.45). Since Na is a monovalent ion known for its mobility, this is indicative that Na released is likely due to surface wash off and the high concentration released originates from the brine. However, since equilibrium was reached, it is possible that the Na ions are incorporated into new, secondary mineral precipitates or are being adsorbed onto the CPB. Low Mg concentrations in the leachates are characteristic of the precipitation of slightly soluble phases such as $Mg(OH)_2$ which are favoured by alkaline pHs. Since Mg is known to be found within the ash matrix, the release continually increases as the water percolates through the CPB as shown in Figure 4.46. The release is more gradual following 7 days further confirming that the dissociation of the glass fraction occurs after a period of time. Al concentrations found in the leachate were low as only a small portion of Al exists as a soluble fraction whereas the majority of the leachable Al is due to the aluminosilicate phases. The Al released is due to the slow dissolution of the glass matrix and crystalline aluminosilicate phases. Equilibrium is reached after 42 days as seen in Figure 4.47.

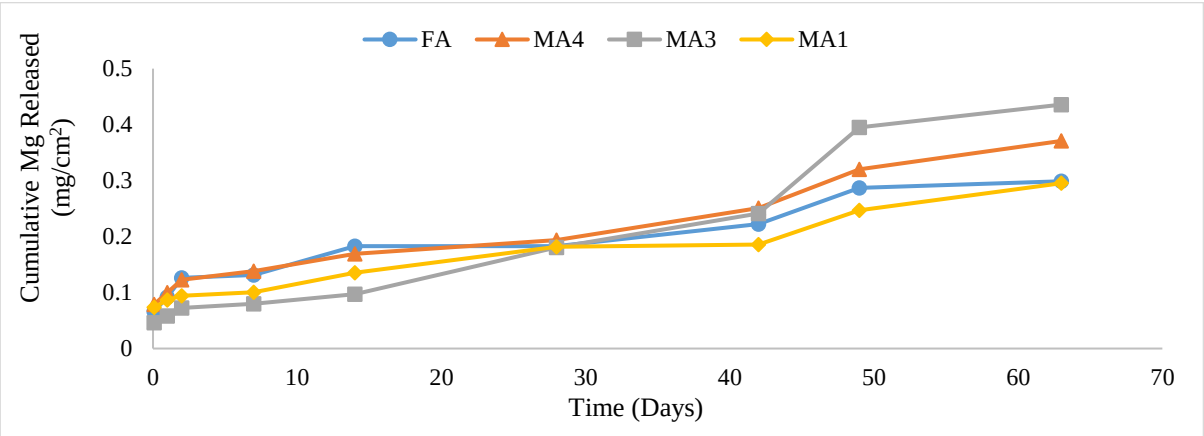

Figure 4-46: Mg Released during the TLT

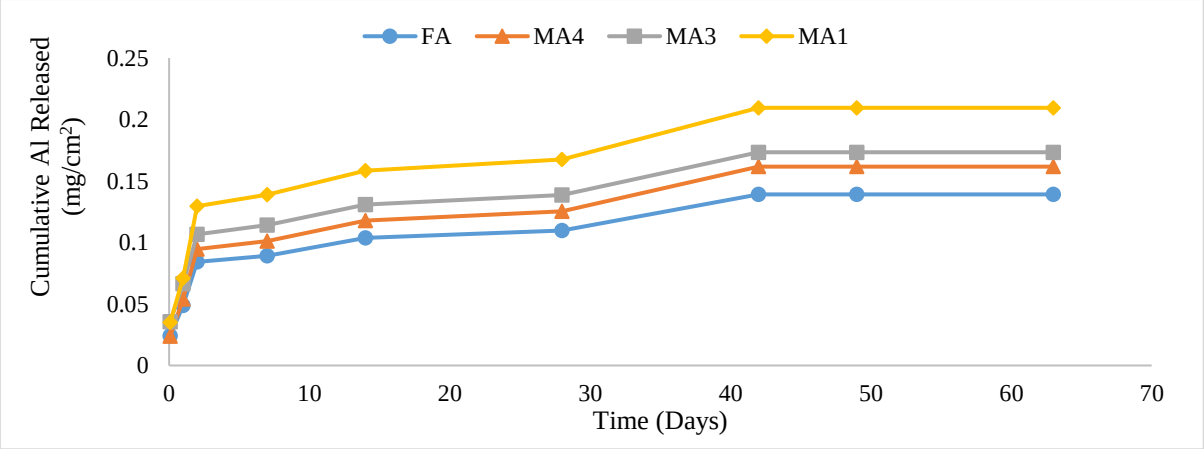

Figure 4-47: Al Released during the TLT

The amount of K released follows a similar pattern to that of the Na release whereby equilibrium is reached after the first few renewal cycles. Na and K leachability is due to the dissolution of the soluble phases of NaCl and KCl. It is likely that because these compounds are independent of pH, the release is initially high and then decreases as the release is availability controlled.

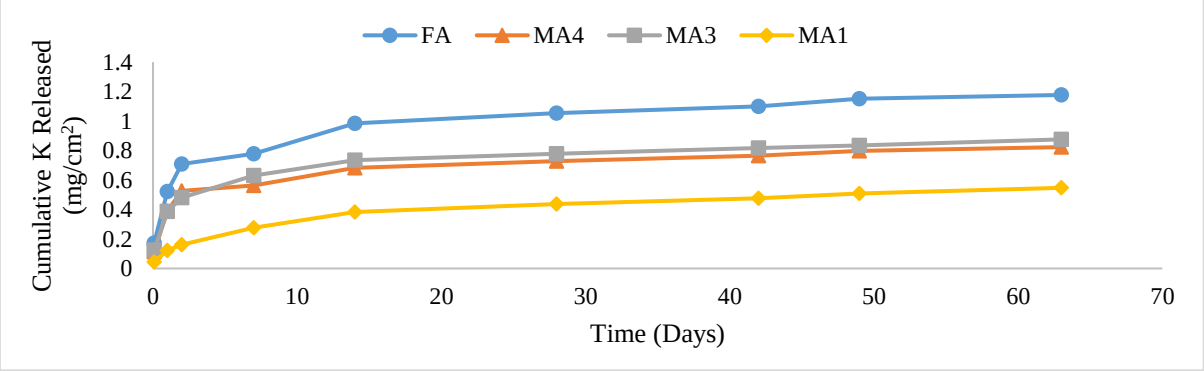

Figure 4-48: K Released during the TLT

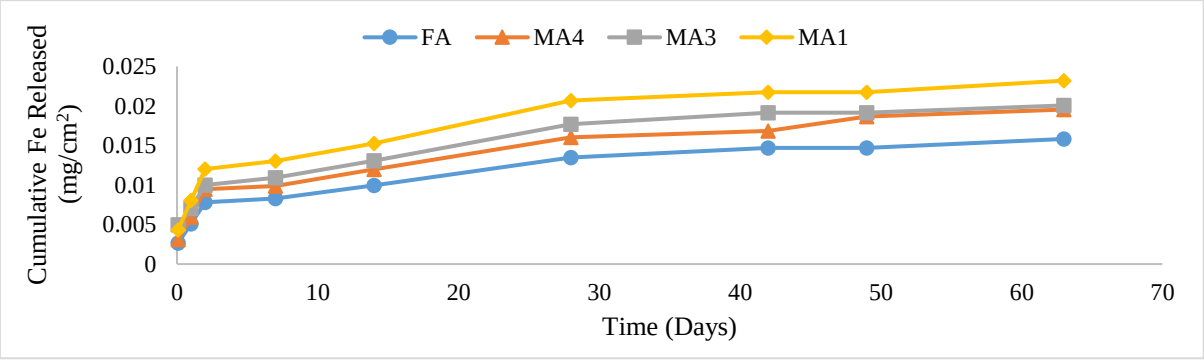

Figure 4-49: Fe Released during the TLT

The metals (Cr, Ni, and As) were below the detection limit and this could be attributed to low concentrations in the ashes and brine as well as the alkaline pH of the leachate which inhibits solubility. Studies have shown that at alkaline pHs, the surface of FA becomes

negatively charged which promotes the adsorption of trace metals from solution (Alinnor, 2007; Lee and Saunders, 2003). Low concentrations were observed for Pb and Ba with an elemental release of <0.003 mg/cm^2 and <0.02 mg/cm^2, respectively. The release occurred during the first 7 days, thereafter no further release occurred. However, if the cementitious phases dissolved, the permeability and release of trace metals may increase in the CPB mixtures. The release of Fe followed a similar trend to that of Al indicating the dissolution of the aluminosilicate matrix.

Overall, MA3 had a high cumulative release of all elements and showed the poorest strength development due to the lack of hydration and pozzolanic reaction products. As a result, MA3 was characterized by having a high porosity and thus higher leachability was observed. This is confirmed by MA3 having the highest EC and consequently a higher concentration of soluble species. This is due to the greater proportion of CA in the mixtures which has a much larger particle size that does not favour the pozzolanic reaction. The cumulative elemental release for FA was the lowest for Al, Pb, Ca, Fe and Ba except for the alkali metals, Na and K, in which the cumulative leaching was found to be the highest. The low cumulative leaching observed for FA could also be attributed to the porosity. Since the CPB mixture containing only FA showed the greatest strength development and high presence of cement hydration and pozzolanic reaction products, the porosity and permeability of the CPB would be lower. This shows that the pozzolanic activity of the FA is able to significantly refine the pore structure of the CPB thus reducing permeability (H. Zhao et al., 2018). As a result, the leaching would be decreased. The MA4 mixture performed very similarly to that of the FA mixture with similar leaching behaviour observed for Al, Pb, Mg, K, Ca, Fe and Ba, however, lower Na and K released was observed. This could indicate that the addition of CA to the FA in CPB may reduce the leachability of alkali metals. This is further confirmed whereby MA1 had the lowest cumulative release of Na, K, and Mg. however, this may also be attributed to coarse containing lower proportions of alkali metals.

The pore solution of the CPB is a result of the brine, dissolution of the ashes and the hydration and pozzolanic reaction products. Hydration products include portlandite and ettringite whereas the pozzolanic reaction products include the CSH gel. Ca, Mg, Fe, and Ba show a continuous increase in release with no plateau being reached. It is likely that these elements are encapsulated within the ash matrix and the soluble fraction on the surface of the monolith. Leaching is thus a combination of surface wash off and diffusion controlled.

Na, Al, K, Pb show a release that is most abundant initially but diminishes towards the end of the TLT. This is indicative of surface wash off of the readily available soluble fraction which is deposited on the surface of the monolith. Once this fraction has been removed, the release decreases. Choi et al. (2002) have suggested that these elements are mainly associated with the surface and these surface-associated fractions will dominate the leachate chemistry at the early stages of interaction with water. Cumulative release of the TLT is in the order of Na, Ca, K, Mg, Al, Fe, Ba, and Pb. Elements that are abundant and easily soluble are Ca, Na, K, and Mg. These elements are high in both the FA, CA and the brine. As a result, these elements contribute significantly to the leachate chemistry.

4.3.4.4. Kinetic Test Results: Weathering Cell Test

Results obtained from the weathering cell tests for all CPB mixtures showed good reproducibility and an average of the results is presented. The cumulative elemental release following 10 cycles for each CPB mixture is shown in Figures 4.52 – 4.59. The cumulative release for Na is the highest in all CPB mixtures followed by Ca, Mg, K, Al, Ba, Fe, and Pb. The trends in pH were similar with a constant pH of approximately 8.3 being reached after the third extraction. The high initial pH of the CPB mixtures is attributed to the dissolution and hydrolysis of alkali earth and alkali earth metal oxides such as calcium and magnesium oxide (Figure 4.50). The EC decreased steadily as the weathering cell test progressed as shown in Figure 4.51. A high EC confirms that a large fraction of soluble salts is easily leached from the CCPs. This is due to the release of species such as Ca, Na, Mg, and K. The initial rapid decrease is due to the release of Na which is high during the first 4 cycles, thereafter the EC drop is more gradual indicating that the amount of soluble species released such as Ca, Mg and K is decreasing. The decrease observed in the EC of the CPB mixtures could indicate the precipitation of soluble salts as a result of the ash-brine interaction in the form of transient mineral phases (Fatoba, 2010).

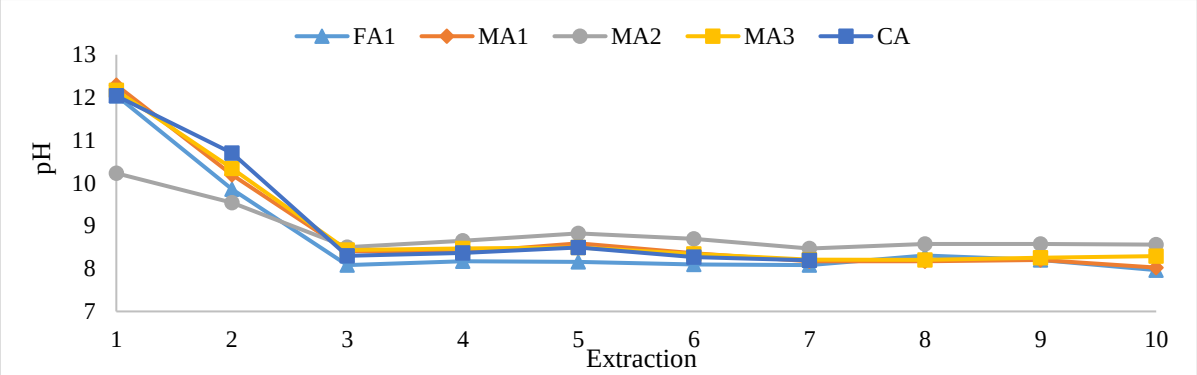

Figure 4-50: pH Evolution During the Weathering Cell Test

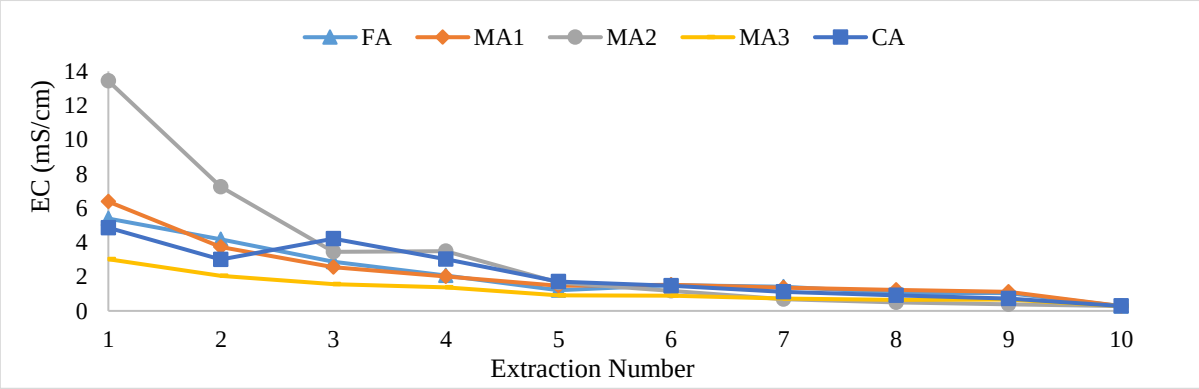

Figure 4-51: EC Evolution During the Weathering Cell Test

The high elemental release observed for Na, Ca, K and Mg is a result of co-disposal with brine which is rich in these elements. Consequently, high pHs of the leachate were observed as these elements contribute significantly to solution alkalinity. However, there was an initial removal of Na ions from the brine solution by the interaction with the CPB. The cumulative release of Na in the CPB for FA, CA, MA1, and MA3 was less than the concentration of Na in the brine prior to use in the CPB (2988 mg/l). This is further confirmed by the EC of the leachates (<7 mS/cm) being lower than that of the brine (12.39 mS/cm) except for MA2. The elemental release of Na increased progressively over the first 15 days and then stabilized, increasing only slightly between days 14 and 35 (Figure 4.52). This is due to Na in the brine being deposited as a water soluble fraction on the ashes which can be easily be leached upon water ingress. The release on Pb followed a similar trend to that of Na with an increase in elemental release during the first 7 days and thereafter no Pb leaching was observed (Figure 4.59).

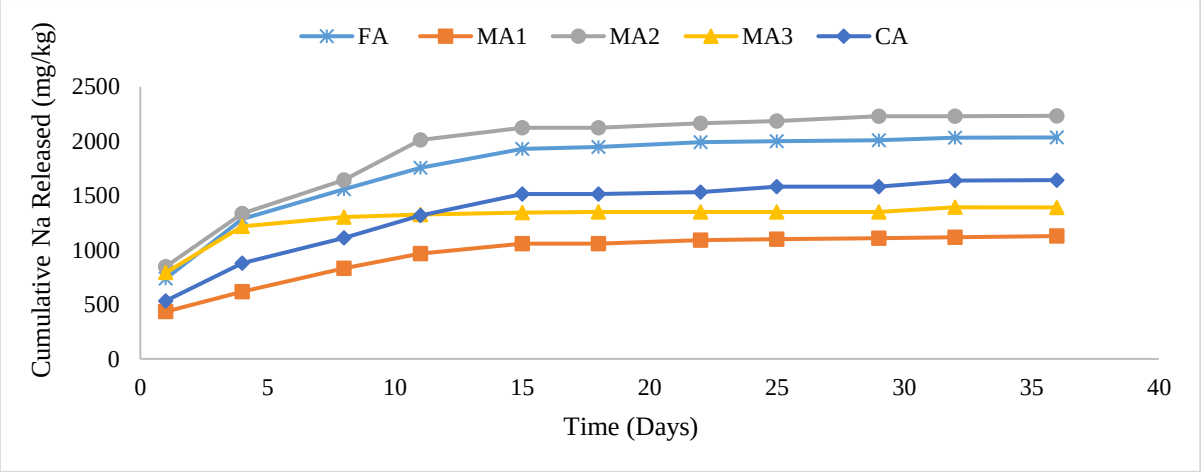

Figure 4-52: Cumulative Na Released for the Weathering Cell Test

The amount of Ca, Mg, K, and Al released showed a stable increase for the duration of the experiment. These elements are trapped within the aluminosilicate matrix and are only released upon long term weathering. The decrease in pH led to the dissolution of the major aluminosilicate ash matrix which influenced the release of these elements previously locked in the ash matrix (Eze et al., 2013). The trend does not show any decrease that could indicate a reduction in the elemental release over time. However, the amount of Ca, Mg and K released between each extraction began to decrease following 14 days which could be attributed to the change in pH. A decrease from the natural pH of 12 to a pH of 8.3 due to the buffering capacity of the binder reduced the amount of Ca, Mg, K released in each extraction. A similar observation was made for the release of Fe and Ba.

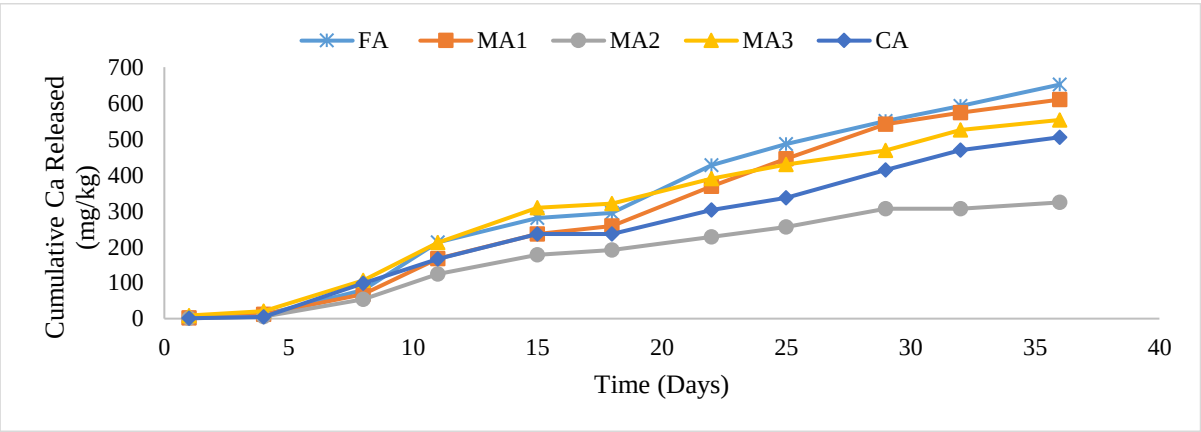

Figure 4-53: Cumulative Ca Released for the Weathering Cell Test

The addition of CA to FA significantly reduced the release of Ca from 912.16 mg/kg in the FA mixture to 452.92 mg/kg in the MA2 mixture as shown in Figure 4.53. Calcium is known to be associated with the surface of FA particles, as well as the main constituents of the

aluminosilicate and glass fractions thus the constant release of Ca can be seen in Figure 4.53. The high initial Ca release is due to the surface wash off of soluble Ca phases such as Ca-sulphates whereas the continuous release is due to the dissolution of free lime (CaO) and other insoluble forms such as calcite.

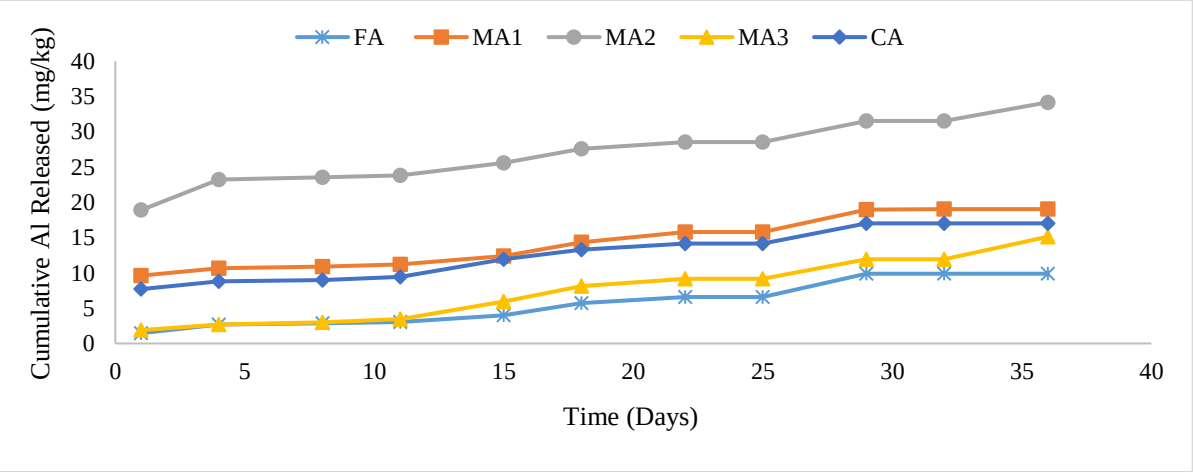

Figure 4-54: Cumulative Al Released for the Weathering Cell Test

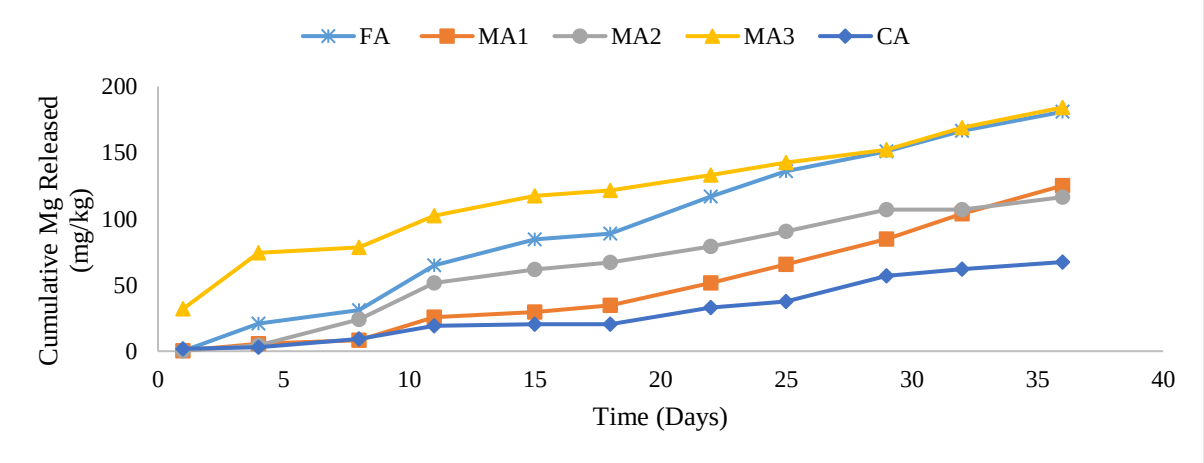

Figure 4-55: Cumulative Mg Released for the Weathering Cell Test

The amount of Al and Mg released during each extraction increased steadily (Figures 4.54 and 4.55). This is a result of the dissolution of the glass phases within the ash matrix. The amount of K increased until day 11, thereafter, the cumulative increase decreased and the amount released reached equilibrium at ~7 mg/kg as shown in Figure 4.56. This is consistent with the decrease in pH at day 11 from natural pH (~11.5) to a pH of ~8.5.

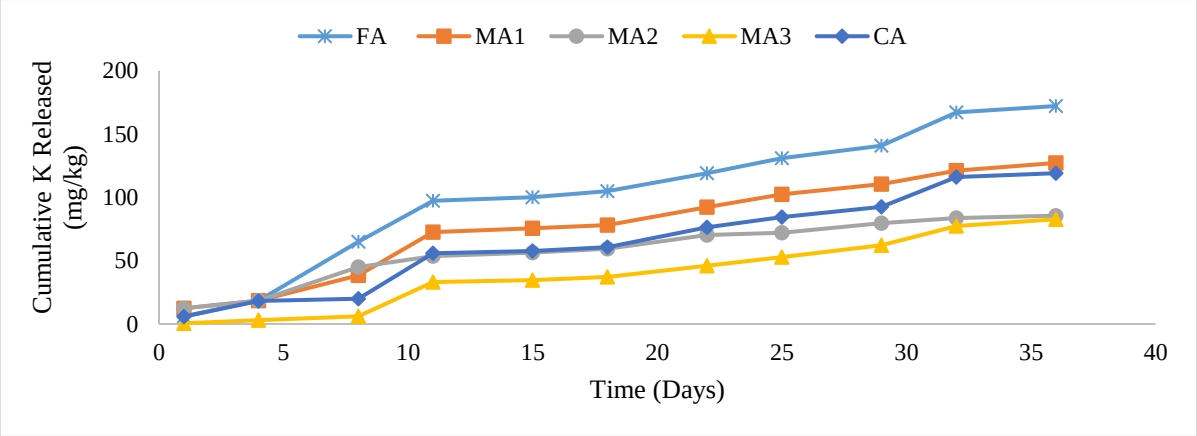

Figure 4-56: Cumulative K Released for the Weathering Cell Test

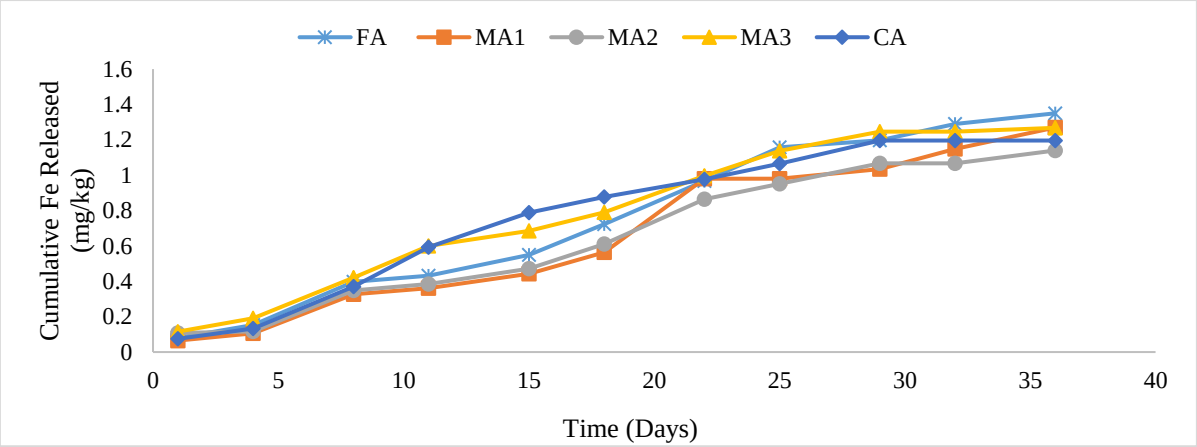

Figure 4-57: Cumulative Fe Released for the Weathering Cell Test

The release of Fe is low as shown in Figure 4.57 and consistent with other studies whereby the cumulative release is <10 mg/kg at alkaline conditions (Kim et al., 2003). Fe is stable and resistant to weathering due to the spinel structure. This is confirmed as the release is consistent between all CPB mixtures.

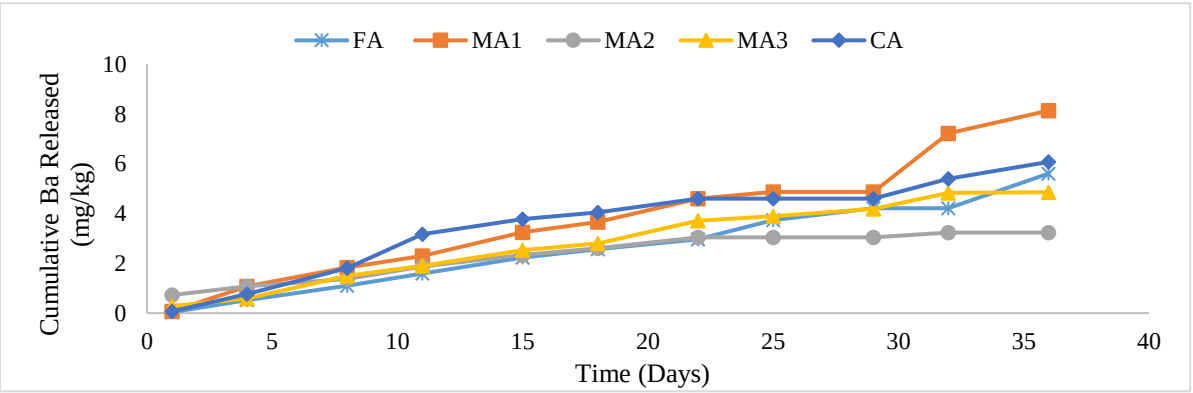

Figure 4-58: Cumulative Ba Released for the Weathering Cell Test

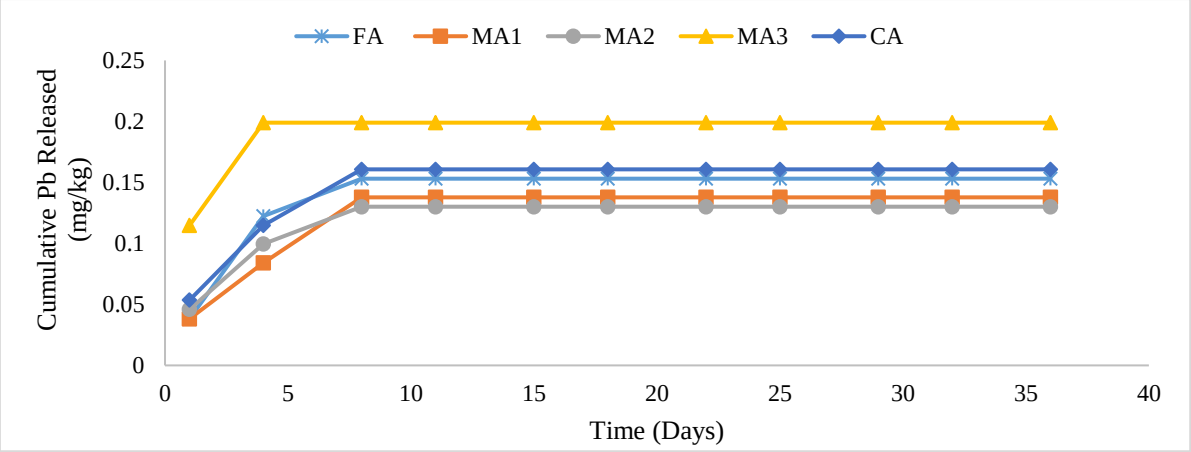

Figure 4-59: Cumulative Pb Released for the Weathering Cell Test

From Figure 4.60, it can be seen that MA2 had the lowest cumulative leaching for Ca, Pb, Fe, and Ba. MA1 and FA exhibited the lowest leaching of Na and Al, respectively. FA had the highest cumulative leaching of K, Fe and Ca. The cumulative leaching for all CPB mixtures was comparable, however, FA and MA2 which contain greater proportions of FA had a higher cumulative leaching for majority of the elements (Na, K, Ca, Al and Fe). MA2 showed the second lowest leaching for K and Fe, and the least for Ca. MA1 performed favourably whereby the highest cumulative leaching only occurred for Ba. This indicates that FA contains more leachable species and the addition of coarser ash particles potentially minimises leachability. Since CA has a much larger particle size, weathering occurs over a longer period of time. CA is more resistant to weathering than FA.

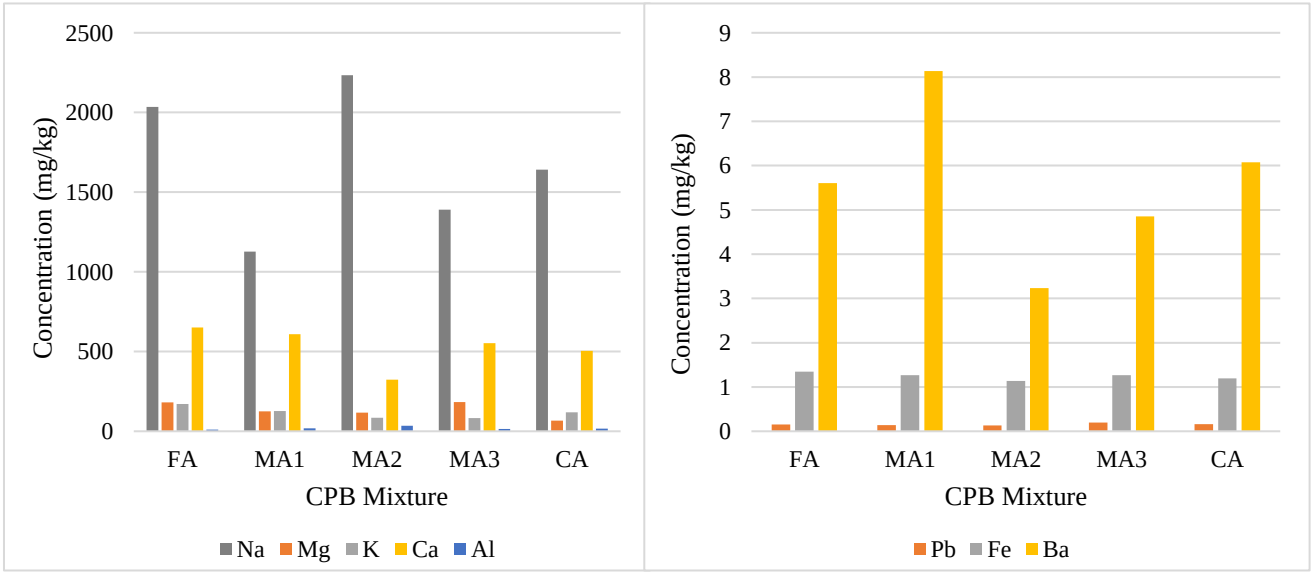

Figure 4-60: Cumulative Elemental Release for Different CPB following the Weathering Cell Test

4.3.4.5. Tank Leach Test and Weathering Cell Test Comparison

Table 4.19 shows a comparison in leachability between the mass transfer based leaching tests, the TLT and the weathering cell test. The leachability values presented in Table 4.19 are the cumulative elemental release in mg/kg. The TLT shows a much smaller leachable concentration in comparison to the weathering cell tests. This indicates that the CPB is a much more environmentally sustainable method of disposal in comparison to the surface ash disposal, thus a NEB is achieved. Similar leachable concentrations are observed for Pb, Al, Fe however there are vast differences in the leachable concentration for Na, Mg and Ca. It can be noted that the CPB encapsulates these elements, particularly from the brine. These elements are precipitated as secondary salts onto the CPB which is why leachability is reduced. The addition of small proportions of CA (in MA1) further enhances the reduction in leachability as a lower release is seen for Na, Mg, K, and Ba in comparison to the FA mixture. The use of CA enhances the texture of the CPB as the irregular shaped, larger porous particles which are very rough can improve interparticle friction and thus create a denser CPB which exhibits lower leachability (Rafieizonooz et al., 2016). The larger particle size of the CA further reduces the dissolution of the glass fraction and aluminosilicate phases. The surface area also plays a role when predicting leaching behaviour. The monolith samples in the TLT represent a case with a small surface area whereas the pulverized ash used in the weathering cell test represents a much larger surface area. It can be said that the smaller exposed surface area decreases leachability. As a result of the different exposed surface areas, releases from the TLT can be said to be diffusion controlled whereas the weathering cell test release is dissolution controlled. Since the glassy fraction of the ashes is known to be susceptible to dissolution, the weathering cell test shows a significantly higher release. A smaller exposed surface area is expected to have lower leaching as water percolation through the CPB is reduced. The pulverized ash used in the weathering cell test has a greater exposed surface area which enhances dissolution. Both scenarios exhibit different permeabilities due to the surface area.

Table 4-19: Comparison of the Cumulative Elemental Release (mg/kg)

Element	CPB Mixture	Weathering Cell Test (mg/kg)	TLT (mg/kg)
Al	FA	9,89	8,07
	MA1	19,0	10,7
	MA3	15,1	9,45
Pb	FA	0,15	0,14
	MA1	0,14	0,14
	MA3	0,20	0,13
Na	FA	2034	284
	MA1	1128	89,3
	MA3	1391	186
Mg	FA	181	17,3
	MA1	125	15,1
	MA3	184	23,8
K	FA	172	68,3
	MA1	127	27,9
	MA3	119	47,8
Ca	FA	652	40,9
	MA1	610	72,0
	MA3	553	95,4
Fe	FA	1,50	0,92
	MA1	1,27	1,18
	MA3	1,27	1,09
Ba	FA	5,61	1,23
	MA1	8,13	0,98
	MA3	4,86	1,04

4.3.4.6. Acid Neutralization Capacity Test: pH Dependence Leaching Test

In accordance with prEN 14429 testing method, nine different final pH values were analysed, covering the pH range 3–11. However, in some cases, the natural pH of the mixtures was below 11 (MA2 and BA) and thus the pH range below the natural value was analysed. pH is an important controlling parameter of leachability as it determines the surface charge of the ashes, the degree of ionization and speciation of elements in the solution (Gitari et al., 2009).

The ANC behaved similarly for the CPB mixtures whereby a smooth and continuous neutralization curve was obtained which decreased exponentially in buffering potential. Throughout the test, FA showed a higher neutralizing capacity than all other mixtures throughout the pH range (Figure 4.61). The FA mixture had the greatest strength development, the highest formation of reaction products and the greatest proportion of soluble calcium and magnesium bearing phases which is the result of the high neutralizing capacity observed. The CPB mixture containing equals amounts of FA and CA (MA1) and the mixture containing only CA only also showed a high neutralizing capacity. This phenomenon suggests that both FA and CA have the potential to provide the necessary alkalinity, especially to minimize the generation of acid mine drainage (AMD) if water is leached into the mine voids (Murarka and Erickson, 2006). This is due to the presence of the readily available Ca, Na, Mg, and K in these ashes. However, the potential higher release of these alkali metals might exert detrimental effects with regards to the utilization of the ash (Lo and Liao, 2007). Therefore, ash ratios should be chosen in order to ensure the purpose of utilization is met as different ratios will have different leaching characteristics. CPB mixtures exhibiting lower ANC buffering capacities (MA2 or MA3) coupled with the lower leaching of alkali metals may be more suited to concrete applications as the presence of alkali metals and alkali earth metal oxides such as sodium oxide (Na_2O) and calcium oxide (CaO) play a significant role in the alkali-silica reaction (ASR) which can cause cracking and be detrimental to the CPB (Shehata and Thomas, 2000).

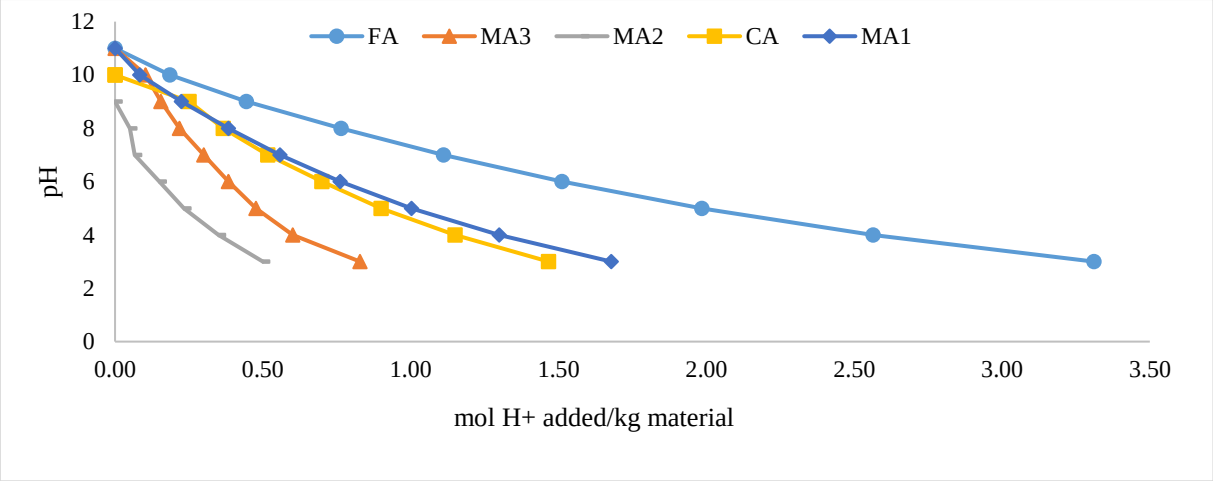

Figure 4-61: Acid Neutralization Capacity of CPB Mixtures

The solubility curves for Na, Mg, K, Fe, B, Ba, Al, Cr, Ni, As and Pb as a function of pH were obtained for each CPB mixture and shown in Figure 4.64 – 4.68. These curves are useful in predicting the leaching behaviour. The calcium releases decrease almost linearly as the pH of the solution increases (Figure 4.62). High correlation coefficients ($R^2 > 0.95$) were obtained for all mixtures except MA2. The precipitation of $CaCO_3$ occurs at high pHs hence low release is observed. The higher release observed at low pHs is indicative that the release is pH-dependent whereby the dissolution of the aluminosilicates phases and other Ca-rich phases such as $CaCO_3$ is favoured. Johnson et al. (1995) state that at pHs lower than 8, the dissolution of calcium silicate is high which is confirmed by Figure 4.62 especially in the case of MA1. The release of Mg follows a similar trend to that of Ca. A linear decrease in the amount of Mg releases is seen as the pH increases. At high pHs, a low release is due to the precipitation of $Mg(OH)_2$ which is stable at alkaline conditions. However, the dissolution of these phases as pH increases causes high amounts of Mg to be released. Elements such as Ca and Mg are cationic elements and thus the chemical behaviour in solution is due to adsorption of these ions onto the aluminosilicate and iron oxide phases. Precipitation of hydroxides and carbonates also determines the mobility of these elements. Figure 4.63 shows that the EC follows a linear relationship whereby the EC decreases as solution pH increases. All mixtures showed high correlation coefficients similarly to that of the Ca release ($R^2 > 0.95$). This high ionic strength is likely due to the high release of the highly soluble Ca and Mg throughout the pH range.

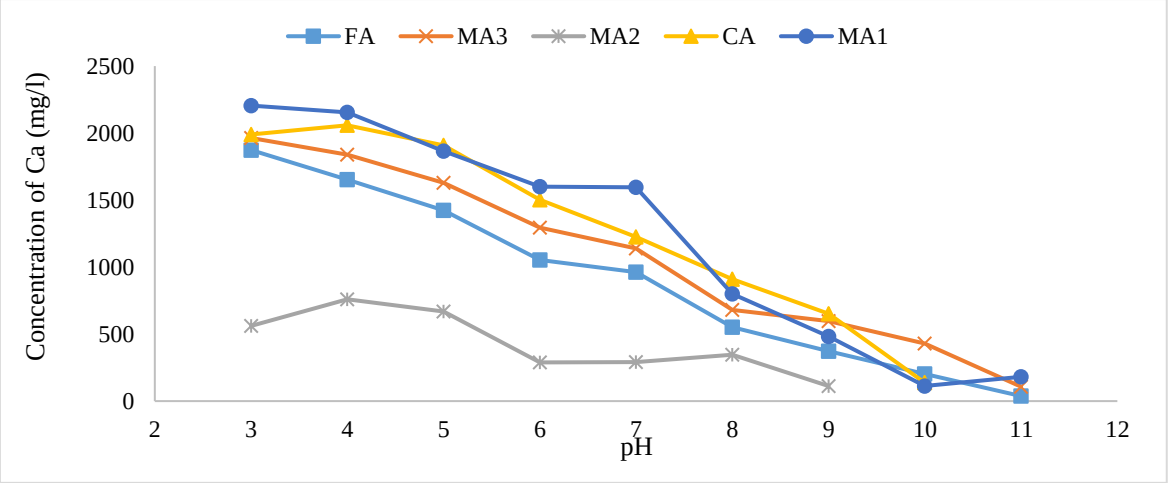

Figure 4-62: Ca Release as a Function of pH

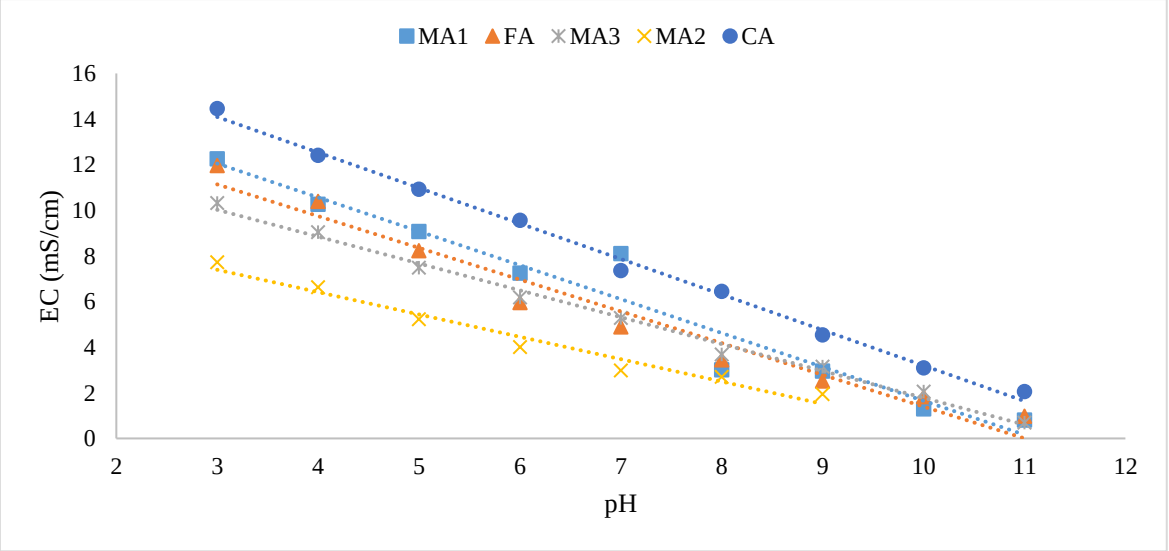

Figure 4-63: EC Release as a Function of pH

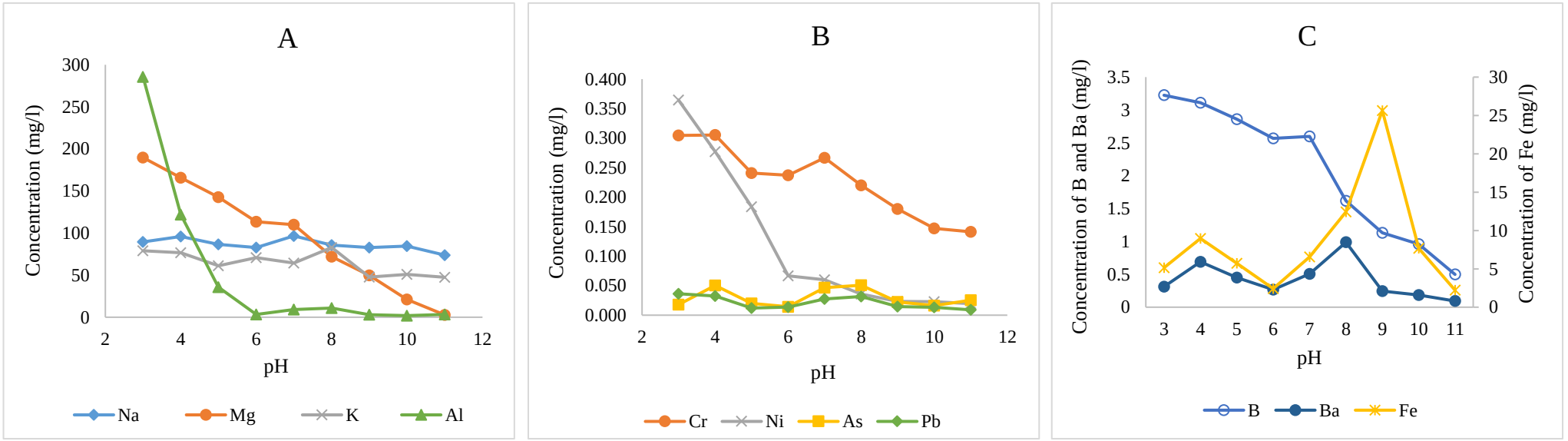

Figure 4-64: Elemental Release of Various Elements from the FA CPB Mixture as a Function of pH

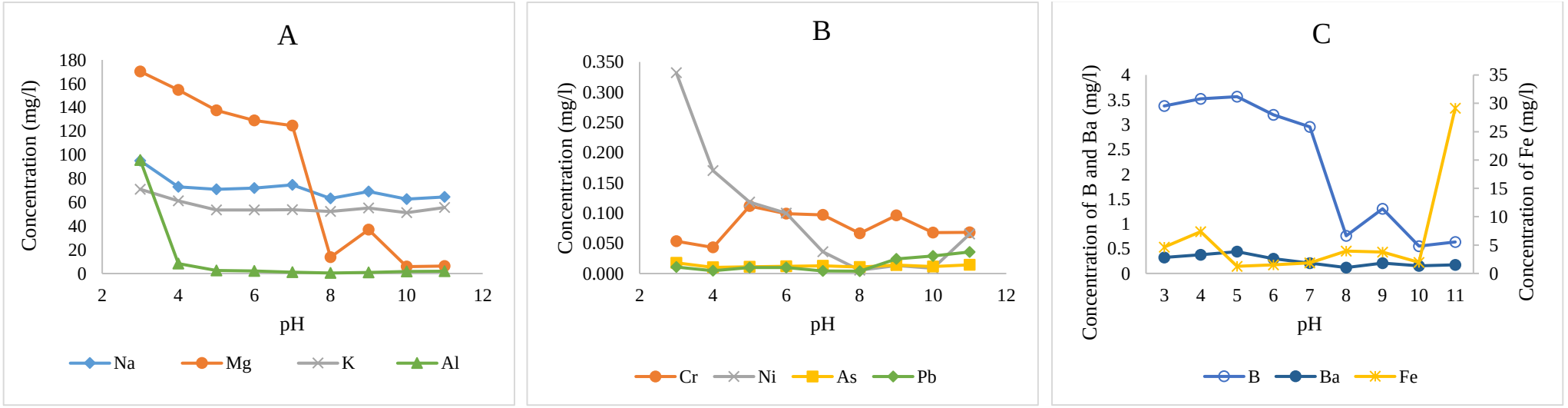

Figure 4-65: Elemental Release of Various Elements from the MA1 CPB Mixture as a Function of pH

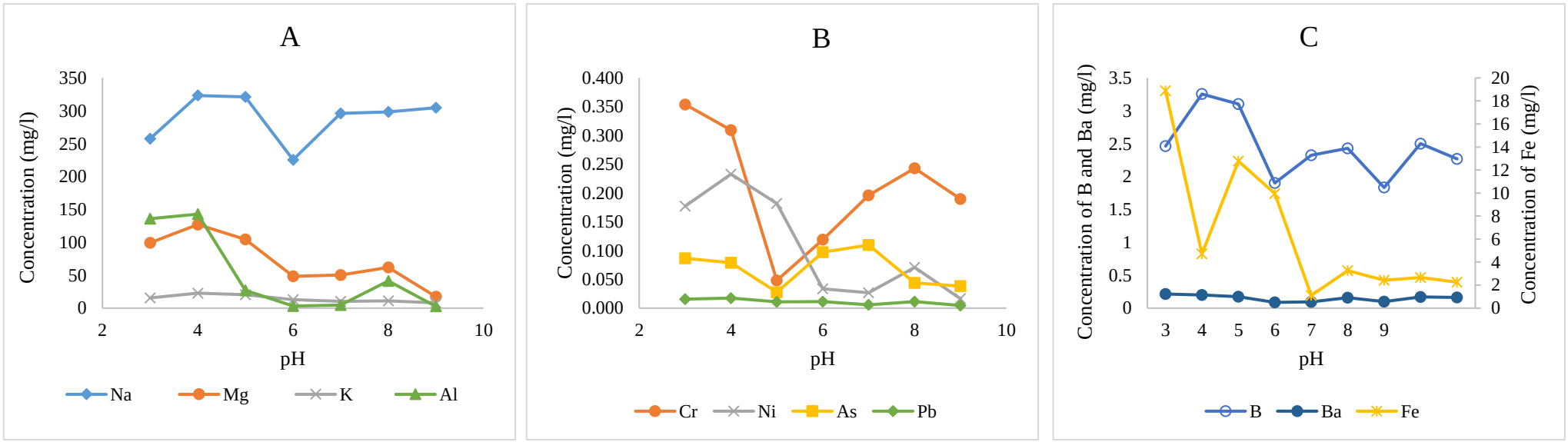

Figure 4-66: Elemental Release of Various Elements from the MA2 CPB Mixture as a Function of pH

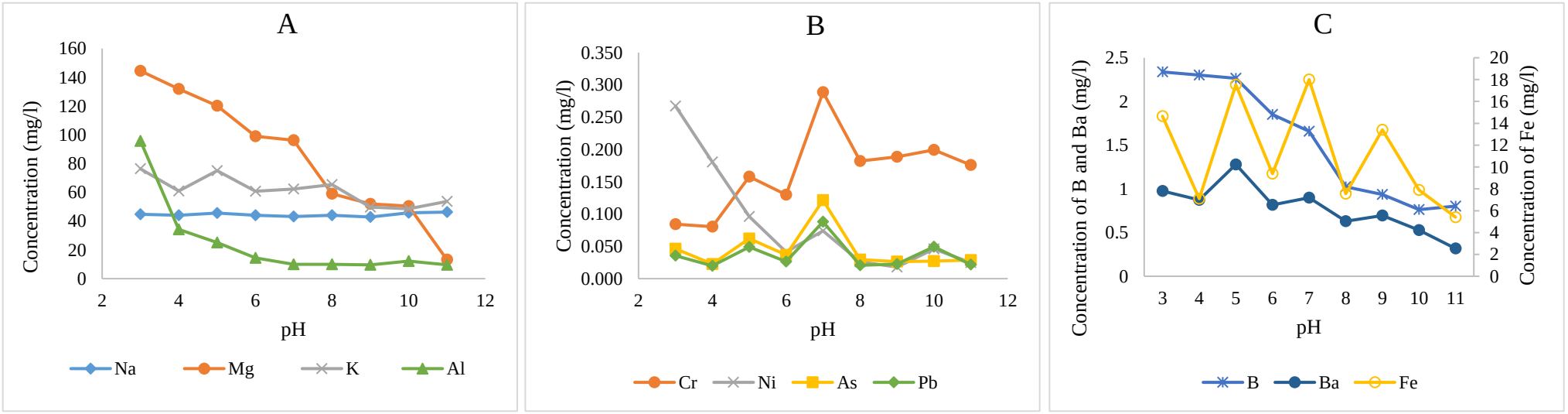

Figure 4-67: Elemental Release of Various Elements from the MA3 CPB Mixture as a Function of pH

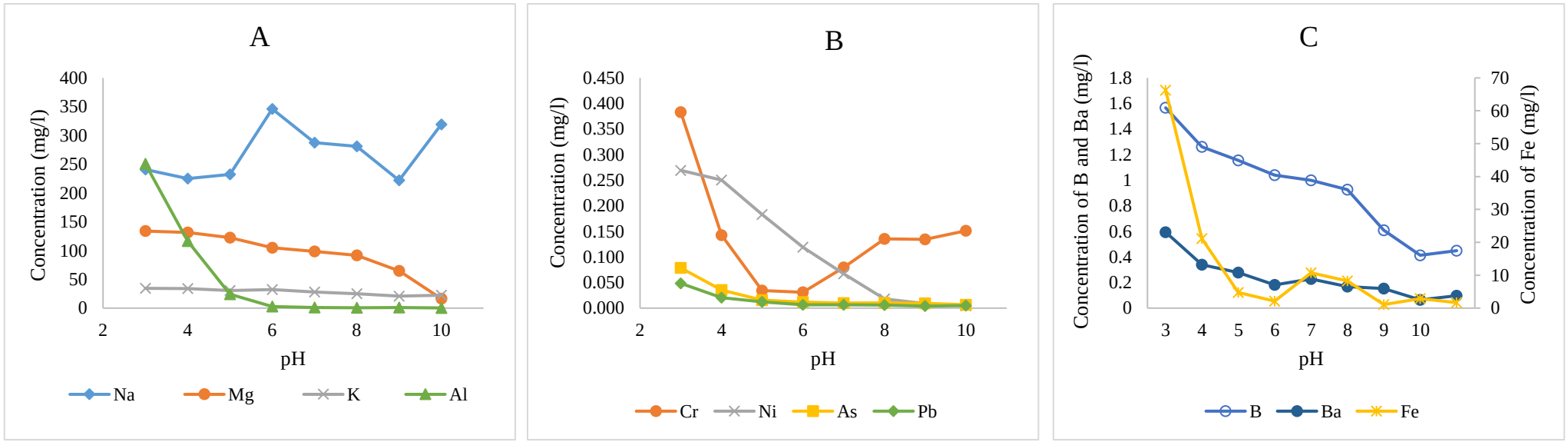

Figure 4-68: Elemental Release of Various Elements from the CA CPB Mixture as a Function of pH

The solubility of K and Na is independent of the solution pH as the released amount is constant across the entire pH range. This suggests that there is no effect on leachability with regards to pH and the released amount is mainly availability controlled. This is confirmed with findings by Gitari et al. (2009) and Tiruta-Barna et al. (2006). The release of Ba followed a similar trend whereby release was independent of pH, however, the higher release was seen at acidic conditions for CPB mixture containing higher proportions of coarse ash (MA3 and CA).

Al releases increases sharply at pH >5. The release is stable at the low to moderate pH range of 6-12 due to the precipitation of amorphous Al phases such as $Al(OH)_3$ and ettringite. At pH >5, the dissolution of the glass fraction becomes significant. The release of Fe fluctuated greatly between all CPB mixtures. A rapid increase in the release at pH 9 was seen for FA and at pH 11 for MA1. CA and MA2 showed a higher release at low pHs whereas the release of Fe in MA3 was independent of pH. All mixtures exhibited low release between pH 5-9 which is a result of oxyhydroxide and metal hydroxide precipitation. The dissolution of these phases at low pHs result in a higher Fe release.

The concentration of Cr, Ni, As and Pb were low in all CPB mixtures which is attributed to the low concentrations in the ashes and minimal occurrence in the glass fractions of the ashes. The release of Pb was very low (<0.05 mg/l) and followed the same trend for all CPB mixtures as that of Fe. The release of Pb is thus said to be dependent on the dissolution of iron oxides. However, due to the low release from the ashes which is also consistent with other studies (Izquierdo and Querol, 2012; Moreno et al., 2005; Ward et al., 2003), the release of Pb does not pose an environmental risk. Pb is said to be insoluble due to its association with the aluminosilicate matrix of the ashes.

As release at moderate to high pH levels was low and showed slightly higher solubility at pH >5. The release of As is dependent on adsorption and precipitation processes. Low release at alkaline pH is attributed to the number of Ca-bearing phases such as $Ca_3(AsO_4)_2$ whereby precipitation is favoured and hence the release of As is lowered (Jankowski et al., 2006). A lower concentration of As was released from the CPB containing a higher amount of FA at alkaline pHs. Since these mixtures contained a greater amount of reaction products and thus presence of ettringite ($Ca_6[Al(OH)_6(SO_4)_3.26H_2O$) which formed at these high pHs, the oxyanion form of As (arsenate) can often substitute for the SO_4 in ettringite and thus

lower release is observed (Gitari et al., 2009). The presence of ettringite can thus significantly reduce the amount of As released (Solem-Tishmack et al., 1995). Arsenate also has an affinity for portlandite ($Ca(OH)_2$).

The release of Ni at pHs 11-8 was low and constant at 0.05 mg/l. However, at pHs <8, the release increased linearly as pH decreased. This was observed for all CPB mixtures. Cr release is characterized by high solubility at low and high pHs with low or moderate solubility at the intermediate pH range between 5 - 7 in the case of MA2 and CA which is consistent with the amphoteric behaviour. Thus, Cr is able to react both as an acid and base. High leaching of metals at acidic conditions (<4) is common as the acidic leachate can easily dissolve metal oxides as well as metals bound to organic compounds.

The release of B increased as the solution pH decreased across the entire pH range. Since this increase was gradual, it is indicative that B is available as a soluble species on the surface of the monoliths as well as encapsulated within the ash matrix. Boron, being an oxyanion, is also known to be able to substitute in the ettringite structure similarly to that of As which is why the lower release is seen at alkaline pHs. The leaching of B is closely related to that of Ca and lower leaching at alkaline pHs is a result of B being trapped by ettringite and/or co-precipitation with $CaCO_3$ (Iwashita et al., 2005).

In general, the solubility of metals increased as solution pH decreased for Ca, Mg and B across the entire pH range. Solubility increased at acidic conditions in the range of 0 - 5 for Al and As and at pH >8 for Ni. Solubility is independent of solution pH with regards to the release of Na, K, and Ba. Cr and Pb exhibited amphoteric behaviour with higher solubility observed at the extreme ends of the pH range. The release of Fe varied greatly between the different mixtures and no general trend was observed.

4.3.5. Conclusions

The present work examined the net environmental benefit of the CPB containing FA, CA, and brine in comparison to the surface ash disposal methods with regards to the environmental and structural properties. This study aimed to reduce the current environmental impact of the surface ash disposal methods by proposing a more environmentally suitable disposal option whereby fly ash, coarse ash and brine and be co disposed of through the development of a CPB. Furthermore, the environmental and

structural properties were examined in order to determine the most desirable ash characteristics and mix design which showed high strength development and lower leaching. The main results of this study can be summarized as follows –

- The CPB is a viable option for brine and ash co-disposal as a NEB is achieved. Major brine and ash elements such as Ca, Na, Mg, and K are encapsulated with the CPB and a lower leachability is observed when compared to the surface ash disposal. Thus, the environmental impact of FA, CA, and brine is reduced when implemented in backfilling applications.
- Surface area and particle size are the major contributing factors responsible for the leaching behaviour observed for CPB. A finer particle size will improve the pozzolanic activity of the ashes thus creating a greater amount of reaction hydration products which reduces the porosity of the CPB and thus leachability. A smaller exposed surface area is expected to have lower leaching as water percolation is reduced.
- Leachability is further reduced with the addition of small proportions of CA, specifically with regards to the alkali metals, Na and K. The addition of CA improves interparticle friction thus creating a denser CPB which reduces permeability, porosity, and leachability. Thus, it will take a considerable amount of time to remove any mobile trace elements from the CPB upon interaction with the surrounding groundwater.
- Small amounts of major (Na, Ca, Mg and K) and minor species (Al, Mg, Ba) were easily released in the leaching test when in contact with water. This is indicative of surface wash off of the readily available soluble fraction which is deposited on the surface of the monolith and ash. Once this fraction has been removed, the release decreases.
- The release of trace elements from FA and CA is a slow and complex process, strongly dependent on the pH developed during the interaction with the leaching solutions used except for highly soluble elements that are mobile under both acidic and basic conditions.
- At lower pHs, the majority of the major and minor species were released into the solution. Lower release observed at high pHs is a result of precipitation and adsorption processes. The solubility of metals increased as solution pH decreased for Ca, Mg and B whereas solubility was independent of solution pH with regards to the

release of Na, K, and Ba. Cr and Pb exhibited amphoteric behaviour with higher solubility observed at the extreme ends of the pH range.

- The CPB has good acid-neutralizing capacities that are able to minimize the generation of AMD as a result of the soluble fraction of Ca, Na, Mg, and K in these ashes. However, the potential higher release of these alkali metals might exert detrimental effects with regards to the utilization of the ash. Therefore, ash ratios should be chosen in order to ensure the purpose of utilization is met as different ratios will have different leaching characteristics
- The UCS strength development is dependent on particle size. Larger CA particles are not suitable and should undergo particle size reduction before implementation. Finer CA samples would significantly improve the pozzolanic activity of the ashes and thus improve workability and strength development.
- CPB could provide a potential economic benefit as the cost of disposal is reduced and the potential implementation of brine wastewater in mining operations will reduce the cost of wastewater treatment.

It must be noted that the surface ash disposal and CPB application have different requirements due to the difference in applications. It is thus necessary to consult the required legislation and relevant literature when deciding the most appropriate disposal method. The physical and chemical properties of the ashes and brine will ultimately determine the further use as these characteristics will affect the characteristics of the CPB formed.

5. Evaluation of Guidelines

This chapter critically compares the feasibility of the guidelines in Section 4.2 to the practical implementation in the CPB which was presented and analysed in Section 4.3. The results presented in Section 4.2 was data obtained from the raw ash prior to any further use whereas Section 4.3 used the various ashes in the construction of the CPB. This chapter compares the results from both sections in order to determine if a Net Environmental Benefit (NEB) was achieved.

5.1. Summary of Guidelines

A detailed summary of the proposed guidelines for the use of FA, CA and brine in the CPB is listed below –

- Class F ashes should be used ($SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$),
- The silicon dioxide content should be greater than 51% ($SiO_2 \geq 51\%$). This promotes the pozzolanic reaction which enhances strength development.
- The calcium oxide content should be limited to less than 10% ($CaO \leq 10\%$). This promotes the adverse alkali-silica reaction.
- Alkalis, sodium and potassium oxides, should be limited to a total equivalent alkali content of less than 1.5% ($Na_2O_{eq} < 1.5\%$). This refers to the equivalent alkali content of both constituents. Furthermore, when implementing a binding agent, the total alkalis present in cement needs to be limited to less than 0.6%.
- The magnesium oxide content should be limited to less than 5% ($MgO < 5\%$) as concrete expansion due to hydration reactions can cause cracking of the CPB.
- A thorough compositional analysis should be conducted in both the ash and brine prior to use in order to determine the total elemental compositions. This is important in ensuring that the environmental limits set out by SANS10234 are not exceeded especially in the case of the more toxic transition metals. Care should be taken to ensure that TCT0 and LCT0 limits are not exceeded, in the case where these limits are exceeded, the appropriate measures should be put into place.
- The total unburnt carbon content present in the ashes should be below 6% ($LOI < 6\%$)
- Ashes with a small particle size are preferable ($< 20\ \mu m$ for FA and $< 45\ \mu m$ for CA). The smaller particle size of the ashes enhances the pozzolanic reaction.
- A CA substitution in the CPB should be limited to < 10% in cases where the CA has not undergone particle size reduction as CA with a large particle size does not display significant pozzolanic activity. However, CA substitution is necessary and advisable in

low quantities as the addition of CA improves interparticle friction thus creating a denser CPB which reduces permeability, porosity, and leachability. This is specifically with regards to the release of alkali metals as lower leaching is observed.

- A minimum binder content of 5% is necessary to provide sufficient calcium hydroxide necessary for the pozzolanic reaction to occur. Lower binder content will not provide the required long term strength development.
- The pH of the system should remain alkaline because at high pHs, precipitation and adsorption processes are favoured and thus the element mobility is reduced.
- The most mobile elements are Na, Ca, Mg, K, Al, Mg and Ba which are found to be deposited on the surface of the ashes. Care should be taken when using these ashes with excessively high concentrations of these constituents as release occurs upon contact with water.
- It is more beneficial to use fresh ashes than weathered ashes due to the higher SiO_2 content.

These guidelines should be considered when designing a CPB. The practical implementations of using these guidelines are discussed below.

5.2. Workability and Structural Suitability

It is evident from the experimental results that the LOI plays and important role in strength development and needs to be less than 6% for use in the CPB. Since the CA used in the study exceeded the LOI limit, it is confirmed that ash with a high LOI has unfavourable characteristics for use in the CPB. This was seen in the case of CPB mixtures containing high proportions of CA as these mixtures were characteristic of high bleed water formation and significantly longer settling times in comparison to the FA only mixtures (MA1 and MA3). Bleed water is defined as the volume of water that forms on top of the cemented paste when the solid material settles. The bleed formation is undesirable as the water may not be reabsorbed by the paste and may require additional treatment. The bleed water formation is expressed as a percentage of water release of the total water content in the CPB.

Figure 5.1 shows the % bleed formation of the different CCPs analysed. The high LOI observed of both FA1 and CA1 (as shown in Table 4.1) caused the high bleed water formation as shown in Figure 5.1. Since this was an undesirable characteristic, those ashes were not analysed further. It can be seen that in the case of MA3 which contained the highest proportion of CA, the highest bleed formation was also seen in comparison to the mixtures

containing higher proportions of FA. This indicates that a high LOI results in poor workability. In the case of the FA only mixture, a 1.03% bleed was only achieved indicating good workability. Furthermore, this small percentage was reabsorbed by the paste which is desirable. Mahlaba et al. (2011b) found that high LOI ashes exhibited reduced slumping behaviour which indicates that more energy will be required to pump the paste. Consequently, the CPB mixtures which contained a higher proportion of CA with a high LOI did not meet the required minimum strength values. In the case of CA and MA3, the mixtures disintegrated upon being cured in the water bath and hence confirmed that the high LOI and a large particle size do not favour the production of pozzolanic reaction products. The converse was observed with the mixtures containing FA whereby a higher strength development was seen due to the fine particle size of FA. Particle size is a major contributor to the pozzolanic reaction as a smaller particle size has a greater surface area available for reaction. The ashes used in this study met the other stipulated guidelines.

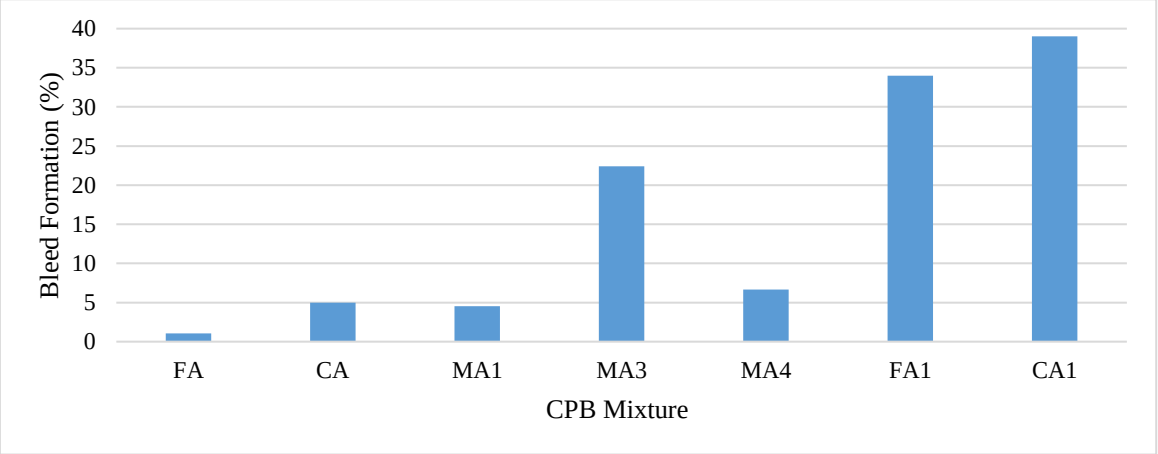

Figure 5-1: CPB Mixtures Bleed Formation

5.3. Net Environmental Benefit

The analysis of the environmental impact in terms of the element mobility was conducted on the raw ashes following surface ash disposal, upon chemical weathering and following the implementation in the CPB. The total elemental concentration in each ash was compared to that of the total elemental concentration leached out for the duration of the various leaching tests and converted to a percentage as shown in Table 5.1. The results are presented graphically in Figures 5.2 and 5.3. A comparison of the percentage leached out in the tank leach test which is used to simulate flooded CPB conditions and the surface ash disposal will allow determination of whether a net environmental benefit is achieved. A net environmental benefit will be achieved if the tank leach test has a lower elemental release

than that of the surface ash disposal. It must be noted that this is based on one criteria, namely that the total leachable fraction is significantly less than the total elemental concentration. There are also other factors which need to be considered when assessing the net environmental benefit. It is suggested that other factors would need to be considered for a holistic view on the NEB.

Table 5-1: Percentage Leached out of Various Elements in Varying Tests

Element	CPB Mixture	% Leached TLT	% Leached WCT	% Leached Surface Disposal
Al	FA	0,006	0,007	0,036
	MA1	0,008	0,013	
	MA3	0,007	0,011	
Pb	FA	0,28	0,23	0,96
	MA1	0,28	0,28	
	MA3	0,26	0,40	
Na	FA	8,27	59,3	54,3
	MA1	2,60	32,8	
	MA3	5,41	40,5	
Mg	FA	0,33	3,46	0,97
	MA1	0,29	2,39	
	MA3	0,45	3,52	
K	FA	1,05	2,66	1,14
	MA1	0,43	1,96	
	MA3	0,74	1,84	
Ca	FA	0,20	3,25	17,6
	MA1	0,36	3,04	
	MA3	0,48	2,76	
Fe	FA	0,004	0,006	0,001
	MA1	0,005	0,005	
	MA3	0,004	0,005	
Ba	FA	0,11	0,49	15,5
	MA1	0,086	0,72	
	MA3	0,091	0,43	

From Figure 5.2, it can be seen that with regards to the release of major elements, the TLT showed the lowest elemental release and thus exhibited the lowest leachability in comparison to the WCT and the surface ash disposal. This indicates that a net environmental

benefit is achieved by implementing both the ash and brine in CPB applications as element mobility is significantly reduced.

The surface ash disposal showed the highest release for all elements followed by the weathering cell test. According to the values reported for Mg, K and Fe, the WCT indicated higher release, and for the FA WCT, the Na release was higher than the surface disposal.

With regards to the release of Na and Ca, it can be seen that a significant portion of the brine remains encapsulated in the CPB. This observation is confirmed by Muriithi et al. (2014) and Fatoba et al. (2015) which suggested that the brine components can be trapped within the ash matrix or may precipitate as salts on the surface of the ash particles. This is extremely beneficial and shows that a net environmental benefit is indeed achieved as the elemental release in the TLT is much lower than that of the surface ash disposal. Furthermore, the CPB mixture containing small proportions of CA (MA1) shows the lowest percentage leached out for Na, Mg, K, Ba and Pb. This further confirms that the presence of CA creates a denser CPB which displays lower leachability. Hence, the addition of CA to CPB mixtures is favourable but should be limited to ensure structural specifications are still met.

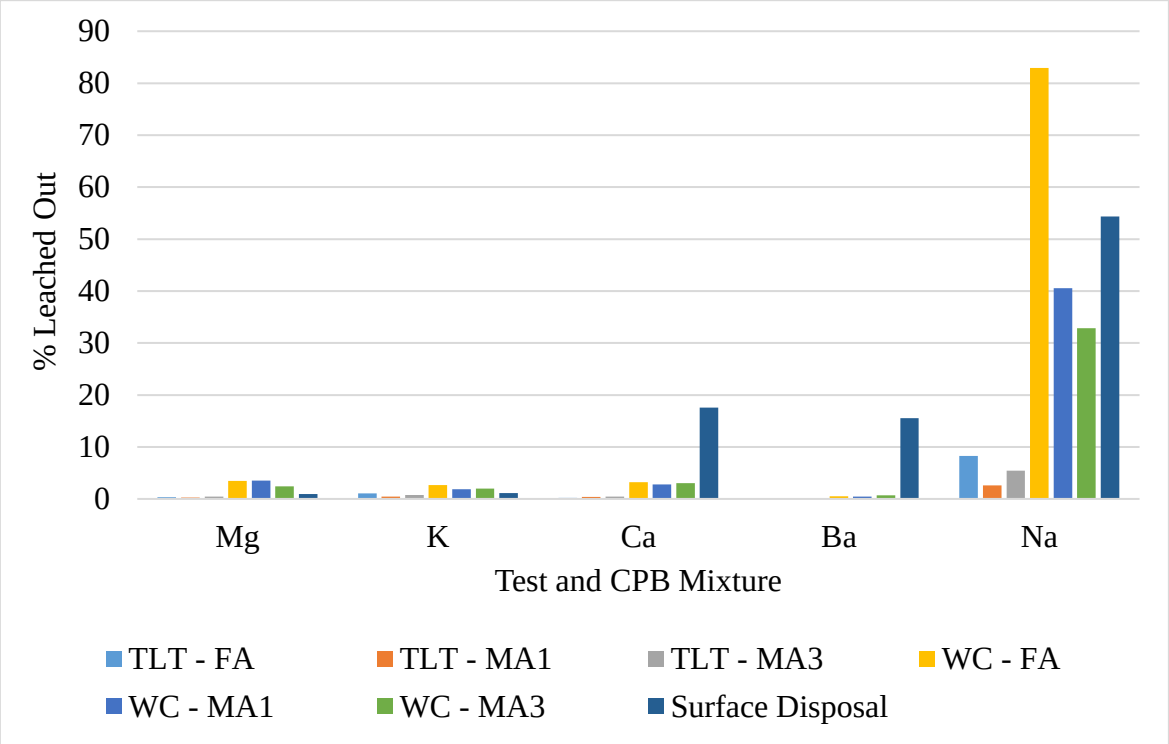

Figure 5-2: Percentage Leached Out of Major Elements from Various Leaching Tests

Figure 5.3 shows that although the glassy matrix breaks down upon chemical weathering, the majority of the total Al and Fe present is not released into solution. This may be why certain brine elements remain encapsulated in this matrix and are not released. Results also show that preference should be given to using fresh ashes due to this glassy matrix being intact.

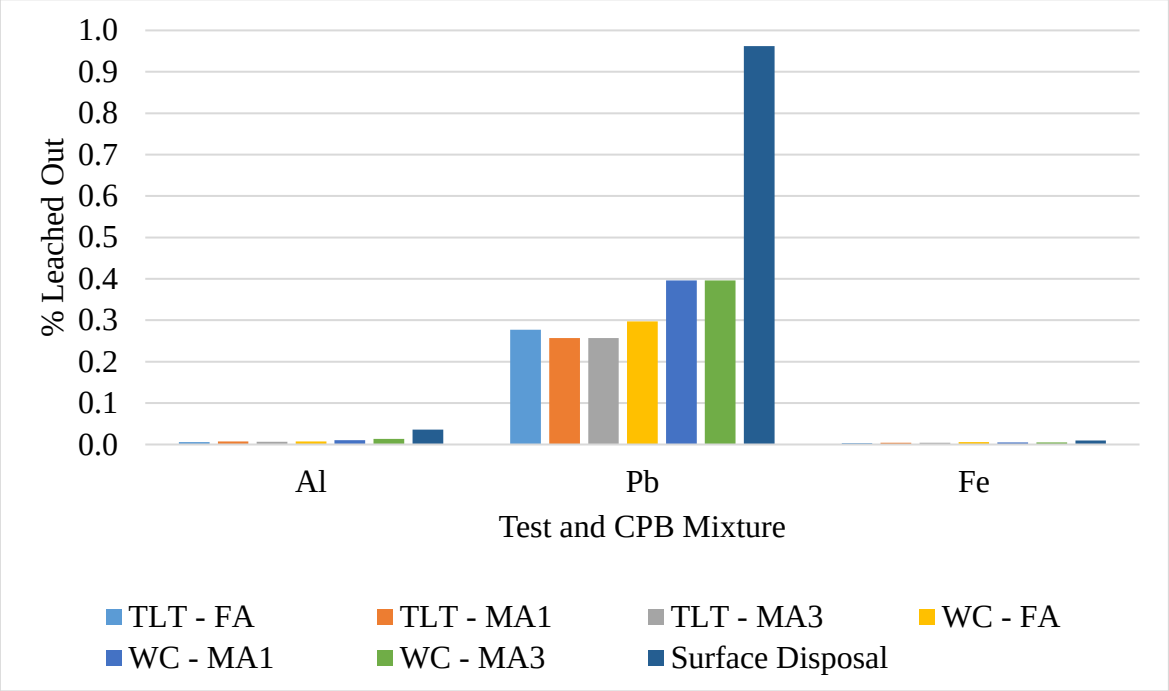

Figure 5-3: Percentage Leached Out of Minor Elements from Various Leaching Tests

6. Discussion and Conclusion

In this chapter the research is considered in its entirety. For clarity, each of the various research questions is restated along with the major findings obtained from this study –

1. What are the chemical or mineralogical factors of the ashes that influence and enhance the pozzolanic reaction?

- The chemical factors of the various ashes that enhance the pozzolanic reaction are a high silica content ($SiO_2 \geq 50\%$), class F ashes ($SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$), the presence of calcium oxide is necessary however should be limited to below 10%. Calcium hydroxide is also necessary for this reaction to occur thus the need for an additional hydration binder such as OPC is mandatory. High alkali content ashes should be avoided as they promote the alkali-silica reaction as opposed to the pozzolanic reaction.
- The mineralogical factors which favour the pozzolanic reaction are a low LOI (< 6%) and the particle size distribution. A high fines content with a high proportion of particles <20 μm in size and spherical particle shape is favourable. The pozzolanic reaction is increased as the particle surface area available for reaction increases. The presence of small proportions of ashes with a larger particle size such as in the case of CA should be limited to <10% substitution as CA does not favour this reaction due to the large particle size. CA should undergo particle size reduction in order to exhibit pozzolanic activity. Approximately 25% of the particles should be <45 μm in size according to the ASTM C618 standards for class F ashes as a pozzolan. This is evident as only the CPB mixtures containing DuraPozz, PozzFill and FA met the required minimum UCS after 28 days with values of 0.94 MPa, 2.17 MPA, and 0.73 MPa, respectively. Furthermore, the FA mixtures showed the greatest proportion of reaction products in comparison to mixtures containing the larger CA particles.

2. What is the relationship between the total leachable fraction and the total elemental concentration of the various elements and compounds found in the CCPs?

- Overall, very few elements exhibited a relationship between the leachable fraction and the total elemental concentration. In the case of fresh ashes, the release of Ca, Na, B, Ga and Sr showed a positive linear relationship whereby a higher leachable fraction was observed as the total concentration of these constituents in the ash increased. This indicates that these elements are deposited on the more soluble phases of the ashes and

are thus easily released upon contact with water. The release is purely availability controlled. In the case of weathered ashes, the release of Si, Fe, K, As, Sb, Ge, Rb, Ce and Li showed a positive linear relationship where leachable fraction increased as the total concentration increased. This relationship indicates that these elements are contained in the glassy fraction of the ash matrix as release only occurs upon long term weathering.

3. What mineral phases form or dissociate through water ingress of the CPB and do the newly formed secondary mineral phases dissociate over time to release contaminants?

- It is evident from the leaching behaviour of the CPB through analysis of the tank leach test and the SEM micrographs that the newly formed secondary mineral phases include the pozzolanic reaction products such as the presence of ettringite, calcium silicate hydrate gel (CSH) and calcium aluminate hydrate. Upon analysis of the leaching behaviour, the dissociation of these phases may occur as a continuous release in Ca and Al is seen which would indicate the dissociation of calcium aluminates or the CSH gel. However, this dissociation is very minimal and these phases do not show any sign of complete dissociation which would lead to the release of contaminants at a later stage. This is shown by the very small percentage leached out (< 0.05%) of Al.

4. How does the co-disposal of CCPs and brine affect the leachability of major and trace elements from the ash-brine interaction in the CPB?

- The leachability is significantly reduced through the co-disposal of both CCPs and brine through the construction of the CPB in comparison to the surface ash disposal methods. It was found that the major constituents in the brine (Ca, Na, Mg and K) are actually removed from the solution and adsorbed onto the fly ash. This is seen as there was a decrease in the TDS of the initial brine solution upon contact with the ashes. Furthermore, the elemental percentage of constituents leached out was significantly lower in the TLT in comparison to the WCT and the surface ash disposal (SD). The results expressed are indicated of the average data for FA, MA1 and MA3 for each test [(Al (TLT – 0.01%, WCT – 0.01%, SD – 0.04%), Pb (TLT – 0.27%, WCT – 0.30%, SD – 0.96%), Na (TLT – 5.43%, WCT – 44.20%, SD – 54.34%), Mg (TLT – 0.36%, WCT – 3.12%, SD – 0.97%), K (TLT – 0.74%, WCT – 2.15%, SD – 1.14%), Ca (TLT – 0.35%, WCT – 3.02%, SD – 17.57%), Fe (TLT – 0.004%, WCT – 0.01%, SD – 0.001%), Ba (TLT – 0.10%, WCT – 0.55%, SD – 15.52%)]. This indicates a large

portion of these constituents are encapsulated in the CPB and are not easily released upon water ingress.

5. What mix design of FA, CA and brine have the most favourable characteristics for the further use of the CPB in terms of structural and environmental suitability?

- Mix designs which produce the most favourable characteristics are designs containing greater proportions of FA (> 90%) and lower proportions of CA (< 10%). This mix design promotes interparticle friction between the ash particles which enhances the flow of the paste backfill and creates a denser backfill which exhibits lower leachability especially in the release of Na, K and Mg which are major brine constituents.

6. Is the co-disposal of brine, FA and CA through the construction of a CPB environmentally and structurally suitable and sustainable?

- The co-disposal of brine, FA and CA through the construction of a CPB is indeed environmentally and structurally suitable and sustainable. It is evident from the various leaching tests that the current surface ash disposal methods have a much higher elemental release and a greater negative risk on the environment. Thus, the CPB poses a much lower environmental risk which would be more sustainable as a long term usage of waste as opposed to the current surface ash disposal techniques. Furthermore, the CPB mixtures did meet the minimum required strength development values thus both these parameters of environmental and structural suitability are satisfied.

The aim of this study was to find a sustainable long term solution for the disposal of brines and CCPs through the development of a CPB. This was effectively done through the various leaching tests and strength tests. The relationship between leachability and concentration or elemental mass composition of the various CCPs was determined through statistical analysis which allowed for the development of guidelines which related the chemical and physical characteristics of the ashes (FA and CA) to the environmental and structural suitability in the CPB. Furthermore, a detailed insight into the leaching and removal of major and trace elements from the CPB ash-brine interaction systems was conducted. Lastly, the optimal mix-design to develop a CPB with the required structural and environmental properties was proposed. All the above stated aims were met through the answering of the various research questions.

In conclusion, a net environmental benefit can be achieved when utilizing waste in a CPB as opposed to the current surface ash disposal methods. This study shows that the CPB can effectively reduce the current environmental impact of surface ash disposal methods by proposing a more environmentally suitable disposal option whereby fly ash, CA and brine and be co-disposed of through the development of a CPB. Furthermore, it is noted that surface ash disposal and CPB application have different requirements due to the difference in applications. It is thus necessary to consult the required legislation and relevant literature when deciding the most appropriate disposal method. The physical and chemical properties of the ashes and brine will ultimately determine the further use as these characteristics will affect the characteristics of the newly formed CPB.

6.1. Recommendations

The aim of this study was to examine the environmental and structural feasibility of CPB applications. The results presented in this study have enabled the author to recommend guidelines when designed a CPB as well as potential outcomes. However, there is a need to continue with the research in this field since there is insufficient data available for a larger full-scale implementation.

Recommendations for future work would include –

- A potential study could further examine the hydration and pozzolanic reaction and the kinetics thereof. The determination of this would allow further understanding into possible ways to enhance or accelerate the pozzolanic reactions through the potential use of additives or the controlling of external factors such as temperature or pressure.
- Construction of a pilot plant which would allow a better understanding of large-scale paste production as the laboratory scale does not accurately simulate the actual field conditions.
- The use of a brine from an actual desalination plant may behave differently to that of the synthetic brine used in this study. It could be useful for the experiments done here to be repeated on a real brine.
- The use of CA which has undergone particle size reduction in order to more closely determine the pozzolanic reactivity of CA.

- To further close the research gap, the potential use of both class C and class F ashes in order to determine the full extent that the CaO content plays in the environmental and structural implications of the CPB.
- Due to the range of different ashes as well as the complexity of the mineralogy of these ashes, there is a limitation proposed by the use of XRD as an analytical technique. Thus, it is advisable that more analysis be done to determine the mineral compositions of both the raw ashes and CPB by using different analytical techniques in order to fully understand the mineral transformation in the ashes and reaction products produced.
- The assessment of the NEB was based on one criteria, namely that the total leachable fraction is significantly less than the total elemental concentration. There are also other factors which need to be considered when assessing the net environmental benefit. It is suggested that other factors would need to be considered for a holistic view on the NEB such as the operating costs of the backfilling operation versus a surface ash disposal facility.

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Appendices

Appendix A: Statistical Analysis Raw Data of CCPs Major Oxides

State And Type		% SiO2	% Al2O3	% Fe(total)	% Fe2O3	% TiO2	% CaO	% MgO	% Na2O	% K2O	% MnO
CA	W	54,7	28,5	2,60	3,72	1,61	6,29	1,70	0,260	0,707	0,043
CA	F	50,4	26,5	3,60	5,14	1,56	8,87	2,04	0,400	0,613	0,037
CA	F	59,3	24,7	4,39	6,28	1,25	3,52	1,03	0,097	0,872	0,072
CA	W	45,6	24,0	2,75	3,93	1,39	8,25	1,46	0,540	0,894	0,035
CA	F	57,2	24,1	4,04	5,77	1,41	7,92	1,29	0,130	0,780	0,050
CA	F	59,8	25,3	4,69	3,28	1,34	5,24	1,47	0,340	0,926	0,054
CA	F	62,2	27,1	5,12	3,58	1,22	2,86	1,05	0,098	0,949	0,083
CA	F	59,7	23,6	6,06	8,67	1,19	3,29	1,01	0,093	0,731	0,077
CA	F	56,5	26,5	3,78	5,40	1,59	6,50	1,67	0,180	0,819	0,043
CA	F	53,7	27,7	2,83	4,04	1,66	6,79	2,06	0,350	0,845	0,033
CA	W	53,6	27,9	3,09	4,42	1,62	7,11	1,83	0,290	0,654	0,035
CA	F	54,3	32,0	2,20	1,54	1,66	5,52	1,85	0,340	0,893	0,036
CA	F	55,8	26,3	4,37	3,05	1,35	8,65	1,55	0,220	0,919	0,057
CA	F	54,7	24,9	4,59	6,56	1,34	5,28	1,52	0,144	0,685	0,060
CA	W	53,1	27,3	4,01	5,73	1,51	4,70	1,40	0,119	0,732	0,052
CA	W	51,2	33,4	2,44	3,48	1,88	2,85	0,83	0,100	0,868	0,034
CA	F	47,5	26,1	2,85	4,08	1,32	4,80	1,82	0,404	0,990	0,033
CA	F	53,7	28,8	1,93	2,77	1,54	3,81	1,35	0,279	0,915	0,032
CA	F	52,2	25,8	6,11	8,73	1,42	7,62	2,47	0,201	0,783	0,058
CA	F	50,8	28,6	5,58	7,98	1,58	4,32	1,00	0,121	0,601	0,049
CA	W	58,1	24,5	4,51	6,46	1,50	4,98	1,76	0,099	0,598	0,054
CA	F	64,643	21,658	4,472	6,396	1,452	3,909	1,488	0,140	0,651	0,050
FA	F	55,8	29,2	5,33	7,62	1,46	3,66	1,06	0,100	0,761	0,067
FA	W	48,5	21,2	3,61	5,17	1,37	9,15	1,96	0,260	0,843	0,044
FA	F	50,8	26,2	2,17	3,10	1,45	6,73	1,20	0,210	0,755	0,031
FA	W	49,4	27,2	2,45	3,50	1,58	7,40	1,83	0,460	0,643	0,031
FA	F	56,1	30,6	3,64	2,55	1,65	4,55	1,27	0,190	0,758	0,043
FA	F	60,0	26,0	4,60	3,22	1,23	3,07	1,14	0,120	1,057	0,121
FA	W	47,9	25,9	2,21	1,54	1,38	5,89	1,05	0,190	0,777	0,034
FA	F	54,8	27,0	3,14	4,49	1,58	6,85	1,42	0,240	0,570	0,038
FA	F	59,4	25,4	3,07	4,39	1,42	5,41	1,15	0,240	0,703	0,030
FA	F	54,1	28,2	3,28	4,69	1,67	5,84	1,54	0,180	0,826	0,046
FA	W	54,3	29,4	2,67	3,81	1,63	6,18	1,69	0,320	0,680	0,029
FA	W	54,2	29,7	3,21	2,24	1,51	6,81	1,68	0,280	0,673	0,045
FA	F	55,4	30,6	2,64	1,85	1,56	6,07	1,69	0,290	0,798	0,038
FA	F	51,1	30,9	2,33	1,63	1,76	9,06	2,09	0,340	1,012	0,044
FA	F	54,8	28,0	4,25	6,08	1,53	5,58	1,56	0,114	0,714	0,056

FA	W	54,5	22,3	5,80	8,30	1,31	5,50	1,48	0,079	0,583	0,067
FA	W	52,1	35,5	1,84	2,64	1,98	2,21	0,68	0,101	0,851	0,029
FA	F	53,4	21,9	4,62	6,60	1,11	5,84	1,70	0,260	1,038	0,045
FA	F	59,8	28,2	3,13	4,48	1,78	3,50	1,13	0,120	1,038	0,057
FA	F	50,2	29,3	3,71	5,30	1,63	7,73	2,52	0,245	0,959	0,073
FA	F	51,41	31,62	3,92	5,61	1,72	3,94	0,88	0,08	0,67	0,06
FA	F	52,2	34,2	3,22	4,61	1,90	3,33	0,80	0,077	0,738	0,025
FA	F	54,9	26,7	2,99	4,27	1,52	3,53	1,51	0,109	0,604	0,040
FA	W	55,8	27,1	3,66	5,23	1,51	4,49	1,74	0,110	0,613	0,045
MA	W	51,4	24,1	3,52	5,03	1,41	4,90	1,29	0,470	0,753	0,040
MA	F	59,2	26,1	2,54	3,63	1,48	4,51	1,12	0,310	0,689	0,026
MA	W	57,1	24,6	3,01	4,30	1,61	7,04	2,09	0,330	0,745	0,036
MA	F	57,2	26,9	4,76	6,81	1,40	3,29	1,06	0,110	0,767	0,065
MA	W	92,7	3,94	1,14	0,80	0,36	0,27	0,09	0,018	0,437	0,013
MA	W	55,2	31,9	4,17	2,92	1,51	3,66	1,03	0,120	0,762	0,067
MA	W	80,3	9,94	1,66	1,16	0,57	1,02	0,43	0,330	1,175	0,062
MA	F	59,1	28,4	2,92	2,04	1,50	5,11	1,16	0,290	0,746	0,034
MA	F	55,9	29,1	3,93	2,75	1,60	4,24	1,25	0,310	0,806	0,041
MA	F	56,2	26,2	4,26	2,98	1,44	4,99	1,49	0,520	0,834	0,054
MA	F	61,7	26,7	4,79	3,35	1,19	2,48	0,78	0,100	0,912	0,069
MA	W	53,1	29,1	4,94	7,06	1,45	4,03	1,35	0,100	0,718	0,063
MA	W	52,6	27,3	3,48	4,97	1,67	6,47	1,66	0,180	0,768	0,049
MA	F	54,3	28,4	3,21	4,58	1,67	5,86	1,56	0,160	0,796	0,043
MA	F	52,13	28,38	2,55	3,64	1,44	5,01	1,77	0,37	1,14	0,05
MA	W	59,0	22,5	5,23	7,48	1,14	5,82	1,76	0,290	1,063	0,058
MA	W	67,3	18,4	6,84	9,79	1,35	3,84	1,28	0,129	0,722	0,055
MA	F	64,0	16,5	6,04	8,63	1,47	4,30	1,26	0,055	0,687	0,036
MA	F	50,8	31,8	1,55	2,21	1,80	4,34	1,58	0,403	1,347	0,052
MA	W	52,3	25,6	5,31	7,59	1,21	6,53	2,07	0,256	0,747	0,057

State And Type		**% P**	**% Ba**	**% Cr**	**% Cu**	**% Ni**	**% Pb**
CA	W	0,258	0,158	0,021	0,006	0,009	0,003
CA	F	0,201	0,195	0,017	0,005	0,004	<0.001
CA	F	0,145	0,111	0,016	0,007	0,007	0,003
CA	W	0,197	0,141	0,016	0,005	0,005	<0.001
CA	F	0,182	0,095	0,017	0,005	0,004	<0.001
CA	F	0,069	0,077	0,023	0,004	0,009	0,001
CA	F	0,144	0,107	0,015	0,006	0,009	0,005
CA	F	0,097	0,101	0,017	0,005	0,008	0,001
CA	F	0,120	0,116	0,018	0,006	0,005	<0.001
CA	F	0,227	0,172	0,019	0,007	0,004	0,001

CA	W	0,170	0,166	0,020	0,005	0,004	0,003
CA	F	0,353	0,180	0,022	0,008	0,007	0,003
CA	F	0,152	0,119	0,020	0,004	0,003	0,001
CA	F	0,321	0,110	0,017	0,003	0,006	0,002
CA	W	0,377	0,121	0,021	0,005	0,007	0,004
CA	W	0,246	0,102	0,019	0,004	0,004	0,004
CA	F	0,326	0,150	0,017	0,004	0,007	0,007
CA	F	0,193	0,212	0,024	0,006	0,010	0,006
CA	F	0,138	0,094	0,017	0,003	0,004	0,003
CA	F	0,188	0,099	0,019	0,005	0,005	0,004
CA	W	0,170	0,107	0,022	0,005	0,008	0,005
CA	F	0,082	0,079	0,022	0,003	0,009	0,005
FA	F	0,179	0,107	0,017	0,006	0,008	0,005
FA	W	0,227	0,139	0,013	0,005	0,006	0,001
FA	F	0,193	0,115	0,013	0,006	0,006	0,001
FA	W	0,241	0,187	0,015	0,006	0,006	<0.001
FA	F	0,184	0,106	0,029	0,006	0,025	0,008
FA	F	0,220	0,115	0,016	0,008	0,010	0,009
FA	W	0,216	0,113	0,019	0,004	0,005	0,003
FA	F	0,203	0,142	0,016	0,005	0,005	<0.001
FA	F	0,117	0,100	0,019	0,005	0,005	0,001
FA	F	0,214	0,121	0,023	0,007	0,006	0,003
FA	W	0,208	0,175	0,016	0,005	0,004	0,004
FA	W	0,199	0,150	0,024	0,004	0,004	0,000
FA	F	0,308	0,165	0,017	0,006	0,005	0,008
FA	F	0,285	0,177	0,017	0,006	0,006	0,001
FA	F	0,343	0,124	0,017	0,004	0,007	0,005
FA	W	0,322	0,111	0,025	0,004	0,006	0,004
FA	W	0,230	0,099	0,020	0,005	0,005	0,007
FA	F	0,194	0,125	0,014	0,003	0,008	0,004
FA	F	0,170	0,076	0,032	0,004	0,009	0,005
FA	F	0,278	0,146	0,030	0,004	0,007	0,004
FA	F	0,21	0,10	0,03	0,00	0,01	0,00
FA	F	0,210	0,119	0,016	0,004	0,006	0,005
FA	F	0,119	0,088	0,019	0,005	0,009	0,006
FA	W	0,203	0,121	0,024	0,006	0,008	0,004
MA	W	0,118	0,109	0,028	0,008	0,008	0,006
MA	F	0,160	0,103	0,024	0,006	0,006	0,003
MA	W	0,161	0,167	0,017	0,005	0,004	0,002
MA	F	0,187	0,118	0,014	0,007	0,007	0,004
MA	W	0,014	0,013	0,015	0,001	0,002	0,000
MA	W	0,239	0,156	0,015	0,006	0,007	0,005
MA	W	0,041	0,047	0,013	0,002	0,002	0,002
MA	F	0,233	0,123	0,024	0,006	0,005	0,001
MA	F	0,202	0,141	0,028	0,006	0,007	0,006

MA	F	0,128	0,099	0,025	0,006	0,009	0,005
MA	F	0,140	0,103	0,017	0,006	0,005	0,002
MA	W	0,192	0,129	0,022	0,007	0,051	0,004
MA	W	0,185	0,116	0,019	0,006	0,005	0,005
MA	F	0,198	0,120	0,017	0,006	0,005	0,002
MA	F	0,20	0,14	0,02	0,005	0,01	0,01
MA	W	0,141	0,118	0,014	0,003	0,007	0,001
MA	W	0,112	0,076	0,024	0,004	0,007	0,001
MA	F	0,104	0,131	0,026	0,004	0,008	0,005
MA	F	0,299	0,144	0,025	0,005	0,007	0,006
MA	W	0,334	0,201	0,022	0,005	0,009	0,004

State And Type		**% Sr**	**% V**	**% Zn**	**% Zr**	**% C**	**% S**	**% LOI**
CA	W	0,180	0,014	0,004	0,038	1,140	0,150	1,4
CA	F	0,229	0,010	0,002	0,037	1,080	0,140	3,9
CA	F	0,046	0,018	0,013	0,038	0,690	0,120	2,6
CA	W	0,228	0,010	0,002	0,026	1,690	0,150	13,4
CA	F	0,128	0,009	0,001	0,039	0,320	0,087	0,7
CA	F	0,078	0,011	0,003	0,022	1,660	0,094	2,1
CA	F	0,041	0,018	0,013	0,037	0,580	0,089	0,8
CA	F	0,040	0,014	0,007	0,037	0,560	0,022	1,3
CA	F	0,126	0,011	0,004	0,034	0,400	0,052	0,9
CA	F	0,196	0,012	0,003	0,033	1,060	0,130	2,3
CA	W	0,184	0,011	0,002	0,036	0,910	0,110	1,9
CA	F	0,201	0,016	0,006	0,037	0,980	0,270	1,1
CA	F	0,154	0,009	0,001	0,025	0,440	0,370	1,3
CA	F	0,099	0,011	0,005	0,041	6,16	0,074	6,86
CA	W	0,114	0,014	0,010	0,044	3,84	0,172	6,59
CA	W	0,183	0,014	0,004	0,051	5,15	0,148	6,69
CA	F	0,185	0,014	0,005	0,034	9,89	0,362	13,86
CA	F	0,202	0,016	0,008	0,042	4,73	0,417	8,72
CA	F	0,152	0,013	0,004	0,048	1,78	0,166	2,26
CA	F	0,169	0,014	0,005	0,053	5,84	0,171	6,18
CA	W	0,108	0,012	0,004	0,043	2,99	0,096	3,84
CA	F	0,080	0,014	0,004	0,046	1,520	0,036	1,576
FA	F	0,044	0,017	0,011	0,041	0,470	0,110	0,5
FA	W	0,212	0,010	0,004	0,026	1,220	0,150	11,6
FA	F	0,170	0,011	0,002	0,027	0,830	0,210	8,8
FA	W	0,212	0,012	0,003	0,037	2,560	0,180	7,2
FA	F	0,113	0,015	0,006	0,031	1,290	0,130	1,0
FA	F	0,042	0,026	0,030	0,039	0,420	0,940	3,0
FA	W	0,158	0,011	0,002	0,023	0,830	0,230	14,3
FA	F	0,171	0,010	0,004	0,039	1,500	0,060	1,9

FA	F	0,097	0,012	0,003	0,030	0,610	0,056	1,1
FA	F	0,138	0,015	0,007	0,035	1,770	0,130	2,6
FA	W	0,184	0,012	0,003	0,035	0,720	0,140	0,9
FA	W	0,174	0,011	0,002	0,038	1,580	0,092	2,2
FA	F	0,186	0,015	0,004	0,035	0,620	0,190	0,8
FA	F	0,268	0,014	0,002	0,030	0,520	0,310	0,7
FA	F	0,110	0,012	0,008	0,045	3,24	0,164	3,82
FA	W	0,099	0,012	0,005	0,045	4,14	0,214	6,75
FA	W	0,183	0,015	0,006	0,050	3,72	0,132	5,53
FA	F	0,148	0,011	0,004	0,039	9,12	0,280	8,33
FA	F	0,076	0,012	0,008	0,052	1,74	0,160	2,44
FA	F	0,158	0,012	0,001	0,042	2,58	0,178	2,77
FA	F	0,15	0,01	0,01	0,05	5,19	0,14	5,29
FA	F	0,092	0,011	0,007	0,042	3,06	0,132	3,30
FA	F	0,086	0,018	0,008	0,040	8,76	0,126	9,28
FA	W	0,129	0,014	0,009	0,041	4,66	0,101	6,48
MA	W	0,107	0,013	0,007	0,028	2,060	0,130	10,0
MA	F	0,104	0,015	0,005	0,030	0,340	0,110	2,5
MA	W	0,190	0,011	0,001	0,039	0,850	0,031	1,3
MA	F	0,048	0,018	0,012	0,039	1,050	0,110	2,6
MA	W	0,004	0,003	0,002	0,006	0,280	0,010	1,5
MA	W	0,062	0,019	0,013	0,039	0,700	0,093	1,8
MA	W	0,021	0,006	0,003	0,009	0,910	0,023	3,3
MA	F	0,120	0,015	0,004	0,031	0,750	0,110	1,2
MA	F	0,125	0,015	0,006	0,029	1,590	0,180	2,9
MA	F	0,094	0,014	0,005	0,027	2,510	0,260	4,0
MA	F	0,041	0,018	0,012	0,036	0,920	0,037	2,4
MA	W	0,058	0,017	0,010	0,041	1,320	0,150	2,6
MA	W	0,149	0,014	0,004	0,036	1,240	0,150	3,4
MA	F	0,134	0,014	0,003	0,035	1,270	0,097	2,3
MA	F	0,16	0,01	0,01	0,04	5,56	0,24	8,90
MA	W	0,140	0,009	0,008	0,042	2,77	0,138	3,60
MA	W	0,070	0,013	0,006	0,051	1,25	0,096	1,62
MA	F	0,123	0,017	0,009	0,037	1,04	0,083	2,83
MA	F	0,184	0,013	0,003	0,041	4,46	0,255	6,82
MA	W	0,213	0,015	0,004	0,045	3,38	0,193	5,06

Appendix B: Statistical Analysis Raw Data of CCPs Leachability

State And Type		Leachability - mg/l									
		Ag	Al	As	Au	B	Ba	Be	Bi	Ca	Cd
CA	W	<0.001	0,735	0,001	<0.001	0,094	0,745	<0.001	<0.001	382	0,0004
CA	F	<0.001	0,343	0,002	<0.001	0,089	0,144	<0.001	<0.001	42,0	0,0002
CA	F	<0.001	1,742	0,013	<0.001	0,139	0,164	<0.001	<0.001	75,6	0,0003
CA	W	<0.001	1,000	0,011	<0.001	0,569	0,072	<0.001	<0.001	9,34	0,0007
CA	F	<0.001	0,893	0,004	<0.001	0,044	0,051	<0.001	<0.001	52,8	0,0002
CA	F	<0.001	0,721	0,003	<0.001	0,052	0,063	<0.001	<0.001	40,3	0,0003
CA	F	<0.001	4,930	0,015	<0.001	0,178	0,101	<0.001	<0.001	80,1	0,0003
CA	F	<0.001	0,803	0,004	<0.001	0,011	0,078	<0.001	<0.001	17,0	0,0003
CA	F	<0.001	0,624	0,003	<0.001	0,049	0,064	<0.001	<0.001	27,2	0,0002
CA	F	<0.001	3,103	<0.001	<0.001	0,016	0,526	<0.001	<0.001	224	0,0003
CA	W	<0.001	3,224	0,003	<0.001	0,188	0,085	<0.001	<0.001	51,6	0,0002
CA	F	<0.001	2,024	0,002	<0.001	0,258	0,942	<0.001	<0.001	357	0,0004
CA	F	<0.001	1,739	0,001	<0.001	0,063	0,073	<0.001	<0.001	65,7	0,0003
CA	F	0,001	0,958	0,003	<0.001	0,057	0,138	<0.001	<0.001	83,3	0,0003
CA	W	0,001	2,416	0,007	<0.001	0,386	0,177	<0.001	<0.001	77,8	0,0003
CA	W	0,001	2,861	0,015	<0.001	0,458	0,130	<0.001	<0.001	64,7	0,0003
CA	F	0,001	1,300	0,007	<0.001	1,169	0,219	<0.001	<0.001	96,2	0,0004
CA	F	<0.001	0,284	0,011	<0.001	1,577	0,195	<0.001	<0.001	280	0,0031
CA	F	<0.001	2,440	0,002	<0.001	0,148	0,203	<0.001	<0.001	65,2	0,0002
CA	F	0,00	0,72	0,01	<0.001	0,14	0,09	<0.001	<0.001	48,96	0,00
CA	W	<0.001	2,555	0,009	<0.001	0,258	0,102	<0.001	<0.001	70,9	0,0002
CA	F	<0.001	0,773	0,004	<0.001	0,050	0,106	<0.001	<0.001	20,1	0,0003
FA	F	<0.001	4,647	0,010	<0.001	0,165	0,154	<0.001	<0.001	165	0,0004
FA	W	<0.001	1,706	0,001	<0.001	0,236	0,088	<0.001	<0.001	63,4	0,0004
FA	F	<0.001	4,227	<0.001	<0.001	0,048	0,173	<0.001	<0.001	122	0,0004
FA	W	<0.001	0,447	0,003	<0.001	0,275	0,107	<0.001	<0.001	55,8	0,0006
FA	F	<0.001	4,229	0,005	<0.001	0,158	0,370	<0.001	<0.001	295	0,0004
FA	F	<0.001	0,225	0,027	<0.001	0,998	0,092	<0.001	<0.001	392	0,0009
FA	W	<0.001	3,937	0,002	<0.001	0,071	0,116	<0.001	<0.001	89,8	0,0003
FA	F	<0.001	0,932	0,002	<0.001	0,038	0,064	<0.001	<0.001	33,2	0,0002
FA	F	<0.001	7,777	0,003	<0.001	0,271	0,087	<0.001	<0.001	87,3	0,0003
FA	F	<0.001	4,005	0,004	<0.001	0,129	0,367	<0.001	<0.001	241	0,0003
FA	W	<0.001	4,862	0,001	<0.001	0,060	0,183	<0.001	<0.001	124	0,0003
FA	W	<0.001	0,919	0,002	<0.001	0,055	0,077	<0.001	<0.001	42,4	0,0002
FA	F	<0.001	0,706	0,001	<0.001	0,104	0,866	<0.001	<0.001	424	0,0004
FA	F	<0.001	0,043	0,000	<0.001	0,080	1,910	<0.001	<0.001	1372	0,0004
FA	F	0,001	0,288	<0.001	<0.001	0,009	1,082	<0.001	<0.001	586	0,0003
FA	W	0,001	0,831	0,005	<0.001	0,175	0,132	<0.001	<0.001	83,8	0,0002
FA	W	0,001	2,515	0,020	<0.001	0,637	0,150	<0.001	<0.001	58,4	0,0004

FA	F	0,001	0,281	0,001	<0.001	0,064	1,463	<0.001	<0.001	1076	0,0004
FA	F	<0.001	0,691	<0.001	<0.001	0,190	1,022	<0.001	<0.001	417	0,0007
FA	F	<0.001	0,597	<0.001	<0.001	0,038	2,511	<0.001	<0.001	1142	0,0003
FA	F	<0.001	2,753	<0.001	<0.001	0,046	0,798	<0.001	<0.001	395	0,0004
FA	F	<0.001	8,343	<0.001	<0.001	0,275	0,614	<0.001	<0.001	284	0,0005
FA	F	<0.001	1,465	<0.001	<0.001	0,083	0,967	<0.001	<0.001	369	0,0007
FA	W	<0.001	4,474	<0.001	<0.001	0,277	0,149	<0.001	<0.001	55,4	0,0004
MA	W	<0.001	2,858	0,001	<0.001	0,145	0,160	<0.001	<0.001	79,4	0,0003
MA	F	<0.001	0,586	0,016	<0.001	0,307	0,090	<0.001	<0.001	34,4	0,0002
MA	W	<0.001	3,751	0,010	<0.001	0,350	0,154	<0.001	<0.001	73,5	0,0003
MA	F	<0.001	1,224	0,002	<0.001	0,008	0,092	<0.001	<0.001	10,8	0,0002
MA	W	<0.001	2,287	0,009	<0.001	0,097	0,143	<0.001	<0.001	83,0	0,0003
MA	W	<0.001	6,941	0,007	<0.001	0,114	0,444	<0.001	<0.001	14,5	0,0003
MA	W	<0.001	0,257	0,012	<0.001	0,035	0,095	<0.001	<0.001	27,1	0,0003
MA	F	<0.001	3,508	0,008	<0.001	0,100	0,333	<0.001	<0.001	14,2	0,0003
MA	F	<0.001	7,988	0,003	<0.001	0,496	0,227	<0.001	<0.001	105	0,0004
MA	F	<0.001	6,514	0,007	<0.001	0,291	0,154	<0.001	<0.001	96,6	0,0002
MA	F	<0.001	2,151	0,007	<0.001	0,279	0,085	<0.001	<0.001	108	0,0005
MA	W	<0.001	0,424	0,019	<0.001	0,030	0,091	<0.001	<0.001	15,0	0,0003
MA	W	<0.001	4,110	0,002	<0.001	0,089	0,081	<0.001	<0.001	86,3	0,0003
MA	F	<0.001	5,705	0,004	<0.001	0,151	0,053	<0.001	<0.001	46,7	0,0004
MA	F	<0.001	3,711	0,001	<0.001	0,048	0,363	<0.001	<0.001	141	0,0003
MA	W	0,001	2,514	0,006	<0.001	0,725	0,088	<0.001	<0.001	67,0	0,0006
MA	W	0,001	0,661	0,004	<0.001	0,227	0,110	<0.001	<0.001	33,3	0,0003
MA	F	<0.001	2,425	0,006	<0.001	0,257	0,159	<0.001	<0.001	69,6	0,0003
MA	F	<0.001	3,292	<0.001	<0.001	0,109	0,360	<0.001	<0.001	126	0,0003
MA	W	<0.001	7,782	<0.001	<0.001	0,614	0,216	<0.001	<0.001	130	0,0007

State And Type		**Leachability - mg/l**									
		Ce	**Co**	**Cr**	**Cs**	**Cu**	**Fe**	**Ga**	**Ge**	**Hf**	**Hg**
CA	W	<0.001	0,001	0,174	<0.001	0,001	0,047	0,021	<0.001	<0.001	0,0007
CA	F	<0.001	<0.001	0,007	<0.001	0,001	0,005	0,003	<0.001	<0.001	0,0002
CA	F	<0.001	<0.001	0,105	0,001	<0.001	0,010	0,016	<0.001	<0.001	0,0009
CA	W	<0.001	<0.001	0,789	0,011	0,001	0,013	0,016	0,002	<0.001	0,0019
CA	F	<0.001	<0.001	0,009	0,001	<0.001	0,006	0,002	0,001	<0.001	0,0004
CA	F	<0.001	<0.001	0,003	<0.001	0,003	0,007	0,001	0,001	<0.001	0,0005
CA	F	<0.001	<0.001	0,065	<0.001	<0.001	0,004	0,024	<0.001	<0.001	0,0012
CA	F	0,001	<0.001	0,003	<0.001	<0.001	0,118	0,001	<0.001	<0.001	0,0001
CA	F	<0.001	<0.001	0,026	<0.001	<0.001	0,023	0,001	0,001	<0.001	<0.0001
CA	F	<0.001	<0.001	0,078	0,001	0,001	0,004	0,008	<0.001	<0.001	0,0003
CA	W	<0.001	<0.001	0,072	<0.001	<0.001	0,007	0,014	<0.001	<0.001	0,0004
CA	F	<0.001	<0.001	0,348	0,001	<0.001	0,001	0,032	<0.001	<0.001	0,0014
CA	F	<0.001	<0.001	0,016	0,001	0,001	0,008	0,003	<0.001	<0.001	0,0012
CA	F	<0.001	<0.001	0,004	<0.001	0,007	0,012	0,003	0,001	<0.001	0,0002
CA	W	<0.001	<0.001	0,097	<0.001	0,002	0,008	0,019	<0.001	<0.001	0,0007

CA	W	0,001	<0.001	0,052	<0.001	0,002	0,003	0,018	<0.001	<0.001	0,0009
CA	F	<0.001	<0.001	0,074	<0.001	0,001	0,005	0,037	<0.001	<0.001	0,0025
CA	F	<0.001	<0.001	1,360	<0.001	0,004	0,013	0,015	0,001	<0.001	0,0025
CA	F	<0.001	<0.001	0,011	<0.001	0,002	0,007	0,003	<0.001	<0.001	0,0004
CA	F	<0.001	<0.001	0,01	<0.001	0,00	0,00	0,00	0,00	<0.001	0,00
CA	W	<0.001	<0.001	0,041	<0.001	0,001	0,007	0,014	<0.001	<0.001	0,0005
CA	F	<0.001	0,003	0,006	<0.001	0,007	0,062	0,001	<0.001	<0.001	0,0001
FA	F	<0.001	<0.001	0,054	<0.001	<0.001	0,017	0,022	<0.001	<0.001	0,0011
FA	W	<0.001	<0.001	0,119	0,002	0,004	0,009	0,021	<0.001	<0.001	0,0004
FA	F	<0.001	<0.001	0,240	0,013	<0.001	0,004	0,025	<0.001	<0.001	0,0003
FA	W	<0.001	<0.001	0,216	0,001	<0.001	0,001	0,008	0,001	<0.001	0,0004
FA	F	<0.001	<0.001	0,268	<0.001	0,001	0,007	0,022	<0.001	<0.001	0,0012
FA	F	<0.001	0,004	0,046	0,005	0,001	0,005	0,008	0,024	<0.001	0,0036
FA	W	<0.001	<0.001	0,252	0,010	0,001	0,010	0,029	<0.001	<0.001	0,0001
FA	F	<0.001	<0.001	0,004	<0.001	<0.001	0,005	0,001	<0.001	<0.001	0,0001
FA	F	<0.001	<0.001	0,090	<0.001	<0.001	0,006	0,016	<0.001	<0.001	0,0002
FA	F	<0.001	<0.001	0,192	<0.001	<0.001	0,004	0,018	<0.001	<0.001	0,0007
FA	W	<0.001	<0.001	0,156	0,001	<0.001	0,006	0,010	<0.001	<0.001	0,0003
FA	W	<0.001	<0.001	0,006	<0.001	<0.001	0,003	0,002	<0.001	<0.001	0,0002
FA	F	<0.001	0,001	0,207	0,001	<0.001	0,005	0,018	<0.001	<0.001	0,0009
FA	F	<0.001	0,001	0,434	0,001	0,002	0,009	0,000	<0.001	<0.001	0,0005
FA	F	0,001	<0.001	0,092	<0.001	0,008	0,014	0,013	<0.001	<0.001	0,0003
FA	W	<0.001	<0.001	0,038	<0.001	0,002	0,027	0,014	<0.001	<0.001	0,0003
FA	W	0,013	<0.001	0,099	<0.001	0,002	0,008	0,027	<0.001	<0.001	0,0012
FA	F	<0.001	0,001	0,091	<0.001	0,001	0,012	0,002	<0.001	<0.001	0,0006
FA	F	<0.001	<0.001	0,367	<0.001	0,002	0,003	0,028	<0.001	<0.001	0,0011
FA	F	<0.001	0,001	0,111	<0.001	0,002	0,010	0,015	<0.001	<0.001	0,0006
FA	F	<0.001	<0.001	0,038	<0.001	0,002	0,004	0,030	<0.001	<0.001	0,0009
FA	F	<0.001	<0.001	0,051	<0.001	0,001	0,003	0,042	<0.001	<0.001	0,0014
FA	F	<0.001	0,001	0,082	<0.001	0,011	0,007	0,056	<0.001	<0.001	0,0008
FA	W	<0.001	<0.001	0,116	<0.001	0,004	0,008	0,028	<0.001	<0.001	0,0006
MA	W	<0.001	<0.001	0,018	<0.001	0,003	0,004	0,008	<0.001	<0.001	0,0004
MA	F	<0.001	<0.001	0,060	0,001	0,001	0,006	0,011	0,006	<0.001	0,0006
MA	W	<0.001	<0.001	0,308	<0.001	0,014	0,007	0,013	<0.001	<0.001	0,0004
MA	F	0,001	<0.001	0,004	<0.001	0,001	0,246	0,001	<0.001	<0.001	<0.0001
MA	W	<0.001	<0.001	0,060	<0.001	<0.001	0,007	0,013	<0.001	<0.001	0,0006
MA	W	0,011	0,001	0,011	<0.001	0,003	3,750	0,001	<0.001	<0.001	0,0001
MA	W	<0.001	<0.001	0,021	<0.001	0,001	0,006	0,004	0,002	<0.001	0,0002
MA	F	0,009	0,001	0,009	0,001	0,005	2,510	0,002	<0.001	<0.001	0,0002
MA	F	<0.001	<0.001	0,114	<0.001	<0.001	0,009	0,024	<0.001	<0.001	0,0008
MA	F	<0.001	<0.001	0,096	<0.001	<0.001	0,009	0,029	<0.001	<0.001	0,0012
MA	F	<0.001	0,001	0,220	<0.001	0,008	0,003	0,013	0,001	<0.001	0,0013
MA	W	<0.001	<0.001	0,006	<0.001	<0.001	0,012	0,003	0,003	<0.001	0,0002
MA	W	<0.001	<0.001	0,055	<0.001	<0.001	0,003	0,027	0,001	<0.001	0,0005
MA	F	<0.001	<0.001	0,191	<0.001	0,014	0,003	0,019	<0.001	<0.001	0,0003

MA	F	<0.001	<0.001	0,160	0,001	<0.001	0,007	0,011	<0.001	<0.001	0,0001
MA	W	<0.001	<0.001	0,235	<0.001	0,001	0,005	0,043	<0.001	<0.001	0,0011
MA	W	<0.001	<0.001	0,003	<0.001	0,002	0,008	0,004	0,001	<0.001	0,0004
MA	F	<0.001	<0.001	0,077	<0.001	0,002	0,005	0,011	<0.001	<0.001	0,0005
MA	F	<0.001	<0.001	0,126	<0.001	0,003	0,004	0,014	<0.001	<0.001	0,0002
MA	W	<0.001	<0.001	0,515	<0.001	0,003	0,007	0,060	<0.001	<0.001	0,0015
State And Type		**Leachability - Mg/l**									
		Ho	**Ir**	**K**	**La**	**Li**	**Mg**	**Mn**	**Mo**	**Na**	**Nb**
CA	W	<0.001	<0.001	1,17	<0.001	0,089	0,07	0,006	0,040	2,21	<0.001
CA	F	<0.001	<0.001	1,66	<0.001	0,022	3,72	0,009	0,005	6,32	<0.001
CA	F	<0.001	<0.001	2,33	<0.001	0,026	0,48	0,001	0,043	2,02	<0.001
CA	W	<0.001	<0.001	63,8	<0.001	4,685	0,58	0,003	0,244	107	<0.001
CA	F	<0.001	<0.001	3,06	<0.001	0,107	0,44	0,006	0,007	9,71	<0.001
CA	F	<0.001	<0.001	3,66	<0.001	0,029	0,48	0,009	0,012	51,4	<0.001
CA	F	<0.001	<0.001	0,82	<0.001	0,015	0,32	0,001	0,041	1,42	<0.001
CA	F	<0.001	<0.001	1,05	<0.001	0,008	1,06	0,001	0,004	5,08	<0.001
CA	F	<0.001	<0.001	1,23	<0.001	0,014	3,94	0,001	0,007	10,8	<0.001
CA	F	<0.001	<0.001	1,39	<0.001	0,063	0,06	0,003	0,015	4,81	<0.001
CA	W	<0.001	<0.001	0,67	<0.001	0,006	0,34	0,002	0,010	3,82	<0.001
CA	F	<0.001	<0.001	0,87	<0.001	0,106	0,04	0,002	0,069	2,15	<0.001
CA	F	<0.001	<0.001	4,74	<0.001	0,104	0,48	0,003	0,012	13,2	<0.001
CA	F	<0.001	<0.001	2,41	<0.001	0,130	0,77	0,003	0,029	7,05	<0.001
CA	W	<0.001	<0.001	2,33	<0.001	0,087	1,98	0,015	0,051	9,11	<0.001
CA	W	<0.001	<0.001	2,93	0,001	0,106	1,62	0,001	0,066	14,3	<0.001
CA	F	<0.001	<0.001	2,51	<0.001	0,050	4,54	0,001	0,072	11,6	<0.001
CA	F	<0.001	<0.001	14,37	<0.001	0,631	17,02	0,014	0,954	36,8	<0.001
CA	F	<0.001	<0.001	2,53	<0.001	0,030	0,49	0,008	0,010	8,02	<0.001
CA	F	<0.001	<0.001	2,74	<0.001	0,15	1,84	0,00	0,04	16,62	<0.001
CA	W	<0.001	<0.001	1,51	<0.001	0,022	1,77	0,010	0,027	7,72	<0.001
CA	F	<0.001	<0.001	1,62	<0.001	0,020	3,55	0,006	0,022	7,68	<0.001
FA	F	<0.001	<0.001	1,04	<0.001	0,057	0,09	0,002	0,065	1,67	<0.001
FA	W	<0.001	<0.001	9,27	<0.001	0,248	0,52	0,017	0,020	12,2	<0.001
FA	F	<0.001	<0.001	14,5	<0.001	0,358	0,05	0,001	0,049	11,7	<0.001
FA	W	<0.001	<0.001	3,72	<0.001	0,072	5,22	0,001	0,106	17,2	<0.001
FA	F	<0.001	<0.001	0,65	<0.001	0,074	0,04	0,002	0,051	1,14	<0.001
FA	F	<0.001	<0.001	7,12	<0.001	0,119	85,86	0,273	0,254	3,80	<0.001
FA	W	<0.001	<0.001	13,0	<0.001	0,338	0,09	0,001	0,042	12,3	<0.001
FA	F	<0.001	<0.001	1,17	<0.001	0,069	1,23	0,002	0,005	6,27	<0.001
FA	F	<0.001	<0.001	1,70	<0.001	0,053	0,08	0,001	0,008	11,7	<0.001
FA	F	<0.001	<0.001	1,42	<0.001	0,083	0,05	<0.001	0,038	3,95	<0.001
FA	W	<0.001	<0.001	2,21	<0.001	0,071	0,08	<0.001	0,021	6,98	<0.001
FA	W	<0.001	<0.001	3,11	<0.001	0,052	1,20	0,001	0,008	18,5	<0.001
FA	F	<0.001	<0.001	0,74	<0.001	0,072	0,04	0,001	0,049	1,68	<0.001
FA	F	<0.001	<0.001	1,87	<0.001	0,175	0,03	0,002	0,064	3,35	<0.001

FA	F	<0.001	<0.001	0,72	0,001	0,113	0,09	0,001	0,052	1,81	<0.001
FA	W	<0.001	<0.001	2,03	<0.001	0,063	1,32	0,007	0,022	4,95	<0.001
FA	W	<0.001	<0.001	1,8	0,007	0,095	2,08	0,005	0,085	10,2	<0.001
FA	F	<0.001	<0.001	2,16	<0.001	0,061	0,04	0,003	0,062	6,16	<0.001
FA	F	<0.001	<0.001	1,18	<0.001	0,086	0,03	0,002	0,167	2,01	<0.001
FA	F	<0.001	<0.001	1,28	<0.001	0,050	0,02	0,001	0,049	3,39	<0.001
FA	F	<0.001	<0.001	1,04	<0.001	0,125	0,03	0,001	0,060	1,66	<0.001
FA	F	<0.001	<0.001	1,19	<0.001	0,154	0,03	<0.001	0,089	1,81	<0.001
FA	F	<0.001	<0.001	0,13	<0.001	0,030	0,03	0,019	0,063	1,60	<0.001
FA	W	<0.001	<0.001	1,91	<0.001	0,028	0,17	0,006	0,036	6,13	<0.001
MA	W	<0.001	<0.001	3,16	<0.001	0,065	0,55	0,002	0,024	11,2	<0.001
MA	F	<0.001	<0.001	7,54	<0.001	0,017	1,83	0,003	0,014	78,9	<0.001
MA	W	<0.001	<0.001	1,32	<0.001	0,080	0,22	0,008	0,027	7,36	<0.001
MA	F	<0.001	<0.001	0,46	<0.001	0,006	1,72	0,005	0,004	0,87	<0.001
MA	W	<0.001	<0.001	1,41	<0.001	0,034	0,467	0,002	0,033	3,06	<0.001
MA	W	<0.001	<0.001	3,86	0,007	0,002	1,20	0,021	0,004	7,26	<0.001
MA	W	<0.001	<0.001	1,29	<0.001	0,015	3,99	0,001	0,013	7,63	<0.001
MA	F	<0.001	<0.001	3,53	0,005	0,004	3,23	0,034	0,003	3,98	0,001
MA	F	<0.001	<0.001	0,80	<0.001	0,088	0,10	0,001	0,024	3,65	<0.001
MA	F	<0.001	<0.001	3,61	<0.001	0,103	0,09	0,002	0,016	33,9	<0.001
MA	F	<0.001	<0.001	4,04	<0.001	0,054	0,23	0,017	0,044	92,5	<0.001
MA	W	<0.001	<0.001	0,59	<0.001	0,003	1,06	0,001	0,005	1,06	<0.001
MA	W	<0.001	<0.001	2,31	<0.001	0,027	0,35	<0.001	0,027	4,85	<0.001
MA	F	<0.001	<0.001	2,23	<0.001	0,024	0,06	0,009	0,018	9,81	<0.001
MA	F	<0.001	<0.001	1,82	<0.001	0,056	0,07	<0.001	0,026	4,13	<0.001
MA	W	<0.001	<0.001	1,95	<0.001	0,036	0,86	0,002	0,118	10,3	<0.001
MA	W	<0.001	<0.001	2,48	<0.001	0,040	3,51	0,003	0,027	10,4	<0.001
MA	F	<0.001	<0.001	0,85	<0.001	0,017	0,49	0,000	0,021	3,48	<0.001
MA	F	<0.001	<0.001	2,78	<0.001	0,036	0,05	0,000	0,051	3,47	<0.001
MA	W	<0.001	<0.001	3,79	<0.001	0,090	0,14	0,001	0,142	9,12	<0.001

State And Type		**Leachability - mg/l**									
		Nd	**Ni**	**Pb**	**Pt**	**Rb**	**Sb**	**Sc**	**Se**	**Si**	**Sn**
CA	W	<0.001	0,005	0,001	<0.001	0,003	0,001	0,002	0,016	3,99	<0.001
CA	F	<0.001	0,003	0,002	<0.001	0,003	0,001	0,001	0,009	2,54	<0.001
CA	F	<0.001	0,001	<0.001	<0.001	0,004	0,005	0,002	0,020	6,15	<0.001
CA	W	<0.001	<0.001	<0.001	<0.001	0,110	0,003	0,002	0,047	6,08	<0.001
CA	F	<0.001	<0.001	0,001	<0.001	0,007	0,001	0,002	0,010	8,76	0,002
CA	F	<0.001	0,003	0,001	<0.001	0,005	0,001	0,003	0,010	9,11	<0.001
CA	F	<0.001	0,001	<0.001	<0.001	0,001	0,008	0,002	0,043	4,33	<0.001
CA	F	<0.001	<0.001	<0.001	<0.001	0,001	0,001	0,002	0,007	5,30	<0.001
CA	F	<0.001	<0.001	<0.001	<0.001	0,002	0,001	0,002	0,008	4,33	<0.001
CA	F	<0.001	0,003	0,001	<0.001	0,004	0,002	0,002	0,014	5,79	<0.001
CA	W	<0.001	<0.001	<0.001	<0.001	0,002	0,004	0,001	0,014	3,26	<0.001
CA	F	<0.001	0,003	<0.001	<0.001	0,003	0,002	0,002	0,019	4,5	<0.001
CA	F	<0.001	0,002	<0.001	<0.001	0,010	0,001	0,003	0,009	9,7	<0.001

CA	F	<0.001	0,001	0,001	<0.001	0,005	0,003	0,003	0,005	8,52	0,001
CA	W	<0.001	0,002	<0.001	<0.001	0,006	0,007	0,001	0,017	1,21	<0.001
CA	W	0,001	0,001	0,002	<0.001	0,004	0,008	0,001	0,020	3,11	<0.001
CA	F	<0.001	0,003	<0.001	<0.001	0,005	0,008	0,001	0,027	2,21	<0.001
CA	F	<0.001	0,007	<0.001	<0.001	0,028	0,009	0,001	0,043	3,76	<0.001
CA	F	<0.001	0,001	<0.001	<0.001	0,005	0,004	0,002	0,007	5,27	0,001
CA	F	<0.001	0,00	0,00	<0.001	0,00	0,00	0,00	0,01	5,75	0,00
CA	W	<0.001	0,001	0,001	<0.001	0,003	0,004	0,001	0,015	2,91	0,001
CA	F	<0.001	0,001	<0.001	<0.001	0,003	0,002	0,001	0,003	3,85	0,001
FA	F	<0.001	0,002	0,001	<0.001	0,002	0,004	0,002	0,031	4,62	<0.001
FA	W	<0.001	0,003	0,001	<0.001	0,019	0,002	0,002	0,018	6,64	0,001
FA	F	<0.001	0,001	<0.001	<0.001	0,048	0,001	0,002	0,015	6,73	<0.001
FA	W	<0.001	0,001	<0.001	<0.001	0,007	0,002	0,001	0,023	1,68	<0.001
FA	F	<0.001	0,003	0,001	<0.001	0,002	0,002	0,002	0,033	4,36	<0.001
FA	F	<0.001	0,017	0,001	<0.001	0,028	0,013	0,001	0,058	3,02	<0.001
FA	W	<0.001	<0.001	<0.001	<0.001	0,041	0,001	0,002	0,021	7,42	<0.001
FA	F	<0.001	0,001	<0.001	<0.001	0,004	0,001	0,001	0,008	3,08	<0.001
FA	F	<0.001	0,007	<0.001	<0.001	0,003	0,002	0,002	0,035	4,38	<0.001
FA	F	<0.001	0,002	<0.001	<0.001	0,003	0,002	0,002	0,039	5,14	<0.001
FA	W	<0.001	0,001	<0.001	<0.001	0,005	0,002	0,002	0,013	6,78	<0.001
FA	W	<0.001	<0.001	<0.001	<0.001	0,005	0,002	0,001	0,010	3,04	<0.001
FA	F	<0.001	0,004	<0.001	<0.001	0,002	0,002	0,002	0,013	3,80	<0.001
FA	F	<0.001	0,012	0,001	<0.001	0,006	0,003	0,001	0,013	1,28	<0.001
FA	F	<0.001	0,008	<0.001	<0.001	0,002	0,003	0,001	0,007	2,15	<0.001
FA	W	<0.001	0,002	0,001	<0.001	0,004	0,006	0,001	0,014	3,53	<0.001
FA	W	0,005	0,002	0,001	<0.001	0,003	0,009	0,001	0,016	1,33	0,001
FA	F	<0.001	0,016	0,001	<0.001	0,004	0,004	0,001	0,009	4,26	<0.001
FA	F	<0.001	0,008	<0.001	<0.001	0,003	0,004	0,001	0,013	3,58	<0.001
FA	F	<0.001	0,017	0,002	<0.001	0,004	0,007	<0.001	0,009	0,97	0,001
FA	F	<0.001	0,006	<0.001	<0.001	0,003	0,005	0,001	0,008	2,42	0,001
FA	F	<0.001	0,006	<0.001	<0.001	0,003	0,005	0,001	0,023	2,24	<0.001
FA	F	<0.001	0,012	0,003	<0.001	0,003	0,004	0,001	0,010	3,70	0,007
FA	W	<0.001	0,002	0,001	<0.001	0,005	0,005	0,002	0,021	5,31	0,005
MA	W	<0.001	0,001	<0.001	<0.001	0,006	0,004	0,001	0,006	3,86	<0.001
MA	F	<0.001	0,001	<0.001	<0.001	0,008	0,003	0,001	0,017	2,29	<0.001
MA	W	<0.001	0,001	<0.001	<0.001	0,002	0,002	0,002	0,024	6,54	<0.001
MA	F	<0.001	0,002	0,001	<0.001	0,001	0,001	0,002	0,012	3,92	<0.001
MA	W	<0.001	0,003	<0.001	<0.001	0,004	0,004	0,002	0,021	5,36	<0.001
MA	W	0,006	0,002	0,003	<0.001	0,005	0,001	0,003	0,010	16,22	<0.001
MA	W	<0.001	0,001	<0.001	<0.001	0,002	0,002	0,001	0,014	3,14	<0.001
MA	F	0,004	0,011	0,003	<0.001	0,009	0,001	0,007	0,013	11,66	0,001
MA	F	<0.001	0,001	<0.001	<0.001	0,002	0,003	0,002	0,049	4,02	<0.001
MA	F	<0.001	0,001	<0.001	<0.001	0,005	0,006	0,001	0,026	2,99	<0.001
MA	F	<0.001	0,007	0,004	<0.001	0,005	0,003	0,002	0,024	4,86	0,001
MA	W	<0.001	<0.001	<0.001	<0.001	0,001	0,002	0,001	0,011	2,35	<0.001

MA	W	<0.001	0,001	<0.001	<0.001	0,004	0,004	0,001	0,023	1,98	<0.001
MA	F	<0.001	<0.001	0,042	<0.001	0,002	0,002	0,001	0,017	9,56	<0.001
MA	F	<0.001	0,001	<0.001	<0.001	0,003	0,002	0,002	0,012	6,47	<0.001
MA	W	<0.001	0,002	<0.001	<0.001	0,004	0,007	0,002	0,019	3,65	<0.001
MA	W	<0.001	0,002	0,001	<0.001	0,005	0,003	0,001	0,007	2,73	0,001
MA	F	<0.001	0,001	<0.001	<0.001	0,002	0,005	0,001	0,016	4,43	0,001
MA	F	<0.001	0,002	<0.001	<0.001	0,009	0,003	0,002	0,010	6,75	<0.001
MA	W	<0.001	0,003	<0.001	<0.001	0,008	0,009	0,001	0,029	3,60	0,001

State And Type		**Leachability - mg/l**									
		Sr	**Ta**	**Te**	**Th**	**Ti**	**Tl**	**U**	**V**	**W**	**Y**
CA	W	3,530	<0.001	<0.001	<0.0001	0,003	<0.001	0,0001	0,013	0,018	<0.001
CA	F	0,528	<0.001	<0.001	<0.0001	0,001	<0.001	0,0003	0,012	0,003	<0.001
CA	F	0,155	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,083	0,019	<0.001
CA	W	0,122	<0.001	<0.001	<0.0001	0,008	<0.001	0,0004	0,134	0,045	<0.001
CA	F	0,279	<0.001	<0.001	<0.0001	0,002	<0.001	<0.0001	0,008	0,005	<0.001
CA	F	0,234	<0.001	<0.001	<0.0001	0,002	<0.001	0,0001	0,009	0,011	<0.001
CA	F	0,092	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,065	0,024	<0.001
CA	F	0,034	<0.001	<0.001	0,0001	0,016	<0.001	0,0001	0,008	0,003	<0.001
CA	F	0,100	<0.001	<0.001	<0.0001	0,002	<0.001	0,0001	0,010	0,005	<0.001
CA	F	1,592	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,008	0,007	<0.001
CA	W	0,491	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,037	0,013	<0.001
CA	F	4,145	<0.001	0,001	<0.0001	0,003	<0.001	0,0001	0,026	0,033	<0.001
CA	F	0,484	<0.001	<0.001	<0.0001	0,002	<0.001	<0.0001	0,010	0,005	<0.001
CA	F	0,450	<0.001	<0.001	<0.0001	0,004	<0.001	<0.0001	0,027	0,007	<0.001
CA	W	0,841	<0.001	<0.001	<0.0001	0,002	<0.001	0,0005	3,311	0,028	<0.001
CA	W	0,439	<0.001	0,001	<0.0001	0,001	<0.001	0,0001	0,090	0,042	<0.001
CA	F	1,180	<0.001	<0.001	<0.0001	0,001	<0.001	0,0004	0,070	0,052	<0.001
CA	F	2,472	<0.001	<0.001	<0.0001	0,003	<0.001	0,0005	0,185	0,095	<0.001
CA	F	0,433	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,014	0,005	<0.001
CA	F	0,25	<0.001	<0.001	<0.001	0,00	<0.001	0,00	0,03	0,01	<0.001
CA	W	0,275	<0.001	<0.001	<0.0001	0,001	<0.001	0,0002	0,042	0,018	<0.001
CA	F	0,137	<0.001	<0.001	<0.0001	0,007	<0.001	0,0001	0,015	0,006	<0.001
FA	F	0,199	<0.001	<0.001	<0.0001	0,002	<0.001	0,0001	0,089	0,026	<0.001
FA	W	1,231	<0.001	<0.001	<0.0001	0,002	<0.001	<0.0001	0,032	0,009	<0.001
FA	F	2,531	<0.001	<0.001	<0.0001	0,002	<0.001	<0.0001	0,017	0,007	<0.001
FA	W	1,052	<0.001	<0.001	<0.0001	0,001	<0.001	0,0003	0,018	0,009	<0.001
FA	F	1,821	<0.001	0,001	<0.0001	0,002	<0.001	0,0002	0,023	0,024	<0.001
FA	F	0,552	<0.001	<0.001	0,0002	0,004	0,002	<0.0001	0,185	0,087	<0.001
FA	W	1,720	<0.001	<0.001	<0.0001	0,002	<0.001	<0.0001	0,030	0,007	<0.001
FA	F	0,301	0,001	<0.001	<0.0001	0,003	<0.001	0,0001	0,004	0,003	<0.001
FA	F	0,325	<0.001	<0.001	<0.0001	0,002	<0.001	<0.0001	0,025	0,009	<0.001
FA	F	1,479	<0.001	<0.001	<0.0001	0,001	<0.001	0,0001	0,027	0,020	<0.001
FA	W	0,715	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,020	0,007	<0.001
FA	W	0,314	<0.001	<0.001	<0.0001	0,001	<0.001	0,0001	0,005	0,006	<0.001
FA	F	3,939	<0.001	<0.001	<0.0001	0,002	<0.001	0,0001	0,012	0,019	<0.001

FA	F	11,499	<0.001	<0.001	<0.0001	0,004	<0.001	0,0001	0,001	0,015	<0.001
FA	F	2,429	<0.001	<0.001	<0.0001	0,002	<0.001	<0.0001	0,033	0,015	<0.001
FA	W	0,679	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,064	0,017	<0.001
FA	W	0,419	<0.001	<0.001	<0.0001	0,002	<0.001	0,0006	0,120	0,054	<0.001
FA	F	4,703	<0.001	<0.001	<0.0001	0,004	<0.001	0,0001	0,014	0,018	<0.001
FA	F	2,331	<0.001	0,001	<0.0001	0,002	<0.001	<0.0001	0,028	0,041	<0.001
FA	F	4,245	<0.001	<0.001	<0.0001	0,003	<0.001	<0.0001	0,004	0,020	<0.001
FA	F	1,735	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,006	0,032	<0.001
FA	F	1,536	<0.001	0,001	<0.0001	0,001	<0.001	<0.0001	0,011	0,047	<0.001
FA	F	2,362	<0.001	0,001	<0.0001	0,002	<0.001	0,0001	0,021	0,026	<0.001
FA	W	0,816	<0.001	0,001	<0.0001	0,001	<0.001	<0.0001	0,087	0,024	<0.001
MA	W	0,596	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,026	0,012	<0.001
MA	F	0,312	<0.001	<0.001	<0.0001	0,003	<0.001	0,0003	0,063	0,017	<0.001
MA	W	0,411	<0.001	<0.001	<0.0001	0,002	<0.001	0,0001	0,055	0,011	<0.001
MA	F	0,090	<0.001	<0.001	0,0001	0,018	<0.001	0,0002	0,003	0,002	<0.001
MA	W	0,121	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,063	0,014	<0.001
MA	W	0,038	<0.001	<0.001	0,0005	0,051	<0.001	0,0004	0,012	0,004	0,003
MA	W	0,057	<0.001	<0.001	0,0000	0,002	<0.001	0,0004	0,048	0,007	<0.001
MA	F	0,061	<0.001	<0.001	0,0017	0,292	<0.001	0,0005	0,013	0,004	0,003
MA	F	0,630	<0.001	0,001	0,0001	0,001	<0.001	<0.0001	0,036	0,019	<0.001
MA	F	1,306	<0.001	<0.001	0,0001	0,002	<0.001	<0.0001	0,043	0,034	<0.001
MA	F	0,622	<0.001	<0.001	<0.0001	0,002	<0.001	0,0001	0,069	0,031	<0.001
MA	W	0,034	<0.001	<0.001	<0.0001	0,001	<0.001	0,0003	0,041	0,006	<0.001
MA	W	0,144	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,032	0,017	<0.001
MA	F	0,374	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,052	0,010	<0.001
MA	F	0,646	<0.001	<0.001	<0.0001	0,001	<0.001	<0.0001	0,020	0,007	<0.001
MA	W	0,585	<0.001	0,001	<0.0001	0,001	<0.001	0,0001	0,118	0,041	<0.001
MA	W	0,311	<0.001	<0.001	<0.0001	0,001	<0.001	0,0001	0,022	0,009	<0.001
MA	F	0,423	<0.001	<0.001	<0.0001	0,001	<0.001	0,0001	0,114	0,018	<0.001
MA	F	1,036	<0.001	<0.001	<0.0001	0,002	<0.001	<0.0001	0,051	0,007	<0.001
MA	W	0,958	<0.001	0,001	<0.0001	0,001	<0.001	<0.0001	0,079	0,054	<0.001

State And Type		**Leachability - mg/l**							
		Zn	**Zr**	**pH**	**pH Temp**	**TDS**	**EC**	**TDS by Sum**	**TDS by EC**
CA	W	0,010	<0.001	12,07	22,4	688	110	787	770
CA	F	0,014	<0.001	8,62	22,8	160	24,6	175	172
CA	F	0,007	<0.001	10,83	22,8	188	35,2	229	246
CA	W	0,022	<0.001	10,26	23,0	496	72,9	499	510
CA	F	0,011	<0.001	10,36	24,7	132	25,0	191	175
CA	F	0,344	<0.001	10,34	24,4	220	36,4	275	255
CA	F	0,002	<0.001	10,73	24,3	222	34,5	250	241
CA	F	0,000	0,001	9,50	22,5	74,0	10,4	79	72,9
CA	F	<0.001	<0.001	5,44	18,9	122	22,4	144	157
CA	F	0,029	<0.001	11,87	21,2	420	70,7	438	495

CA	W	0,001	<0.001	10,15	21,6	151	23,1	173	162
CA	F	0,001	<0.001	11,96	21,8	794	128	821	895
CA	F	0,008	<0.001	10,27	22,1	200	26,0	228	182
CA	F	0,003	<0.001	10,60	23,9	192	24,4	209	171
CA	W	0,007	<0.001	9,41	23,8	288	39,4	307	276
CA	W	0,004	<0.001	9,70	23,7	230	31,2	240	218
CA	F	0,005	<0.001	9,70	23,8	350	49,9	377	350
CA	F	0,008	<0.001	9,39	23,6	934	139	1054	972
CA	F	0,001	<0.001	10,26	23,0	230	30,4	245	213
CA	F	0,01	<0.001	8,88	21,17	182,00	25,39	205,55	177,70
CA	W	0,006	<0.001	9,77	21,0	216	27,6	225	193
CA	F	0,003	<0.001	9,32	20,9	92,0	13,1	100	91,8
FA	F	0,016	<0.001	11,53	22,4	370	64,1	419	449
FA	W	0,029	<0.001	10,57	22,7	202	37,0	260	259
FA	F	<0.001	<0.001	11,56	23,6	315	50,5	315	353
FA	W	0,017	<0.001	8,31	24,6	220	36,4	266	255
FA	F	0,010	<0.001	11,82	24,7	598	90,0	650	630
FA	F	0,018	<0.001	7,71	24,5	1928	256	1964	1793
FA	W	0,005	<0.001	11,17	24,0	264	37,3	275	261
FA	F	0,013	0,001	9,58	23,5	112	18,0	128	126
FA	F	0,002	<0.001	11,06	23,3	294	44,2	284	309
FA	F	0,007	<0.001	11,77	20,9	544	79,7	567	558
FA	W	0,004	<0.001	11,50	21,3	280	41,7	271	292
FA	W	0,016	<0.001	9,74	22,3	168	28,1	198	197
FA	F	0,012	<0.001	12,09	22,4	882	129	873	900
FA	F	0,007	<0.001	10,63	22,5	2664	427	2704	2990
FA	F	0,003	<0.001	12,09	23,7	1036	151	1067	1056
FA	W	0,004	<0.001	9,82	23,9	264	38,0	284	266
FA	W	0,016	<0.001	9,54	23,8	220	30,4	241	213
FA	F	0,007	<0.001	12,27	23,7	2064	295	1959	2064
FA	F	0,003	<0.001	11,92	24,0	864	124,3	858	870
FA	F	0,009	<0.001	12,32	23,1	2188	311	2144	2178
FA	F	0,001	<0.001	11,87	22,6	748	106	788	742
FA	F	0,002	<0.001	11,73	21,4	628	93,3	665	653
FA	F	0,045	<0.001	11,95	21,3	748	104	729	729
FA	W	0,015	<0.001	10,30	21,1	182	25,5	198	179
MA	W	0,000	<0.001	10,21	23,3	286	41,3	306	289
MA	F	0,005	<0.001	9,34	23,1	352	54,5	367	382
MA	W	0,004	<0.001	11,07	23,2	190	32,8	211	229
MA	F	0,009	<0.001	8,09	23,9	38,0	5,10	44	35,7
MA	W	0,011	<0.001	10,56	24,5	226	32,8	250	230
MA	W	0,065	0,001	7,28	25,4	114	13,6	106	95,1
MA	W	0,005	<0.001	8,77	25,2	108	17,4	127	122
MA	F	0,053	0,009	7,38	25,0	90,0	11,9	87	83,4
MA	F	0,008	<0.001	11,08	24,9	288	49,6	316	347

MA	F	0,005	<0.001	10,69	24,7	374	56,5	415	396
MA	F	0,083	<0.001	10,45	24,6	598	86,5	615	606
MA	W	0,001	<0.001	7,96	24,2	58,0	7,5	54	52,8
MA	W	0,000	<0.001	9,95	22,4	298	40,4	309	283
MA	F	0,117	<0.001	9,45	21,1	152	23,8	193	167
MA	F	0,001	<0.001	11,50	21,2	292	45,7	323	320
MA	W	0,005	<0.001	10,00	23,8	224	32,0	254	224
MA	W	0,016	<0.001	9,34	23,8	162	23,1	167	162
MA	F	0,002	<0.001	10,06	23,9	196	28,0	201	196
MA	F	0,000	<0.001	11,37	23,8	284	41,5	297	291
MA	W	0,010	<0.001	10,94	23,5	416	60,2	450	421

Appendix C: Statistical Analysis Raw Data of CCPs Concentration

State And Type		**Concentration (mg/kg)**								
		Ag	**As**	**Au**	**B**	**Ba**	**Be**	**Bi**	**Cd**	**Ce**
CA	W	1,17	1,71	0,01	35,02	735,71	5,01	0,28	0,12	52,60
CA	F	1,38	18,9	0,02	216	1412	7,70	3,14	0,23	32,1
CA	F	1,10	1,5	0,01	27,9	1039	5,43	0,24	0,13	36,6
CA	W	1,37	1,81	0,02	49,3	950	6,55	0,24	0,16	12,4
CA	F	1,16	15,4	0,02	153	2054	8,08	2,54	0,35	17,3
CA	F	1,52	2,2	0,01	63,1	868	5,95	0,38	0,20	64,4
CA	F	0,08	1,90	0,01	44,9	937	4,13	0,77	0,11	24,3
CA	F	0,05	3,41	0,00	46,5	1173	3,70	0,90	0,06	31,9
CA	F	0,07	3,12	0,01	35,6	1144	4,61	1,58	0,10	16,6
CA	F	0,16	15,4	0,01	61,1	1090	7,65	2,53	0,34	7,69
CA	W	0,16	4,88	0,01	114	1899	4,71	1,45	0,20	52,0
CA	F	0,08	16,6	0,00	142	1764	6,12	4,06	0,17	18,4
CA	F	0,08	2,93	0,01	16,6	997	4,69	0,72	0,14	6,24
CA	F	0,07	17,3	0,00	44,0	1055	6,07	1,83	0,21	10,2
CA	W	0,04	1,76	0,00	31,4	760	5,56	0,46	0,06	10,1
CA	W	0,09	8,58	0,00	95,9	1687	5,14	3,50	0,14	13,8
CA	F	1,22	10,0	0,01	95,6	835	6,47	1,99	0,30	19,4
CA	F	1,11	10,0	0,01	124	1184	6,12	1,77	0,20	28,1
CA	F	1,15	8,3	0,01	52,4	1182	6,75	1,79	0,26	28,6
CA	F	1,30	10,06	0,02	65,53	917,55	7,11	2,18	0,22	7,27
CA	W	1,44	13,77	0,02	74,5	1160	8,10	2,77	0,25	7,38
CA	F	1,10	13,44	0,02	100	714	7,85	2,03	0,33	14,9
FA	F	1,52	8,3	0,02	128	1366	7,47	2,79	0,25	46,6
FA	W	0,09	7,70	0,01	127	1121	4,77	3,54	0,12	38,3
FA	F	0,07	8,90	0,00	168	1733	4,85	4,54	0,07	48,3
FA	W	0,07	4,14	0,02	67,8	981	3,41	1,57	0,12	7,32

FA	F	0,08	10,8	0,01	70,6	1188	4,86	4,25	0,16	24,3
FA	F	0,17	15,2	0,01	48,7	1053	6,72	2,34	0,32	5,54
FA	W	0,11	1,86	0,01	52,7	1396	4,38	0,60	0,14	13,2
FA	F	0,07	13,9	0,00	112	1622	5,94	3,08	0,15	22,9
FA	F	0,08	44,9	0,00	88,5	1135	7,88	6,63	0,55	17,4
FA	F	0,07	18,3	0,00	88,7	1041	7,53	3,04	0,26	15,9
FA	W	1,45	15,58	0,02	160,29	1300,54	8,25	3,29	0,24	32,29
FA	W	0,80	7,07	0,01	51,5	1263	5,00	0,88	0,17	24,0
FA	F	1,69	15,95	0,02	176	1333	9,36	4,26	0,33	25,5
FA	F	0,10	10,6	0,01	177	1016	4,70	2,98	0,17	9,51
FA	F	0,06	12,3	0,00	177	1212	4,60	3,34	0,11	8,59
FA	W	0,08	9,97	0,00	73,8	1171	5,21	3,70	0,16	13,4
FA	W	0,10	16,1	0,00	40,8	1159	5,79	2,96	0,24	9,63
FA	F	0,07	16,6	0,00	22,8	1016	6,18	2,00	0,21	6,42
FA	F	0,06	12,8	0,00	64,9	972	6,03	2,12	0,20	13,9
FA	F	0,07	20,7	0,00	77,5	1390	5,99	2,80	0,17	9,77
FA	F	1,26	3,9	0,01	51,2	1010	5,51	0,81	0,16	28,5
FA	F	1,13	8,86	0,02	62,3	1150	6,88	1,98	0,27	24,0
FA	F	1,42	12,08	0,02	79,5	988	7,77	2,98	0,24	5,17
FA	W	0,12	7,98	0,01	124	1355	5,45	3,70	0,16	67,8
MA	W	0,12	10,6	0,01	106	1544	5,81	3,21	0,19	33,5
MA	F	0,09	7,80	0,00	78,2	1629	4,99	2,74	0,13	22,4
MA	W	1,23	9,3	0,01	76,8	1148	6,52	2,02	0,25	26,1
MA	F	1,03	5,94	0,01	43,8	1046	5,53	1,24	0,19	40,9
MA	W	1,43	14,7	0,02	81,4	965	8,59	3,81	0,31	3,48
MA	W	0,05	8,32	0,00	98,5	1107	4,20	3,23	0,07	37,6
MA	W	0,12	8,68	0,01	140	1340	5,28	3,20	0,14	71,0
MA	F	0,10	9,25	0,01	116	1833	4,96	2,93	0,17	34,7
MA	F	0,08	2,82	0,00	48,5	1475	4,48	0,53	0,10	27,4
MA	F	0,09	9,02	0,00	106	1715	5,20	4,04	0,14	12,2
MA	F	1,24	2,6	0,01	67,9	1104	5,85	0,38	0,36	48,2
MA	W	0,88	3,6	0,01	43,4	719	5,16	0,52	0,15	20,1
MA	W	1,21	2,81	0,01	56,3	1941	5,53	0,82	0,14	21,9
MA	F	0,02	3,35	0,00	16,9	465	1,41	0,53	0,05	3,41
MA	F	0,09	11,3	0,01	68,2	1134	5,33	3,47	0,16	27,7
MA	W	0,02	2,67	0,00	3,60	126	0,66	0,21	0,05	11,3
MA	W	0,14	1,60	0,01	62,5	1643	4,65	0,58	0,15	20,8
MA	F	0,08	14,6	0,01	26,6	1264	5,25	3,06	0,25	8,94
MA	F	0,09	15,8	0,00	24,3	1529	5,89	2,65	0,24	5,02
MA	W	0,12	18,0	0,01	82,4	1064	8,95	3,16	0,38	12,9

State And Type		**Concentration (mg/kg)**								
		Co	**Cr**	**Cs**	**Cu**	**Ga**	**Ge**	**Hf**	**Hg**	**Ho**
CA	W	18,44	207,16	0,94	27,89	18,34	2,59	7,11	0,02	0,62
CA	F	17,6	157	1,42	39,9	43,0	10,9	8,03	0,98	0,49
CA	F	11,3	159	0,67	25,4	19,4	1,69	7,08	0,03	0,50

CA	W	9,26	177	0,61	26,6	17,6	1,28	8,84	0,03	0,11
CA	F	18,1	219	1,12	41,1	42,7	12,0	7,57	0,49	0,20
CA	F	14,9	147	1,73	29,6	19,3	2,13	9,12	0,03	0,85
CA	F	8,48	166	2,69	48,8	19,9	1,55	12,4	0,06	0,35
CA	F	9,59	198	2,82	36,1	17,9	1,49	10,2	0,04	0,44
CA	F	7,54	174	1,15	59,9	19,3	1,87	16,5	0,05	0,22
CA	F	22,7	151	1,13	59,7	41,5	4,23	17,1	0,07	0,05
CA	W	12,6	167	2,45	48,6	30,0	2,66	16,2	0,08	0,85
CA	F	15,3	208	2,39	73,3	38,0	6,15	16,0	0,04	0,24
CA	F	16,8	163	0,86	45,8	18,4	1,34	17,2	0,05	0,07
CA	F	18,8	145	0,82	56,1	31,4	3,41	15,6	0,04	0,03
CA	W	16,9	226	0,57	36,4	17,0	1,23	8,79	0,03	0,19
CA	W	9,99	180	0,77	67,2	32,3	3,67	16,9	0,05	0,42
CA	F	21,6	177	0,47	39,6	35,7	8,51	7,96	0,32	0,22
CA	F	14,6	131	1,25	30,0	28,1	6,94	6,58	0,36	0,29
CA	F	12,7	157	0,59	33,5	31,8	6,22	7,51	0,08	0,31
CA	F	8,52	247,00	0,38	33,37	32,69	4,45	8,97	0,13	0,07
CA	W	8,67	145	0,36	36,7	38,6	5,45	10,1	0,08	0,06
CA	F	20,8	300	0,68	41,6	44,5	11,3	6,65	0,23	0,13
FA	F	13,9	284	1,63	38,7	38,6	7,62	9,96	0,22	0,54
FA	W	11,7	127	2,41	58,1	36,9	4,55	11,4	0,08	0,46
FA	F	14,8	166	2,41	59,7	36,8	4,29	12,7	0,04	0,55
FA	W	7,68	187	1,69	49,6	18,3	1,42	14,8	0,14	0,10
FA	F	9,63	218	1,57	65,0	30,4	4,17	17,3	0,09	0,28
FA	F	22,1	157	0,64	58,6	37,4	3,47	16,6	0,08	0,02
FA	W	10,4	154	2,43	42,5	20,3	1,69	17,9	0,07	0,15
FA	F	15,4	166	1,35	57,4	33,2	4,99	16,2	0,03	0,13
FA	F	27,5	150	1,15	74,5	68,5	8,57	16,1	0,03	0,12
FA	F	19,5	283	0,50	59,3	36,5	6,39	13,7	0,06	0,19
FA	W	14,88	195,11	1,35	37,61	42,45	11,31	8,71	0,60	0,48
FA	W	23,4	245	0,76	27,1	23,9	6,98	4,66	0,08	0,37
FA	F	13,4	230	2,52	51,8	54,1	12,8	10,7	0,32	0,32
FA	F	10,0	226	0,65	59,5	33,4	3,20	12,8	0,08	0,12
FA	F	9,59	231	0,68	51,8	32,5	3,27	14,0	0,07	0,13
FA	W	9,43	166	0,86	54,2	31,4	3,66	16,9	0,05	0,38
FA	W	18,6	138	0,87	60,5	36,5	3,67	18,3	0,05	0,11
FA	F	18,2	159	0,84	51,7	32,6	3,58	15,6	0,04	0,02
FA	F	20,6	238	0,57	52,8	28,8	4,57	12,3	0,12	0,24
FA	F	16,5	274	0,51	53,0	32,2	4,58	13,1	0,06	0,13
FA	F	18,1	208	0,49	27,8	22,4	3,83	7,82	0,11	0,48
FA	F	13,5	197	1,03	34,1	32,7	6,83	7,51	0,10	0,30
FA	F	8,16	176	0,54	37,7	37,7	5,33	9,86	0,28	0,04
FA	W	13,5	148	4,09	47,5	40,0	4,00	12,8	0,08	1,05
MA	W	15,5	199	1,46	58,6	34,9	4,81	17,1	0,05	0,57

MA	F	9,67	194	0,89	47,5	28,5	3,06	17,4	0,05	0,50
MA	W	21,3	222	0,49	33,1	33,7	7,22	7,86	0,33	0,32
MA	F	13,7	232	0,67	27,8	25,1	4,64	6,32	0,07	0,53
MA	W	7,99	184	0,44	40,7	44,7	6,44	10,4	0,22	0,04
MA	W	10,3	179	1,57	39,6	32,0	4,15	10,4	0,05	0,41
MA	W	12,0	125	3,21	48,7	36,6	3,95	11,6	0,08	1,11
MA	F	9,58	149	2,29	59,6	33,3	4,01	16,0	0,09	0,39
MA	F	10,6	237	1,46	37,8	19,5	1,66	15,8	0,02	0,41
MA	F	9,89	154	0,78	50,1	34,3	4,10	17,5	0,05	0,28
MA	F	14,8	130	1,62	25,6	18,9	2,69	6,58	0,06	0,60
MA	W	21,2	224	0,71	24,2	19,1	3,40	5,30	0,08	0,29
MA	W	17,5	204	0,55	26,9	24,1	3,69	6,72	0,08	0,40
MA	F	5,17	125	1,12	17,6	10,6	1,09	5,83	0,04	0,03
MA	F	9,74	186	2,15	58,1	28,4	3,94	16,9	0,08	0,47
MA	W	4,29	143	0,83	9,62	5,1	0,87	5,56	0,02	0,04
MA	W	9,22	159	1,38	48,2	20,8	1,44	16,8	0,07	0,31
MA	F	16,6	213	0,82	66,1	30,7	3,24	19,3	0,08	0,11
MA	F	16,0	145	1,42	54,6	30,7	3,39	17,1	0,03	0,08
MA	W	23,1	267	0,73	72,3	38,7	6,47	13,9	0,12	0,32

State And Type		**Concentration (mg/kg)**								
		Ir	**La**	**Li**	**Mn**	**Mo**	**Nb**	**Nd**	**Ni**	**Pb**
CA	W	0,03	28,21	50,63	356,44	2,44	27,38	16,49	71,60	20,35
CA	F	0,03	18,1	95,3	240	5,82	32,1	12,6	63,6	94,3
CA	F	0,03	19,5	122	438	3,22	31,9	14,2	48,0	15,9
CA	W	0,04	4,50	130	358	4,63	41,1	3,23	36,8	10,6
CA	F	0,03	5,01	127	233	30,79	35,7	4,25	66,4	69,6
CA	F	0,03	35,6	80,1	412	11,75	35,4	24,9	68,8	13,5
CA	F	0,02	9,52	154	378	4,45	38,5	9,53	23,1	17,6
CA	F	0,01	12,9	159	432	4,42	32,2	12,8	22,2	14,0
CA	F	0,05	4,87	85,3	326	2,50	36,1	4,90	20,4	39,6
CA	F	0,04	0,92	48,5	537	5,80	39,7	1,01	37,1	72,0
CA	W	0,04	22,9	161	276	4,08	46,8	20,6	25,1	26,8
CA	F	0,01	6,48	142	275	5,96	40,1	5,85	29,4	81,9
CA	F	0,07	1,56	34,0	586	2,71	29,9	1,61	34,1	37,5
CA	F	0,01	0,66	37,0	633	5,23	32,2	0,77	33,2	56,3

CA	W	0,01	3,92	59,4	409	2,95	28,8	4,11	28,8	14,6
CA	W	0,02	4,74	139	249	3,40	40,5	6,02	20,1	57,7
CA	F	0,03	8,85	66,6	293	4,59	31,3	6,41	76,7	64,5
CA	F	0,03	12,2	81,5	329	5,17	27,6	8,37	55,2	37,4
CA	F	0,03	12,7	129	411	4,47	36,1	8,91	56,7	57,8
CA	F	0,03	2,74	130,48	419,66	4,72	44,13	1,95	44,29	51,65
CA	W	0,03	2,50	138	179	5,56	47,8	1,74	43,7	64,5
CA	F	0,04	3,84	111	423	9,23	36,6	3,11	69,8	64,5
FA	F	0,03	20,1	105	541	5,62	41,1	14,2	63,8	51,2
FA	W	0,02	14,0	194	233	5,66	38,6	12,9	28,6	35,5
FA	F	0,01	16,4	222	335	5,49	40,6	16,6	33,5	38,1
FA	W	0,38	3,09	113	228	1,71	31,8	2,49	21,6	37,0
FA	F	0,20	10,7	93,6	351	4,07	38,7	8,14	23,8	66,4
FA	F	0,12	0,32	62,9	502	5,54	41,8	0,32	43,9	63,6
FA	W	0,04	4,31	176	288	3,48	46,8	3,83	24,0	24,1
FA	F	0,01	3,32	132	289	4,72	41,2	3,32	30,2	69,1
FA	F	0,01	2,26	37,3	909	9,98	33,7	2,63	42,5	126
FA	F	0,02	4,45	95,1	326	4,26	37,9	4,01	37,7	92,5
FA	W	0,03	15,90	105,05	346,92	9,21	35,93	12,14	50,23	61,65
FA	W	0,02	10,3	62,8	245	6,03	26,1	8,37	82,8	31,5
FA	F	0,04	9,17	124	389	9,74	46,8	7,27	85,80	81,4
FA	F	0,02	2,36	124	197	3,27	35,9	2,38	27,2	56,3
FA	F	0,02	2,17	129	257	3,24	34,5	2,37	23,3	50,5
FA	W	0,02	4,59	105	325	3,85	38,8	5,36	21,0	63,3
FA	W	0,05	3,67	52,4	493	5,48	41,7	3,45	36,4	66,8
FA	F	0,01	0,90	36,7	527	2,29	32,1	0,86	25,7	58,2
FA	F	0,01	4,43	80,8	409	3,70	34,4	5,06	37,9	66,6
FA	F	0,01	2,35	90,6	311	2,88	36,7	2,57	32,2	69,2
FA	F	0,03	13,5	66,4	390	3,17	32,1	10,8	68,2	30,9
FA	F	0,03	8,74	127	382	4,75	36,6	6,80	59,0	55,8
FA	F	0,03	1,66	121	255	4,3	46,4	1,24	43,9	55,4
FA	W	0,03	29,4	433	260	12,2	42,1	27,1	28,9	39,6
MA	W	0,07	14,0	139	325	5,10	46,2	8,61	37,2	59,3
MA	F	0,02	7,55	133	264	2,70	39,8	8,55	19,4	48,8
MA	W	0,03	11,7	72,9	329	7,40	32,6	8,70	77,4	58,1
MA	F	0,03	20,2	100	488	8,23	30,2	15,0	54,3	35,3
MA	W	0,03	1,62	133	217	5,44	49,6	1,12	41,9	70,0
MA	W	0,01	11,5	173	258	4,90	33,5	12,2	26,0	32,3
MA	W	0,04	29,6	214	323	4,84	36,7	28,3	28,3	34,2
MA	F	0,08	15,1	146	235	7,58	43,8	12,0	21,8	49,8
MA	F	0,01	9,51	149	342	4,36	39,5	10,3	22,1	21,4

MA	F	0,02	4,03	133	218	3,24	40,6	4,31	20,5	64,4
MA	F	0,03	25,5	86,7	421	4,20	27,5	17,8	54,2	14,9
MA	W	0,03	9,24	73,1	395	6,22	25,7	6,97	73,9	19,7
MA	W	0,03	10,2	105	413	6,72	31,1	8,62	67,7	22,1
MA	F	0,01	1,02	36,5	469	1,82	10,3	0,88	9,45	18,0
MA	F	0,11	11,1	97,1	372	3,40	37,1	10,3	21,6	62,1
MA	W	0,01	2,85	6,86	96,8	4,08	5,8	1,90	14,0	14,0
MA	W	0,03	7,67	95,6	270	2,37	43,4	7,25	20,8	18,3
MA	F	0,09	3,42	46,2	481	4,14	34,6	2,88	32,1	76,8
MA	F	0,02	1,09	50,0	494	2,71	36,3	1,24	31,7	72,0
MA	W	0,03	4,94	104	300	2,70	42,2	5,94	42,6	104

State And Type		**Concentration (mg/kg)**								
		Pt	**Rb**	**Sb**	**Sc**	**Se**	**Sn**	**Sr**	**Ta**	**Te**
CA	W	0,03	4,04	0,38	19,97	0,37	3,09	768,71	2,03	0,02
CA	F	0,04	3,26	1,59	14,3	1,40	12,1	1789	2,39	0,44
CA	F	0,04	2,68	0,55	17,0	0,39	2,84	959	2,37	0,09
CA	W	0,05	2,49	0,32	16,9	0,09	2,52	1666	2,97	0,11
CA	F	0,04	3,35	1,36	20,0	1,16	11,5	1986	2,57	0,44
CA	F	0,05	2,16	0,43	18,3	0,62	3,70	1458	2,51	0,13
CA	F	0,05	4,78	0,48	4,82	0,21	3,49	1254	2,27	0,20
CA	F	0,03	7,15	0,53	2,41	0,25	2,99	1501	1,93	0,28
CA	F	0,05	5,18	0,52	2,43	0,35	4,25	1253	2,75	0,42
CA	F	0,09	3,37	1,83	8,05	0,20	8,49	459	2,31	0,33
CA	W	0,07	8,50	0,78	7,39	0,28	4,92	2197	2,86	0,29
CA	F	0,04	6,85	1,58	2,08	0,43	9,33	1991	2,36	0,40
CA	F	0,07	5,86	0,72	3,01	0,02	3,25	394	1,98	0,37
CA	F	0,04	5,72	1,67	2,69	0,24	6,23	405	1,69	0,36
CA	W	0,03	3,57	0,38	2,71	0,39	1,74	769	1,65	0,20
CA	W	0,04	4,64	1,21	2,60	0,57	7,38	1910	2,79	0,46
CA	F	0,04	3,12	1,11	15,4	0,44	9,73	836	2,39	0,26
CA	F	0,03	5,92	0,97	15,9	0,83	7,50	1439	1,98	0,25
CA	F	0,04	3,04	1,21	17,1	0,64	9,31	1078	2,63	0,29
CA	F	0,05	2,80	1,13	16,74	0,52	9,76	1508,99	3,22	0,31
CA	W	0,05	3,03	1,54	16,3	0,54	11,8	911	3,48	0,37
CA	F	0,04	3,47	0,99	26,6	0,49	10,8	742	2,49	0,44
FA	F	0,06	3,10	1,26	17,2	0,95	10,9	1526	3,15	0,43
FA	W	0,06	7,77	1,16	4,97	0,72	7,45	1642	2,27	0,39
FA	F	0,04	6,83	1,60	2,35	1,01	8,34	2627	2,45	0,51
FA	W	0,08	6,53	0,61	2,89	0,55	4,17	964	2,39	0,58
FA	F	0,05	7,65	1,12	2,35	1,06	8,15	1369	2,90	0,69

FA	F	0,09	2,63	1,44	12,4	0,23	6,97	438	2,62	0,31
FA	W	0,07	3,52	0,45	3,96	0,18	3,01	1696	2,80	0,25
FA	F	0,05	6,71	1,36	2,37	0,57	7,39	1850	2,44	0,42
FA	F	0,05	6,88	3,91	2,59	28,9	14,6	412	1,84	0,65
FA	F	0,05	9,00	1,37	3,01	0,56	7,80	1119	2,29	0,40
FA	W	0,04	3,64	1,58	15,57	1,06	12,01	1554,35	2,69	0,41
FA	W	0,03	2,8	0,57	24,5	0,48	5,47	1201	1,70	0,22
FA	F	0,06	4,2	2,17	18,9	1,16	16,2	1786	3,59	0,68
FA	F	0,06	2,88	0,94	5,79	0,37	7,44	1032	2,16	0,34
FA	F	0,04	5,17	1,01	2,84	0,74	6,75	1187	2,14	0,46
FA	W	0,06	4,25	1,00	2,71	0,52	7,58	1307	2,73	0,43
FA	W	0,07	5,42	1,62	4,97	0,28	7,76	480	2,28	0,33
FA	F	0,05	8,25	1,81	2,58	0,38	7,26	407	1,70	0,39
FA	F	0,04	5,77	0,99	2,72	0,44	8,34	928	2,15	0,36
FA	F	0,04	4,69	1,32	2,45	0,44	6,89	1237	2,27	0,39
FA	F	0,04	1,58	0,62	16,6	0,68	4,94	1045	2,40	0,10
FA	F	0,04	2,38	1,16	15,8	0,59	10,1	1116	2,73	0,26
FA	F	0,05	2,9	1,35	15,2	0,64	12,2	1820	3,50	0,36
FA	W	0,06	12,8	1,10	6,24	0,65	7,90	2148	2,55	0,36
MA	W	0,10	4,40	1,27	16,5	0,45	8,03	1764	3,23	0,30
MA	F	0,06	5,24	1,0	2,78	0,61	6,22	1783	2,78	0,45
MA	W	0,04	2,19	0,97	15,7	0,77	8,99	1256	2,49	0,24
MA	F	0,03	2,52	0,84	17,0	0,88	6,92	955	2,18	0,19
MA	W	0,05	2,95	1,58	15,3	0,70	13,9	1823	3,67	0,44
MA	W	0,03	7,87	1,17	2,18	0,87	6,83	1547	1,99	0,39
MA	W	0,06	10,1	1,01	7,33	0,90	6,75	1999	2,40	0,33
MA	F	0,06	6,15	1,26	3,80	0,42	8,28	2087	2,72	0,34
MA	F	0,04	4,84	0,54	2,41	0,37	2,81	1704	2,38	0,24
MA	F	0,06	5,17	1,23	2,63	0,54	8,17	1794	2,88	0,50
MA	F	0,04	4,47	0,43	17,8	0,49	2,98	1342	2,03	0,05
MA	W	0,03	2,83	0,38	26,9	0,26	3,40	675	1,68	0,24
MA	W	0,03	2,01	0,68	18,3	0,38	4,92	2065	2,23	0,16
MA	F	0,02	11,1	0,41	3,22	0,38	1,73	202	0,59	0,36
MA	F	0,05	5,04	1,01	2,44	0,58	7,58	1470	2,67	0,45
MA	W	0,02	13,7	0,56	3,85	0,27	44,1	36	0,35	0,49
MA	W	0,07	4,27	0,44	5,19	0,10	3,00	1855	2,58	0,22

MA	F	0,07	5,47	1,57	2,49	0,71	7,12	577	2,44	0,50
MA	F	0,05	3,64	1,45	0,40	0,43	7,45	611	2,11	0,28
MA	W	0,07	3,07	1,37	6,31	0,28	7,79	1044	2,56	0,32
State And Type		**Concentration (mg/kg)**								
		Th	**Tl**	**U**	**V**	**W**	**Y**	**Zn**	**Zr**	**Th**
CA	W	9,32	0,30	5,13	130,70	2,75	12,61	30,44	430,75	9,32
CA	F	11,2	1,45	7,82	139	8,01	8,63	41,3	313	11,2
CA	F	11,9	0,31	6,32	107	4,13	8,93	34,9	385	11,9
CA	W	5,31	0,16	9,02	123	5,59	2,03	32,3	498	5,31
CA	F	7,20	1,60	8,03	173	11,43	3,25	68,9	393	7,20
CA	F	13,2	0,16	6,71	117	4,78	17,08	29,2	447	13,2
CA	F	9,10	0,27	5,56	82,8	3,66	5,91	20,7	395	9,10
CA	F	9,04	0,30	5,03	80,5	5,59	7,79	15,2	286	9,04
CA	F	8,99	0,37	7,24	89,2	4,07	2,90	20,0	383	8,99
CA	F	3,00	1,12	7,33	174	5,05	0,94	116	494	3,00
CA	W	15,5	0,29	6,95	106	7,47	16,3	38,3	468	15,5
CA	F	8,98	1,12	9,12	138	6,36	4,41	45,4	446	8,98
CA	F	3,67	0,68	6,98	113	3,01	1,15	48,5	426	3,67
CA	F	2,47	1,19	7,43	157	3,98	0,66	94,3	452	2,47
CA	W	4,96	0,30	4,22	86,3	3,36	3,56	21,6	265	4,96
CA	W	16,1	0,54	7,85	101	6,65	5,22	27,4	400	16,1
CA	F	6,10	0,97	7,97	172	5,09	3,76	66,3	374	6,10
CA	F	5,62	0,84	7,18	102	5,05	5,33	31,8	367	5,62
CA	F	8,88	0,89	7,64	125	5,31	5,76	63,7	424	8,88
CA	F	5,00	0,50	9,66	126,20	6,43	1,37	41,98	473,05	5,00
CA	W	5,41	0,59	11,1	134	7,05	1,29	52,2	384	5,41
CA	F	5,82	1,27	7,31	126	6,78	2,49	67,3	495	5,82
FA	F	10,9	0,60	9,82	145	7,26	10,34	22,6	385	10,9
FA	W	13,7	0,61	5,55	97,9	5,03	8,59	27,2	332	13,7
FA	F	16,8	0,56	8,05	115	6,12	9,04	29,3	358	16,8
FA	W	4,85	0,43	6,08	102	5,16	1,54	24,4	344	4,85
FA	F	13,0	0,73	9,78	113	6,85	4,26	43,0	397	13,0
FA	F	1,91	0,85	7,02	164	4,86	0,43	108	500	1,91
FA	W	5,85	0,27	6,79	89,4	4,24	2,71	24,5	479	5,85
FA	F	5,74	0,92	9,93	130	5,64	2,24	41,0	437	5,74
FA	F	4,82	2,36	9,14	229	8,52	1,76	226	454	4,82
FA	F	7,66	0,86	7,48	125	6,27	3,18	59,7	383	7,66
FA	W	12,25	1,04	8,61	129,87	7,62	7,95	44,81	385,14	12,25
FA	W	6,52	0,70	4,75	136	6,48	7,45	65,5	352	6,52
FA	F	10,6	1,00	11,2	166	8,26	5,57	40,2	372	10,6
FA	F	5,59	0,52	5,91	129	4,59	1,93	49,9	363	5,59
FA	F	5,89	0,48	5,85	124	5,02	2,04	35,3	378	5,89
FA	W	16,6	0,60	7,73	113	6,01	4,66	31,1	410	16,6
FA	W	3,84	1,14	7,68	153	4,98	1,89	90,8	489	3,84

FA	F	2,25	1,14	7,60	164	4,60	0,58	98,0	443	2,25
FA	F	7,80	0,96	7,05	117	5,63	3,74	49,9	331	7,80
FA	F	6,15	0,97	7,02	120	5,10	1,85	48,3	351	6,15
FA	F	9,80	0,40	6,26	116	4,40	8,27	35,7	404	9,80
FA	F	8,6	0,90	7,14	137	5,78	5,4	73,5	414	8,6
FA	F	4,47	0,65	11,1	131	7,39	0,9	36,1	477	4,47
FA	W	21,9	0,60	6,60	109	6,41	19,4	31,5	352	21,9
MA	W	9,49	0,64	7,50	137	5,57	6,99	62,4	523	9,49
MA	F	17,6	0,48	8,06	95,0	5,57	6,28	23,6	423	17,6
MA	W	8,04	0,93	7,89	134	6,09	5,61	68,4	384	8,04
MA	F	11,8	0,53	6,46	124	5,31	9,9	66,3	428	11,8
MA	W	4,68	0,73	11,6	134	7,72	0,95	48,2	465	4,68
MA	W	13,8	0,68	6,88	97,8	4,73	6,50	22,3	288	13,8
MA	W	20,6	0,51	6,57	103	4,54	19,9	54,8	335	20,6
MA	F	12,2	0,62	8,46	102	5,53	6,82	33,6	436	12,2
MA	F	11,1	0,26	6,95	96,7	3,82	6,85	26,4	449	11,1
MA	F	12,0	0,57	7,95	104	6,71	3,47	26,5	412	12,0
MA	F	10,7	0,29	6,29	91	4,33	10,83	52,7	397	10,7
MA	W	6,16	0,47	4,53	118	6,31	5,91	42,9	489	6,16
MA	W	7,95	0,23	7,22	130	4,90	7,21	43,4	425	7,95
MA	F	1,16	0,35	1,89	49,1	1,60	0,64	31,7	139	1,16
MA	F	16,4	0,65	7,92	112	5,82	6,38	33,9	404	16,4
MA	W	1,46	0,24	1,18	31,2	1,44	0,81	33,9	122	1,46
MA	W	7,77	0,15	6,56	86,6	3,41	5,44	21,9	483	7,77
MA	F	5,93	1,02	9,75	145	5,61	1,63	69,8	460	5,93
MA	F	2,92	0,70	7,37	167	4,47	1,37	158	479	2,92
MA	W	8,81	1,10	7,45	125	5,51	5,16	76,1	381	8,81

Appendix D: Mass Percentage and Leachability For Major Oxides

An average value is presented in this section.

%	SiO_2	CaO	Alkalis	Al_2O_3	Fe_2O_3	Fe total	TiO	MgO	MnO	Na_2O	K_2O
Fresh CA	55,51	5,56	0,75	26,29	5,20	4,16	1,43	1,55	0,05	0,22	0,80
Fresh FA	54,54	5,28	0,72	27,81	4,38	3,46	1,56	1,43	0,05	0,19	0,82
Fresh MA	57,31	4,41	0,84	28,10	4,06	3,65	1,50	1,28	0,05	0,26	0,88
Weathered CA	52,72	5,70	0,72	27,59	4,63	3,23	1,58	1,49	0,04	0,23	0,74
Weathered FA	52,08	5,95	0,69	26,11	4,05	3,18	1,53	1,51	0,04	0,23	0,71
Weathered MA	54,90	4,36	0,74	26,83	5,11	3,93	1,23	1,46	0,06	0,22	0,84

Leach (mg/l)	Si	Ca	Al	Fe	Ti	Mg	Mn	Mn Conc (mg/kg)	Na	K
Fresh CA	5,62	98,43	1,46	0,02	0,003	2,45	0,004	383,58	12,18	2,89
Fresh FA	3,62	448,45	2,61	0,01	0,002	5,16	0,019	368,97	4,03	2,48
Fresh MA	4,66	94,41	4,04	0,01	0,001	0,33	0,004	349,98	16,85	1,81
Weathered CA	3,43	109,43	2,13	0,01	0,003	1,06	0,006	312,50	24,07	12,06
Weathered FA	4,47	71,61	2,46	0,01	0,001	1,34	0,005	301,17	11,07	4,63
Weathered MA	5,98	41,64	2,83	0,65	0,037	1,69	0,008	371,19	13,84	2,04

% Change		CA	FA	MA
SiO_2	Mass	-2,79%	-2,46%	-2,41%
	Leachability	-39%	23%	28%
CaO	Mass	0,14%	0,68%	-0,05%
	Leachability	11%	-84%	-56%

Fe_2O_3	Mass	-0,58%	-0,33%	1,05%
	Leachability	-20%	29%	9383%
Al_2O_3	Mass	1,31%	-1,70%	-1,27%
	Leachability	46%	-6%	-30%
Total Fe	Mass	-0,93%	-0,28%	0,28%
	Leachability	-	-	-
TiO_2	Mass	0,16%	-0,03%	-0,27%
	Leachability	-18%	-33%	2578%
MgO	Mass	-0,05%	0,09%	0,17%
	Leachability	-57%	-74%	412%
MnO	Mass	-0,01%	-0,01%	0,01%
	Leachability	36%	-74%	126%
	Concentration	-19%	-18%	6%
Na_2O	Mass	0,01%	0,04%	-0,04%
	Leachability	98%	175%	-18%
K_2O	Mass	-0,06%	-0,11%	-0,05%
	Leachability	318%	87%	13%

Appendix E: Concentration and Leachability Data for Semi Metals

Conc (mg/kg)	B	Ge	As	Sb	Te
Fresh CA	73,46	3,80	7,71	0,93	0,29
Fresh FA	90,51	5,58	9,74	1,32	0,41
Fresh MA	102,16	6,06	13,02	1,34	0,41
Weathered CA	83,52	4,64	8,52	1,09	0,31
Weathered FA	88,79	4,52	8,51	1,08	0,33
Weathered MA	45,20	2,64	6,50	0,77	0,30

Leach (mg/l)	B	Ge	As	Sb	Te
Fresh CA	0,25	0,0010	0,005	0,0035	0,0010
Fresh FA	0,16	0,0025	0,004	0,0039	0,0009
Fresh MA	0,30	0,0012	0,006	0,0041	0,0008
Weathered CA	0,33	0,0012	0,008	0,0046	0,0009
Weathered FA	0,22	0,0010	0,004	0,0037	0,0009
Weathered MA	0,14	0,0011	0,006	0,0026	0,0010

% Change		CA	FA	MA
B	Concentration	14%	-2%	-56%
	Leachability	29%	40%	-53%
Ge	Concentration	22%	-19%	-56%
	Leachability	26%	-61%	-12%
As	Concentration	11%	-13%	-50%
	Leachability	43%	21%	0%
Sb	Concentration	17%	-19%	-43%
	Leachability	32%	-5%	-37%
Te	Concentration	6%	-19%	-25%
	Leachability	-3%	3%	18%

Appendix F: Concentration and Leachability for Basic Metals

Conc (mg/kg)	Ga	Sn	TI	Pb	Bi
Fresh CA	27,27	5,74	2,39	41,85	1,54
Fresh FA	35,46	8,65	2,61	56,75	2,83
Fresh MA	35,85	8,81	2,37	58,70	2,83
Weathered CA	32,70	8,23	2,86	48,29	2,57
Weathered FA	32,40	7,84	2,59	45,70	2,63
Weathered MA	20,94	9,14	1,85	35,33	1,54

Leach (mg/l)	Ga	Sn	TI	Pb	Bi
Fresh CA	0,01	0,001	0,001	0,001	0,001
Fresh FA	0,02	0,001	0,001	0,001	0,001
Fresh MA	0,02	0,001	0,001	0,001	0,001
Weathered CA	0,02	0,001	0,001	0,001	0,001
Weathered FA	0,02	0,001	0,001	0,001	0,001
Weathered MA	0,01	0,001	0,001	0,006	0,001

% Change		CA	FA	MA
Ga	Concentration	20%	-9%	-42%
	Leachability	65%	-12%	-62%
Sn	Concentration	43%	-9%	4%
	Leachability	-5%	-2%	-7%
TI	Concentration	-6%	-27%	-45%
	Leachability	0%	-4%	0%
Pb	Concentration	15%	-19%	-40%
	Leachability	5%	-22%	498%
Bi	Concentration	67%	-7%	-46%
	Leachability	0%	0%	0%

Appendix G: Concentration and Leachability for Alkali Metals

Concentration and Leachability	Li (mg/kg)	Li Leach (mg/l)	Rb (mg/kg)	Rb Leach (mg/l)	Cs (mg/kg)	Cs Leach (mg/l)
Fresh CA	101,53	0,09	4,67	0,006	1,44	0,001
Fresh FA	118,49	0,10	4,87	0,008	1,27	0,002
Fresh MA	91,11	0,06	4,57	0,004	1,07	0,001
Weathered CA	170,01	0,83	4,89	0,021	1,42	0,003
Weathered FA	140,11	0,12	5,23	0,011	1,36	0,002
Weathered MA	70,19	0,02	5,84	0,004	1,18	0,001

% Change		CA	FA	MA
Li	Concentration	67%	18%	-23%
	Leachability	783%	18%	-63%
Rb	Concentration	5%	7%	28%
	Leachability	270%	40%	6%
Cs	Concentration	-1%	8%	10%
	Leachability	178%	10%	-1%

Appendix H: Concentration and Leachability for Alkali Earth Metals

Concentration and Leachability	Be (mg/kg)	Be Leach (mg/l)	Sr (mg/kg)	Sr Leach (mg/l)	Sr Mass (%)	Ba (mg/kg)	Ba Leach (mg/l)	Ba Mass (%)
Fresh CA	5,69	0,001	1332,80	0,82	0,13	1222,78	0,20	0,13
Fresh FA	6,21	0,001	1269,23	2,68	0,13	1174,39	0,77	0,12
Fresh MA	6,11	0,001	1119,26	0,55	0,11	1183,17	0,19	0,12
Weathered CA	6,07	0,001	1612,71	0,95	0,17	1279,39	0,22	0,13
Weathered FA	5,60	0,001	1645,63	0,87	0,17	1328,51	0,13	0,14
Weathered MA	4,87	0,001	981,50	0,23	0,10	1098,90	0,16	0,11

% Change		CA	FA	MA
Be	Concentration	7%	-10%	-20%
	Leachability	0%	0%	0%
Sr	Concentration	21%	30%	-12%
	Leachability	16%	-68%	-58%
	Mass	0,03%	0,04%	-0,01%
Ba	Concentration	5%	13%	-7%
	Leachability	11%	-84%	-14%
	Mass	0,01%	0,02%	-0,01%

Appendix I: Mass Percentage, Concentration and Leachability for Transition Metals

Mass %	Cr	Cu	Ni	V	Zn	Zr
Fresh CA	0,019	0,005	0,006	0,013	0,005	0,038
Fresh FA	0,020	0,005	0,008	0,014	0,007	0,039
Fresh MA	0,022	0,005	0,006	0,015	0,006	0,035
Weathered CA	0,020	0,005	0,006	0,012	0,004	0,040
Weathered FA	0,020	0,005	0,005	0,012	0,004	0,037
Weathered MA	0,019	0,005	0,010	0,012	0,006	0,034

Conc (mg/kg)	Cr	Cu	Ni	V	Zn	Zr
Fresh CA	174,42	45,72	39,98	122,20	44,19	414,47
Fresh FA	184,39	47,93	43,89	131,43	57,95	413,49
Fresh MA	198,75	49,28	44,05	139,32	56,94	398,97
Weathered CA	187,09	42,19	42,79	120,82	43,79	432,06
Weathered FA	185,21	42,16	36,55	111,84	43,29	399,52
Weathered MA	169,85	36,78	36,16	103,40	54,28	377,60

Leach (mg/l)	Cr	Cu	Ni	V	Zn	Zr
Fresh CA	0,14	0,002	0,002	0,04	0,01	0,001
Fresh FA	0,14	0,002	0,008	0,03	0,01	0,001
Fresh MA	0,19	0,003	0,002	0,06	0,00	0,001
Weathered CA	0,20	0,001	0,002	0,06	0,01	0,001
Weathered FA	0,13	0,002	0,002	0,05	0,01	0,001
Weathered MA	0,04	0,003	0,002	0,04	0,03	0,002

% Change after Weathering		CA	FA	MA
Cr	Concentration	7%	0%	-15%
	Leachability	45%	-10%	-77%
	Mass	0,0010%	-0,0003%	-0,0032%
Cu	Concentration	-8%	-12%	-25%
	Leachability	-46%	-22%	10%
	Mass	0,0001%	-0,0003%	-0,0008%
Ni	Concentration	18%	-11%	-17%
	Leachability	0%	0%	0%
	Mass	-0,0002%	-0,0023%	0,0037%
V	Concentration	-1%	-15%	-26%
	Leachability	132%	125%	-38%
	Mass	-0,0007%	-0,0017%	-0,0031%
Zn	Concentration	-1%	-25%	-5%
	Leachability	27%	33%	503%
	Mass	-0,0008%	-0,0025%	-0,0006%
Zr	Concentration	4%	-3%	-5%
	Leachability	1%	0%	95%
	Mass	0,0020%	-0,0016%	-0,0011%

Conc (mg/kg)	Ag	Au	Cd	Co	Hf	Hg	Ir
Fresh CA	0,54	0,01	0,17	14,26	12,39	0,14	0,03
Fresh FA	0,57	0,01	0,23	14,68	12,04	0,13	0,07
Fresh MA	0,45	0,01	0,20	15,45	12,72	0,16	0,02
Weathered CA	0,69	0,01	0,19	13,08	12,07	0,11	0,04
Weathered FA	0,52	0,01	0,17	11,92	11,99	0,11	0,03
Weathered MA	0,39	0,01	0,19	13,76	11,12	0,06	0,04
	Mo	Nb	Pt	Sc	Ta	W	Y
Fresh CA	6,26	35,52	0,05	9,46	2,39	5,50	6,52
Fresh FA	5,16	38,57	0,05	10,60	2,61	5,96	4,06

Fresh MA	4,97	36,30	0,05	9,73	2,37	5,94	4,01
Weathered CA	5,37	40,54	0,06	12,20	2,86	5,85	7,88
Weathered FA	5,75	38,30	0,05	8,28	2,59	5,56	7,50
Weathered MA	3,84	29,41	0,04	8,95	1,85	4,21	4,47

Leach (mg/l)	Ag	Au	Cd	Co	Hf	Hg	Ir
Fresh CA	0,001	0,001	0,0005	0,001	12,39	0,001	0,001
Fresh FA	0,001	0,001	0,0004	0,001	12,04	0,001	0,001
Fresh MA	0,001	0,001	0,0004	0,001	12,72	0,001	0,001
Weathered CA	0,001	0,001	0,0004	0,001	12,07	0,001	0,001
Weathered FA	0,001	0,001	0,0004	0,001	11,99	0	0,001
Weathered MA	0,001	0,001	0,0003	0,001	11,12	0	0,001
	Mo	Nb	Pt	Sc	Ta	W	Y
Fresh CA	0,08	0,001	0,001	0,002	0,001	0,02	0,001
Fresh FA	0,07	0,001	0,001	0,001	0,001	0,03	0,001
Fresh MA	0,05	0,001	0,001	0,002	0,001	0,02	0,001
Weathered CA	0,07	0,001	0,001	0,001	0,001	0,03	0,001
Weathered FA	0,04	0,001	0,001	0,002	0,001	0,02	0,001
Weathered MA	0,02	0,001	0,001	0,002	0,001	0,01	0,001

% Change after Weathering		CA	FA	MA
Ag	Concentration	29%	-10%	-13%
	Leachability	2%	-1%	-1%

Au	Concentration	30%	-20%	-8%
	Leachability	0%	0%	0%
Cd	Concentration	13%	-24%	-4%
	Leachability	-20%	-16%	-21%
Co	Concentration	-8%	-19%	-11%
	Leachability	-18%	-16%	1%
Hf	Concentration	-3%	0%	-13%
	Leachability	0%	0%	0%
Hg	Concentration	-19%	-14%	-64%
	Leachability	6%	-47%	-51%
Ir	Concentration	19%	-49%	51%
	Leachability	0%	0%	0%
		CA	FA	MA
Mo	Concentration	-14%	12%	-23%
	Leachability	-12%	-37%	-68%
Nb	Concentration	14%	-1%	-19%
	Leachability	0%	0%	1%
Pt	Concentration	18%	-11%	-17%
	Leachability	0%	0%	0%
Sc	Concentration	29%	-22%	-8%
	Leachability	-29%	25%	22%
Ta	Concentration	20%	-1%	-22%
	Leachability	0%	2%	0%
W	Concentration	6%	-7%	-29%
	Leachability	45%	-35%	-54%
Y	Concentration	21%	85%	12%
	Leachability	0%	0%	43%

Appendix J: LOI, pH, TDS and EC

	pH	LOI	TDS	EC
Fresh CA	9,88	3,53	197,23	43,92
Fresh FA	11,40	3,49	469,88	81,28
Fresh MA	10,56	3,65	247,25	37,75
Weathered CA	10,23	5,64	344,83	50,70
Weathered FA	10,12	6,88	225,00	34,30
Weathered MA	8,99	3,42	160,44	22,75

Appendix K: Correlation Coefficients

Major Oxide	Element	Pearson Correlation	Spearman Correlation
SiO2	Si	0,571	0,294
Al2O3	Al	0,001	0,130
Fe2O3	Fe	0,137	0,248
TiO2	Ti	-0,530	-0,120
CaO	Ca	0,210	-0,003
MgO	Mg	-0,083	-0,069
Na2O	Na	0,416	0,388
K2O	K	0,083	0,213
MnO	Mn	-0,042	-0,270

Element	SiO_2 and Si		CaO and Ca	
Ash State and Type	r	r_s	r	r_s
Fresh FA	0,23	0,30	0,54	0,22
Fresh CA	0,27	0,36	-0,07	0,00
Fresh MA	0,26	0,24	0,70	0,60
Weathered FA	-0,15	0,06	-0,34	-0,22
Weathered CA	0,68	0,51	0,12	0,04
Weathered MA	0,84	0,50	0,31	0,17
	Al_2O_3 and Al		**Na_2O Na**	
Fresh FA	0,28	0,18	0,40	0,49
Fresh CA	0,19	-0,04	0,29	0,25
Fresh MA	0,40	0,42	0,69	0,83
Weathered FA	0,29	0,26	0,20	0,59
Weathered CA	0,23	0,09	-0,01	-0,21
Weathered MA	-0,52	-0,16	0,62	0,15
	Fe_2O_3 and Fe		**K_2O and K**	
Fresh FA	0,57	0,29	0,15	0,50
Fresh CA	0,49	19,00	0,22	0,05
Fresh MA	-0,38	-0,45	0,33	0,23

Weathered FA	0,78	0,50	0,58	0,35
Weathered CA	-0,31	0,22	0,77	0,84
Weathered MA	-0,08	0,26	-0,01	0,11
	Fe(total) and Fe		**MgO and Mg**	
Fresh FA	0,65	0,46	-0,16	-0,18
Fresh CA	0,39	0,17	-0,05	-0,06
Fresh MA	-0,10	-0,21	-0,24	-0,10
Weathered FA	0,81	0,31	0,06	0,03
Weathered CA	-0,31	0,28	-0,46	-0,50
Weathered MA	-0,16	0,18	-0,24	-0,25
	TiO_2 and Ti		**MnO and Mn**	
Fresh FA	-0,40	-0,36	-0,28	-0,43
Fresh CA	-0,35	0,14	-0,19	-0,19
Fresh MA	0,13	0,15	-0,49	-0,75
Weathered FA	-0,20	-0,20	-0,07	0,12
Weathered CA	-0,33	-0,42	0,07	0,16
Weathered MA	-0,64	-0,08	-0,06	-0,48

Element	B		As		Te	
	r	r_s	r	r_s	r	r_s
Fresh FA	-0,05	0,05	0,39	0,38	0,19	0,10
Fresh CA	0,87	0,44	0,58	0,08	0,00	0
Fresh MA	0,84	0,86	0,39	0,39	-0,72	-0,61
Weathered FA	0,22	0,18	0,73	0,07	0,43	0,41
Weathered CA	-0,50	-0,30	0,16	0,10	-0,29	-0,35
Weathered MA	0,43	0,60	0,70	0,70	0	0
Element	Ga		Sn		TI	
	r	r_s	r	r_s	r	r_s
Fresh FA	0,09	0,23	0,09	0,14	0,18	0,31
Fresh CA	0,84	0,79	-0,19	-0,03	-0,02	-0,15
Fresh MA	-0,02	-0,04	-0,74	-0,61	0,33	0,20
Weathered FA	0,50	0,50	-0,06	-0,12	0,08	0,11

Weathered CA	0,83	0,70	-0,64	-0,71	0,68	0,62
Weathered MA	0,72	0,60	-0,35	-0,71	-0,46	-0,60
Element	Li		Rb		Ce	
	r	r_s	r	r_s	r	r_s
Fresh FA	0,56	0,49	0,30	0,38	-0,17	-0,31
Fresh CA	0,59	0,48	0,02	-0,13	0	0
Fresh MA	0,81	0,79	-0,22	-0,14	0	0
Weathered FA	0,18	0,86	0,56	0,82	-0,57	-0,61
Weathered CA	0,41	0	-0,54	-0,70	0,92	0,71
Weathered MA	0,75	0,90	0,31	0,20	-0,73	-0,72
Element	Sc		V		Cr	
	r	r_s	r	r_s	r	r_s
Fresh FA	-0,63	-0,65	0,82	0,37	0,44	0,50
Fresh CA	-0,29	-0,33	0,86	0,90	-0,40	-0,46
Fresh MA	0,73	0,71	0,24	0,18	0,43	0,43
Weathered FA	-0,53	-0,29	0,47	0,46	-0,65	-0,86
Weathered CA	-0,31	-0,40	0,43	0,40	0,19	0,00
Weathered MA	-0,39	0,00	0,79	0,70	0,37	0,60
	Co		Ni		Cu	
Fresh FA	0,56	0,20	0,51	0,50	-0,63	-0,73
Fresh CA	0,34	0,39	-0,23	-0,26	-0,33	-0,30
Fresh MA	-0,53	-0,61	0,75	0,64	0,40	0,22
Weathered FA	0,00	0,00	0,36	0,68	-0,51	-0,63
Weathered CA	-0,35	-0,35	-0,14	0,10	-0,07	0,10
Weathered MA	-0,06	0,22	-0,62	-0,90	0,12	-0,30
	Zn		Y		Zr	
Fresh FA	0,30	0,34	0,00	0,00	0,00	0,00
Fresh CA	-0,17	-0,13	0,00	0,00	-0,34	-0,31
Fresh MA	-0,11	0,14	0,00	0,00	0,00	0,00
Weathered FA	-0,19	-0,11	0,00	0,00	0,00	0,00
Weathered CA	0,83	0,80	0,00	0,00	0,00	0,00
Weathered MA	-0,36	-0,10	-0,94	-0,78	-0,58	-0,78

	Nb		Ag		Cd	
Fresh FA	0,00	0,00	-0,38	-0,33	0,38	0,43
Fresh CA	0,00	0,00	0,06	0,05	0,82	0,68
Fresh MA	0,00	0,00	0,00	0,00	0,01	0,18
Weathered FA	0,00	0,00	-0,22	-0,27	-0,12	-0,14
Weathered CA	0,00	0,00	-0,29	-0,45	0,60	0,50
Weathered MA	-0,53	-0,35	0,00	0,00	-0,39	-0,40
	Hg		Ta		W	
Fresh FA	0,88	0,34	0,00	0,00	0,50	0,16
Fresh CA	-0,27	-0,18	-0,11	-0,17	0,77	0,58
Fresh MA	0,67	0,61	0,00	0,00	0,20	0,36
Weathered FA	0,12	0,75	0,00	0,00	0,14	-0,07
Weathered CA	0,81	0,60	0,00	0,00	0,83	0,70
Weathered MA	0,87	0,70	0,00	0,00	0,80	0,60

	Ge		Sb	
	r	r_s	r	r_s
Fresh FA	0,29	0,38	0,88	0,57
Fresh CA	0,25	0,58	0,66	0,35
Fresh MA	-0,26	-0,40	0,13	0,25
Weathered FA	-0,26	-0,27	0,35	-0,14
Weathered CA	0	0	0,20	0,30
Weathered MA	0,86	0,71	0,98	0,70
	Sr		Ba	
Fresh FA	0,77	0,41	0,39	0,18
Fresh CA	0,59	0,75	0,54	0,35
Fresh MA	0,81	0,93	0,38	0,82
Weathered FA	0,13	0,39	-0,05	-0,21
Weathered CA	0,34	0,10	0,46	-0,10
Weathered MA	0,51	0,70	-0,91	-0,70

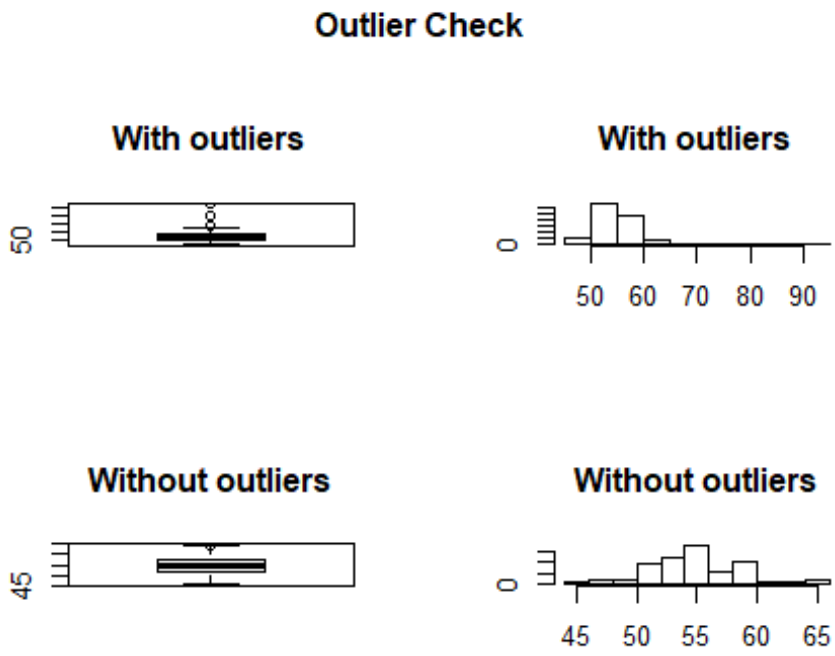
Appendix L: Code Used in R Studio

The following code was used for every major oxide, and element for leachability and concentration data. The code given below is an example used in the case of SiO_2.

```
#Code Used for Major Oxides
setwd("C:/Users/Cherante'/Documents/WITS/R Data") #Set Workspace
# Import all necessary packages into R Studi0
library(car)

## Loading required package: carData

library(ggplot2)
library(rcompanion)
library(WRS2)
library(Rfit)

##
## Attaching package: 'Rfit'

## The following object is masked from 'package:car':
##
##     subsets

library(pastecs)
library(ggpubr)

## Loading required package: magrittr

##
## Attaching package: 'magrittr'

## The following object is masked from 'package:pastecs':
##
##     extract
```

```
# Import data from a txt file while containes the major oxides,
leachability and concentration
anovadata = read.table("Final.txt", header = TRUE, fill=TRUE)
#Import Data
fix(anovadata) #Check table
 # Import outlier function
outlierKD <- function(dt, var) {
  var_name <- eval(substitute(var),eval(dt))
  na1 <- sum(is.na(var_name))
  m1 <- mean(var_name, na.rm = T)
  par(mfrow=c(2, 2), oma=c(0,0,3,0))
  boxplot(var_name, main="With outliers")
  hist(var_name, main="With outliers", xlab=NA, ylab=NA)
  outlier <- boxplot.stats(var_name)$out
  mo <- mean(outlier)
  var_name <- ifelse(var_name %in% outlier, NA, var_name)
  boxplot(var_name, main="Without outliers")
```

```
  hist(var_name, main="Without outliers", xlab=NA, ylab=NA)
  title("Outlier Check", outer=TRUE)
  na2 <- sum(is.na(var_name))
  cat("Outliers identified:", na2 - na1, "n")
  cat("Propotion (%) of outliers:", round((na2 - na1) / sum(!is.na(var_n
ame))*100, 1), "n")
  cat("Mean of the outliers:", round(mo, 2), "n")
  m2 <- mean(var_name, na.rm = T)
  cat("Mean without removing outliers:", round(m1, 2), "n")
  cat("Mean if we remove outliers:", round(m2, 2), "n")
  response <- readline(prompt="Do you want to remove outliers and to rep
lace with NA? [yes/no]: ")
  if(response == "y" | response == "yes"){
    dt[as.character(substitute(var))] <- invisible(var_name)
    assign(as.character(as.list(match.call())$dt), dt, envir = .GlobalEn
v)
    cat("Outliers successfully removed", "n")
    return(invisible(dt))
  } else{
    cat("Nothing changed", "n")
    return(invisible(var_name))
  }
}

outlierKD(anovadata, SiO2)
```




```
## Outliers identified: 3 nPropotion (%) of outliers: 4.7 nMean of the o
utliers: 80.09 nMean without removing outliers: 55.92 nMean if we remove
outliers: 54.79 nDo you want to remove outliers and to replace with NA?
[yes/no]:
## Nothing changed n
```

```
#Generate tables to analyse data
A=aggregate(anovadata$SiO2, by=list(anovadata$Comb), FUN=mean)
B=aggregate(anovadata$SiO2, by=list(anovadata$Comb), FUN=range)

Ratio = anovadata$SiO2/anovadata$Al2O3
Ratio1 = anovadata$CaO/anovadata$Al2O3
anovadata=cbind(anovadata,Ratio,Ratio1)

interaction.plot (x.factor = anovadata$State,
                  trace.factor = anovadata$Type,
                  response = anovadata$Ratio1,
                  fun = mean, type = "b", las=1,
                  xlab = "State of Ash", ylab=expression("SiO" [2]*" Per
centage (%)"),
                  pch=c(1,19), col = c("blue", "orange", "darkgreen"),
                  legend=FALSE, xaxt='n',cex.main=1.4, cex.lab=1.35, cex
.axis=1.4)
axis(1, at=1:2, labels=c("Fresh", "Weathered"),cex.axis=1.35)
legend("topleft", c("Coarse Ash", "Fly Ash","Mixed Ash"), lty=1, bty="n"
, pch=c(1,19),
       col = c("blue", "orange", "darkgreen"))


#Check for skewness, kurtosis and Shapiro-Wilk Test
by(anovadata$SiO2, list(anovadata$Type, anovadata$State), stat.desc, bas
ic=F, norm=T)

## : CA
## : F
##       median         mean      SE.mean CI.mean.0.95          var
std.dev
##  54.73082160  55.50814584   1.18567961   2.54302983  21.08754189   4.
59211737
##     coef.var     skewness     skew.2SE     kurtosis     kurt.2SE   no
rmtest.W
##   0.08272871   0.27698332   0.23872960  -0.77609532  -0.34619384   0.
98386291
##   normtest.p
##   0.98921882
## ------------------------------------------------------------
## : FA
## : F
##       median         mean      SE.mean CI.mean.0.95          var
std.dev
##  54.77169600  54.54016578   0.83189853   1.78424490  10.38082758   3.
22192917
##     coef.var     skewness     skew.2SE     kurtosis     kurt.2SE   no
rmtest.W
##   0.05907443   0.41234103   0.35539327  -1.11673904  -0.49814522   0.
91288634
##   normtest.p
##   0.14993550
## ------------------------------------------------------------
```

```
## : M
## : F
##       median         mean      SE.mean CI.mean.0.95          var
std.dev
##  58.15000000  57.30776782   1.62881453   3.85153433  21.22429406   4.
60698318
##     coef.var     skewness     skew.2SE     kurtosis     kurt.2SE   no
rmtest.W
##   0.08039020  -0.04855796  -0.03228152  -1.62460498  -0.54852671   0.
96181878
##   normtest.p
##   0.82723774
## ------------------------------------------------------------
## : CA
## : W
##       median         mean      SE.mean CI.mean.0.95          var
std.dev
##  53.36836000  52.72073807   1.69984565   4.36959234  17.33685130   4.
16375447
##     coef.var     skewness     skew.2SE     kurtosis     kurt.2SE   no
rmtest.W
##   0.07897755  -0.46601292  -0.27569696  -1.10403486  -0.31710987   0.
94555562
##   normtest.p
##   0.70419922
## ------------------------------------------------------------
## : FA
## : W
##       median         mean      SE.mean CI.mean.0.95          var
std.dev
##  53.13699280  52.08430355   1.09492524   2.58908677   9.59089021   3.
09691624
##     coef.var     skewness     skew.2SE     kurtosis     kurt.2SE   no
rmtest.W
##   0.05945968  -0.22375820  -0.14875533  -1.90504622  -0.64321404   0.
88046111
##   normtest.p
##   0.19024937
## ------------------------------------------------------------
## : M
## : W
##       median         mean      SE.mean CI.mean.0.95          var
std.dev
##  57.10000000  63.29229898   4.75820727  10.97244565 203.76482816  14.
27462182
##     coef.var     skewness     skew.2SE     kurtosis     kurt.2SE   no
rmtest.W
##   0.22553489   0.99207624   0.69169211  -0.65514335  -0.23402851   0.
79181086
##   normtest.p
##   0.01645902
```

```
leveneTest(SiO2 ~ State*Type, data = anovadata) #Test of Homogeneity Var
iance
```

```
## Levene's Test for Homogeneity of Variance (center = median)
##       Df F value  Pr(>F)
## group  5  2.6265 0.03359 *
##       55
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
K= subset(anovadata$SiO2, anovadata$Type=="FA",anovadata$State=="F")
K1=stat.desc(K,basic=F,norm=T,desc=F)
K1=t(K1) #FFA
leveneTest(SiO2 ~ State*Type, data = anovadata) #Test of Homogeneity Var
iance
```

```
## Levene's Test for Homogeneity of Variance (center = median)
##       Df F value  Pr(>F)
## group  5  2.6265 0.03359 *
##       55
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
#Visually check assumptions
qqnorm(anovadata$SiO2, main = expression("Normal Q-Q Plot for SiO"[2]*"
Content"))
#QQ plot (Needs to be diagonal)
qqline(anovadata$SiO2)
shapiro.test(anovadata$SiO2)
```

```
##
##  Shapiro-Wilk normality test
##
## data:  anovadata$SiO2
## W = 0.73984, p-value = 4.619e-09
```

```
#Histogram (Should have normal distribution)
ggplot(anovadata, aes(SiO2)) + geom_histogram(aes(y=..density..),
                                              binwidth=1, color="black",
fill="white")+ stat_function(fun = dnorm,

args = list(mean = mean(anovadata$SiO2), sd = sd(anovadata$SiO2))) + xla
b("SiO2 Content(%)")


#If the data violates assumptions - Robust testing
#Robust Two Way Anova
t2way(SiO2 ~ Type+State+Type:State, data = anovadata, tr=0.2)
```

```
## Call:
## t2way(formula = SiO2 ~ Type + State + Type:State, data = anovadata,
##     tr = 0.2)
##
##             value p.value
## Type       4.7622   0.133
## State      0.0120   0.915
## Type:State 0.9977   0.629
```

```
mcp2atm(SiO2 ~ Type+State+Type:State, data = anovadata) #Post hoc
```

```
## Aggregation requires fun.aggregate: length used as default

## Call:
## mcp2atm(formula = SiO2 ~ Type + State + Type:State, data = anovadata)
##
##                psihat ci.lower ci.upper p-value
## Type1         -0.22222 -1.58345  1.13900 0.67327
## Type2          0.11111 -1.33781  1.56004 0.84566
## Type3          0.33333 -0.67033  1.33700 0.40360
## State1         1.00000 -0.24514  2.24514 0.11124
## Type1:State1   0.22222 -1.13900  1.58345 0.67327
## Type2:State1   0.77778 -0.67115  2.22670 0.18149
## Type3:State1   0.55556 -0.44811  1.55922 0.16932

pbad2way(SiO2 ~ Type+State+Type:State, data = anovadata)

## Aggregation requires fun.aggregate: length used as default

## Call:
## pbad2way(formula = SiO2 ~ Type + State + Type:State, data = anovadata
)
##
##            p.value
## Type        0.6511
## State       0.2788
## Type:State  0.6745

mcp2a(SiO2 ~ Type+State+Type:State, data = anovadata, est = "median")

## Aggregation requires fun.aggregate: length used as default

## Call:
## mcp2a(formula = SiO2 ~ Type + State + Type:State, data = anovadata,
##     est = "median")
##
##               psihat ci.lower ci.upper p-value
## Type1             -1       -2        1 0.12521
## Type2             -1       -2        2 0.23873
## Type3              0       -1        2 0.39065
## State1             1       -1        3 0.30718
## Type1:State1       1       -1        2 0.49082
## Type2:State1       1       -1        3 0.29549
## Type3:State1       0       -1        2 0.48915

med2way(SiO2 ~ Type:State, data = anovadata)

## Call:
## med2way(formula = SiO2 ~ Type:State, data = anovadata)
##
##    value       df p.value
## 1 0.3598 F(2,Inf)  0.6978
## 2 0.2002 F(1,Inf)  0.6546
## 3 0.2248 Chisq(2)  0.8937

mcp2a(SiO2 ~ Type+State+Type:State, data = anovadata, est = "mom")

## Aggregation requires fun.aggregate: length used as default
```

```
## Call:
## mcp2a(formula = SiO2 ~ Type + State + Type:State, data = anovadata,
##     est = "mom")
##
##              psihat ci.lower ci.upper p-value
## Type1            -1 -2.00000  1.13333 0.26377
## Type2            -1 -2.00000  2.00000 0.32387
## Type3             0 -1.00000  2.00000 0.36561
## State1            1 -1.00000  3.00000 0.26043
## Type1:State1      1 -1.26667  2.00000 0.42571
## Type2:State1      1 -1.06667  3.00000 0.22871
## Type3:State1      0 -1.00000  2.00000 0.41903
```

```
lincon(SiO2 ~ State, data = anovadata)
```

```
## Call:
## lincon(formula = SiO2 ~ State, data = anovadata)
##
##          round(df[, -c(1:2)], 5)
## psihat                   1.09463
## ci.lower                -1.25413
## ci.upper                 3.44339
## p.value                  0.35029
```

```
raov(SiO2 ~ Type+State+Type:State, data = anovadata)
```

```
##
## Robust ANOVA Table
##            DF       RD Mean RD       F p-value
## Type        2 19.21241 9.60621 3.89283 0.02623
## State       1  2.57423 2.57423 1.04318 0.31155
## Type:State  2  2.37585 1.18793 0.48140 0.62050
```

```
#If assumptions are met and the distribution is normal
#Run Two Way, Type III Anova
my_anova = aov(SiO2 ~ Type+State+Type:State, data = anovadata)
options(contrasts = c("contr.sum", "contr.poly"))
A = Anova(my_anova, type = "III") #Type III sum of squares
summary(my_anova)
```

```
##             Df Sum Sq Mean Sq F value  Pr(>F)
## Type         2  498.3  249.16   5.775 0.00529 **
## State        1    0.0    0.03   0.001 0.98085
## Type:State   2  216.4  108.21   2.508 0.09070 .
## Residuals   55 2373.1   43.15
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
#Post hoc analysis if ANOVA showed significant results
TukeyHSD(my_anova)
```

```
##   Tukey multiple comparisons of means
##     95% family-wise confidence level
##
## Fit: aov(formula = SiO2 ~ Type + State + Type:State, data = anovadata
)
##
```

```
## $Type
##            diff        lwr       upr     p adj
## FA-CA -1.025791 -5.8012847  3.749703 0.8631935
## M-CA   5.764305  0.6022434 10.926367 0.0252071
## M-FA   6.790096  1.7294364 11.850756 0.0058055
##
## $State
##           diff       lwr      upr     p adj
## W-F 0.04097065 -3.436714 3.518655 0.9812494
##
## $`Type:State`
##                  diff         lwr       upr     p adj
## FA:F-CA:F -0.9679801  -8.0496866  6.113726 0.9985472
## M:F-CA:F   1.7996220  -6.6910459 10.290290 0.9886192
## CA:W-CA:F -2.7874078 -12.1556249  6.580809 0.9500895
## FA:W-CA:F -3.4238423 -11.9145101  5.066826 0.8394376
## M:W-CA:F   7.7841531  -0.3930972 15.961403 0.0707122
## M:F-FA:F   2.7676020  -5.7230658 11.258270 0.9277434
## CA:W-FA:F -1.8194277 -11.1876449  7.548789 0.9923736
## FA:W-FA:F -2.4558622 -10.9465301  6.034806 0.9556227
## M:W-FA:F   8.7521332   0.5748829 16.929384 0.0292649
## CA:W-M:F  -4.5870298 -15.0610150  5.886955 0.7875175
## FA:W-M:F  -5.2234643 -14.9204903  4.473562 0.6082099
## M:W-M:F    5.9845312  -3.4392842 15.408347 0.4281151
## FA:W-CA:W -0.6364345 -11.1104197  9.837551 0.9999727
## M:W-CA:W  10.5715609   0.3499980 20.793124 0.0386771
## M:W-FA:W  11.2079954   1.7841801 20.631811 0.0110210
```

```
#Check the ANOVA for the leaching of the corresponding element based on major oxide
my_anova1 = aov(SiLeach ~ Type+State+Type:State, data = anovadata)
options(contrasts = c("contr.sum", "contr.poly"))
B = Anova(my_anova1, type = "III") #Type III sum of squares
summary(my_anova1)
```

```
##             Df Sum Sq Mean Sq F value Pr(>F)
## Type         2   35.1  17.558   2.645  0.080 .
## State        1    0.9   0.944   0.142  0.708
## Type:State   2   31.3  15.630   2.355  0.104
## Residuals   55  365.1   6.638
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
TukeyHSD(my_anova1)
```

```
##   Tukey multiple comparisons of means
##     95% family-wise confidence level
##
## Fit: aov(formula = SiLeach ~ Type + State + Type:State, data = anovad
ata)
##
## $Type
##             diff        lwr       upr     p adj
## FA-CA -1.0373912 -2.9105375 0.8357551 0.3826743
## M-CA   0.8362468 -1.1885275 2.8610210 0.5832263
## M-FA   1.8736380 -0.1113621 3.8586381 0.0680877
```

```
##
## $State
##          diff       lwr      upr     p adj
## W-F 0.2513326 -1.112759 1.615424 0.7133641
##
## $`Type:State`
##                    diff        lwr       upr     p adj
## FA:F-CA:F -1.959096667 -4.7368349 0.8186416 0.3115071
## M:F-CA:F  -0.541331667 -3.8717228 2.7890595 0.9966811
## CA:W-CA:F -1.956790000 -5.6313923 1.7178123 0.6198515
## FA:W-CA:F -0.916556667 -4.2469478 2.4138345 0.9640130
## M:W-CA:F   1.004715556 -2.2027403 4.2121714 0.9384020
## M:F-FA:F   1.417765000 -1.9126262 4.7481562 0.8066022
## CA:W-FA:F  0.002306667 -3.6722957 3.6769090 1.0000000
## FA:W-FA:F  1.042540000 -2.2878512 4.3729312 0.9385654
## M:W-FA:F   2.963812222 -0.2436436 6.1712681 0.0857878
## CA:W-M:F  -1.415458333 -5.5237886 2.6928720 0.9102010
## FA:W-M:F  -0.375225000 -4.1787998 3.4283498 0.9997019
## M:W-M:F    1.546047222 -2.1503630 5.2424575 0.8178172
## FA:W-CA:W  1.040233333 -3.0680970 5.1485636 0.9748646
## M:W-CA:W   2.961505556 -1.0478143 6.9708254 0.2632043
## M:W-FA:W   1.921272222 -1.7751380 5.6176825 0.6438505
```

```
pairwise.t.test(anovadata$SiO2,anovadata$Type, p.adj = "none")
```

```
##
##  Pairwise comparisons using t tests with pooled SD
##
## data:  anovadata$SiO2 and anovadata$Type
##
##    CA     FA
## FA 0.6129 -
## M  0.0105 0.0024
##
## P value adjustment method: none
```

```
pairwise.t.test(anovadata$SiO2,anovadata$State, p.adj = "none")
```

```
##
##  Pairwise comparisons using t tests with pooled SD
##
## data:  anovadata$SiO2 and anovadata$State
##
##   F
## W 0.56
##
## P value adjustment method: none
```

```
#Normality Test
plot(my_anova,2) #QQ
plot(my_anova,1) #Residual plot (Must have no pattern)
plot(my_anova,3)

#Histogram of residuals, should be normal
x = residuals(my_anova)
plotNormalHistogram(x)
```

```
#Plots
#Boxplot
Lab = c("Coarse Ash", "Fly Ash", "Mixed Ash")
ggplot(anovadata, aes(y = SiO2, x =Type, fill = State), outline =FALSE)+
  theme(axis.title.x = element_text(vjust=-2))+
  theme(panel.grid.major = element_blank(),panel.grid.minor = element_bl
ank(),panel.background = element_blank(),
        axis.line = element_line(colour = "black"),legend.background=ele
ment_blank(),
        legend.key=element_blank())+theme(text = element_text(size = 16)
)+geom_boxplot()+
  labs(y=expression("SiO" [2]*" Percentage (%)"))+scale_x_discrete(label
s= Lab)+
  theme(axis.title.x = element_text(vjust=-2))+
  theme(axis.text.x = element_text(color="black"))+theme(axis.text.y = e
lement_text(color="black"))+
  scale_fill_discrete(name="State",breaks=c("F", "W"), labels = c("Fresh
", "Weathered"))+
  theme(legend.title=element_blank(),legend.position="top", legend.text=
element_text(size=12))+
  coord_flip()+theme(axis.text = element_text(size=16))+theme(legend.tex
t = element_text(size=16))+
  annotate("text",x=1,y=60, label="**", size=8)+
  annotate("text",x=2,y=57, label="**",size=8)+
  annotate("text",x=3,y=60, label="**", size=8)+
  theme(axis.ticks.length=unit(.25, "cm"))


#Mass % Interaction plot
interaction.plot (x.factor = anovadata$State,
                  trace.factor = anovadata$Type,
                  response = anovadata$SiO2,
                  fun = mean, type = "b", las=1,
                  xlab = "State of Ash", ylab=expression("SiO" [2]*" Per
centage (%)"),
                  pch=c(1,19), col = c("blue", "orange", "darkgreen"),
                  legend=FALSE, xaxt='n',cex.main=1.4, cex.lab=1.35, cex
.axis=1.4)
axis(1, at=1:2, labels=c("Fresh", "Weathered"),cex.axis=1.35)
legend("bottomleft", c("Coarse Ash", "Fly Ash","Mixed Ash"), lty=1, bty=
"n", pch=c(1,19),
       col = c("blue", "orange", "darkgreen"))
text(2.1,54.5,"**",cex=1.8)
text(2.1,53,"**",cex=1.8)
text(2.1,52,"**",cex=1.8)
par(mar=c(4,7,2,4))

#Leach interaction plot for corresponding element
interaction.plot (x.factor = anovadata$State,
                  trace.factor = anovadata$Type,
                  response = anovadata$SiLeach,
                  fun = mean, type = "b", las=1,
                  xlab = "State of Ash", ylab=expression("Si (ppm)"),
                  pch=c(1,19), col = c("blue", "orange", "darkgreen"),
```

```
                  legend=FALSE, xaxt='n',cex.main=1.4, cex.lab=1.35, cex
.axis=1.4)
axis(1, at=1:2, labels=c("Fresh", "Weathered"),cex.axis=1.35)
legend("bottomleft", c("Coarse Ash", "Fly Ash","Mixed Ash"), lty=1, bty=
"n", pch=c(1,19),
       col = c("blue", "orange", "darkgreen"))
par(mar=c(4,7,2,4))
```

Appendix M:pH, TDS, EC and leachability of Tank Leach Test

	pH									
Days	0,08	1	2	7	14	28	35	42	49	63
FA	10,13	10,33	10,99	9,41	10,63	10,18	10,07	9,57	9,65	9,22
FA	10,14	10,35	11,00	9,50	10,83	10,26	10,07	9,82	9,97	10,07
Average	10,14	10,34	11,00	9,46	10,73	10,22	10,07	9,70	9,81	9,65
MA1	10,69	11,03	11,18	9,38	10,90	10,30	10,14	9,80	9,88	9,23
MA1	10,83	11,06	11,22	9,31	11,04	10,38	10,19	9,84	9,82	9,83
Average	10,76	11,05	11,20	9,35	10,97	10,34	10,17	9,82	9,85	9,53
MA3	11,27	11,58	11,31	9,20	11,14	10,58	10,17	9,81	9,89	9,78
MA3	10,92	11,15	11,40	9,16	11,27	10,78	10,46	10,05	10,04	10,37
Average	11,10	11,37	11,36	9,18	11,21	10,68	10,32	9,93	9,97	10,08
MA4	10,49	10,83	11,09	9,38	10,81	10,41	10,22	9,97	9,95	9,73
MA4	10,83	11,01	11,10	9,48	10,72	10,20	10,00	9,77	9,84	10,07
Average	10,66	10,92	11,10	9,43	10,77	10,31	10,11	9,87	9,90	9,90
	EC									
FA	173,4	508	532	400	341	290	240	226	248	266
FA	316	523	602	487	535	469	339	259	242	220
Average	244,7	515,5	567	443,5	438	379,5	289,5	242,5	245	243
MA1	272	251	410	238	323	207	196,3	208	205	223
MA1	238	569	415	232	301	206	201	209	207	204
Average	255	410	412,5	235	312	206,5	198,65	208,5	206	213,5
MA3	347	893	486	209	358	209	192	204	190,8	198,8
MA3	411	895	613	194,8	418	228	196,2	205	201	206
Average	379	894	549,5	201,9	388	218,5	194,1	204,5	195,9	202,4
MA4	337	540	404	246	310	221	208	212	196,7	207
MA4	257	518	414	241	257	214	208	211	200	226
Average	297	529	409	243,5	283,5	217,5	208	211,5	198,35	216,5
	TDS									
FA	347	948	266	200	170,4	144,9	120,2	113	124,1	142,1
FA	158	666	301	244	267	235	169,3	129,5	121,1	99,1
Average	252,5	807	283,5	222	218,7	189,95	144,75	121,25	122,6	120,6
MA1	136,1	320,1	205	119,2	161,6	103,3	98,1	104,2	102,6	120,6
MA1	119,1	658,1	207	116,2	150,4	102,6	100,5	104,8	103,4	100,4
Average	127,6	489,1	206	117,7	156	102,95	99,3	104,5	103	110,5
MA3	173,7	962,7	243	104,6	178,8	104,5	96	101,8	95,4	103,4
MA3	205	995	307	97,4	209	114,2	98,1	102,5	100,16	95,16
Average	189,35	978,85	275	101	193,9	109,35	97,05	102,15	97,78	99,28
MA4	168,6	573,6	202	122,8	155,2	110,6	104,3	105,7	98,3	108,6
MA4	128,8	596,8	207	120,6	128,2	106,9	104,3	105,3	100,1	74,1
Average	148,7	585,2	204,5	121,7	141,7	108,75	104,3	105,5	99,2	91,35

TLT Leachability results										
Mg/l	Days	0,08	1	2	7	14	28	42	49	63
Al	FA	2,39	2,46	3,49	0,48	1,47	0,58	2,91	0,00	0,00
	MA4	2,07	2,63	3,56	0,57	1,44	0,66	3,16	0,00	0,00
	MA3	3,30	2,88	3,74	0,72	1,53	0,73	3,24	0,00	0,00
	MA1	3,06	3,12	5,10	0,83	1,70	0,77	3,67	0,00	0,00
Pb	FA	0,05	0,06	0,05	0,01	0,05	0,00	0,00	0,00	0,00
	MA4	0,05	0,08	0,05	0,03	0,04	0,00	0,00	0,00	0,00
	MA3	0,05	0,06	0,06	0,02	0,02	0,00	0,00	0,00	0,00
	MA1	0,05	0,06	0,08	0,02	0,03	0,00	0,00	0,00	0,00
Na	FA	42,02	162,75	74,64	25,09	138,21	24,40	7,78	9,87	0,00
	MA4	42,79	92,87	35,42	7,02	53,62	3,23	7,27	6,49	0,00
	MA3	52,70	118,39	25,56	60,97	42,98	0,00	3,68	13,06	0,00
	MA1	19,20	25,06	7,26	43,79	43,75	1,68	4,09	7,57	0,00
Mg	FA	6,56	2,55	3,37	0,53	5,10	0,04	3,88	6,40	1,17
	MA4	6,87	1,86	1,99	1,34	2,66	2,17	4,97	6,00	4,44
	MA3	4,31	1,09	1,33	0,72	1,60	7,77	5,65	14,29	3,80
	MA1	6,40	1,15	0,67	0,51	3,04	4,03	0,39	5,29	4,23
K	FA	17,16	34,56	18,43	7,01	20,38	7,00	4,45	5,24	2,47
	MA4	9,93	24,08	11,90	3,08	10,52	4,01	3,07	2,95	2,20
	MA3	11,51	24,51	8,77	13,99	9,64	4,06	3,72	1,50	3,87
	MA1	3,87	6,69	3,50	10,00	9,33	4,76	3,26	2,92	3,34
Ca	FA	10,76	10,43	10,74	0,39	3,61	1,89	6,58	22,59	2,87
	MA4	23,80	14,84	14,93	7,97	25,76	1,85	19,11	22,16	17,98
	MA3	15,02	24,40	7,70	28,82	16,98	1,89	21,16	34,20	12,68
	MA1	4,97	17,88	8,74	23,61	21,23	5,96	2,31	21,71	16,57
Fe	FA	0,27	0,24	0,27	0,05	0,17	0,35	0,12	0,00	0,11
	MA4	0,27	0,25	0,31	0,03	0,19	0,35	0,07	0,16	0,08
	MA3	0,46	0,20	0,28	0,09	0,20	0,43	0,14	0,00	0,09
	MA1	0,38	0,32	0,35	0,09	0,19	0,48	0,09	0,00	0,13
Ba	FA	0,00	0,00	0,04	0,17	0,00	1,31	0,57	0,00	0,00
	MA4	0,00	0,00	0,25	0,32	0,09	0,49	0,47	0,00	0,00
	MA3	0,00	0,29	0,32	0,46	0,01	0,28	0,42	0,00	0,00
	MA1	0,11	0,13	0,16	0,38	0,03	0,32	0,55	0,00	0,00

Appendix N: pH, TDS, EC and leachability of Weathering Cell Test

	pH									
Extraction	1	2	3	4	5	6	7	8	9	10
FA	12,01	9,64	8,01	8,14	8,05	8,07	8,03	8,29	8,12	7,95
FA	12,08	10,07	8,16	8,21	8,27	8,12	8,14	8,33	8,29	7,98
Average	12,05	9,86	8,09	8,18	8,16	8,10	8,09	8,31	8,21	7,97
MA1	12,29	10,40	8,43	8,53	8,90	8,61	8,15	8,15	8,19	7,97
MA1	12,29	9,98	8,40	8,24	8,29	8,11	8,20	8,20	8,21	8,08
Average	12,29	10,19	8,42	8,39	8,60	8,36	8,18	8,18	8,20	8,03
MA3	10,28	9,46	8,51	8,72	8,97	8,70	8,45	8,59	8,58	8,55
MA3	10,18	9,63	8,49	8,58	8,68	8,70	8,49	8,57	8,58	8,57
Average	10,23	9,55	8,50	8,65	8,83	8,70	8,47	8,58	8,58	8,56
MA4	12,16	10,05	8,32	8,67	8,69	8,37	8,20	8,20	8,27	8,28
MA4	12,17	10,64	8,55	8,28	8,30	8,32	8,22	8,21	8,24	8,30
Average	12,17	10,35	8,44	8,48	8,50	8,35	8,21	8,21	8,26	8,29
CA	12,28	11,02	8,25	8,31	8,51	8,22	8,18	8,17	8,25	8,16
CA	11,80	10,38	8,35	8,42	8,48	8,32	8,21	8,23	8,30	8,23
Average	12,04	10,70	8,30	8,37	8,50	8,27	8,20	8,20	8,28	8,20
	EC									
FA	5,06	4,36	2,98	2,04	1,28	1,32	1,32	1,34	1,09	0,28
FA	5,73	4,00	2,76	2,08	1,12	1,68	1,51	0,77	1,00	0,28
Average	5,40	4,18	2,87	2,06	1,20	1,50	1,41	1,05	1,04	0,28
MA1	6,63	3,79	2,50	2,03	1,56	1,70	1,42	1,26	1,10	0,28
MA1	6,14	3,67	2,62	1,99	1,39	1,35	1,28	1,18	1,12	0,28
Average	6,39	3,73	2,56	2,01	1,47	1,53	1,35	1,22	1,11	0,28
MA3	13,09	7,40	3,23	3,12	1,26	1,13	0,61	0,43	0,36	0,28
MA3	13,78	7,08	3,69	3,86	2,05	1,22	0,75	0,55	0,43	0,28
Average	13,44	7,24	3,46	3,49	1,65	1,17	0,68	0,49	0,39	0,28
MA4	3,05	1,85	1,59	1,43	0,89	0,97	0,72	0,62	0,58	0,28
MA4	2,99	2,25	1,51	1,32	0,92	0,81	0,70	0,68	0,74	0,28
Average	3,02	2,05	1,55	1,38	0,90	0,89	0,71	0,65	0,66	0,28
CA	4,71	2,91	6,15	4,42	1,00	1,10	0,92	0,83	0,70	0,29
CA	5,01	3,10	2,27	1,62	2,43	1,82	1,30	0,98	0,75	0,28
Average	4,86	3,01	4,21	3,02	1,72	1,46	1,11	0,90	0,72	0,28
	TDS									
FA	2,530	2,180	1,489	1,019	0,637	0,657	0,676	0,669	0,546	0,140
FA	3,310	1,998	1,381	1,039	0,560	0,842	0,752	0,382	0,499	0,140
Average	2,920	2,089	1,435	1,029	0,599	0,750	0,714	0,526	0,523	0,140
MA1	3,310	1,897	1,251	1,013	0,778	0,852	0,710	0,629	0,548	0,139
MA1	3,070	1,836	1,308	0,996	0,696	0,674	0,638	0,591	0,559	0,140
Average	3,190	1,867	1,280	1,005	0,737	0,763	0,674	0,610	0,554	0,140
MA3	6,540	3,700	1,614	1,560	0,627	0,566	0,305	0,217	0,178	0,141
MA3	6,890	3,540	1,843	1,930	1,028	0,608	0,373	0,274	0,214	0,140

Average	6,715	3,620	1,729	1,745	0,828	0,587	0,339	0,246	0,196	0,141
MA4	1,522	0,925	0,796	0,717	0,444	0,484	0,359	0,309	0,291	0,141
MA4	1,496	1,126	0,756	0,658	0,457	0,406	0,352	0,342	0,370	0,141
Average	1,509	1,026	0,776	0,688	0,451	0,445	0,356	0,326	0,331	0,141
CA	2,360	1,455	3,070	2,210	0,502	0,548	0,458	0,416	0,350	0,143
CA	2,510	2,100	1,133	0,809	1,214	0,912	0,650	0,488	0,373	0,143
Average	2,435	1,778	2,102	1,510	0,858	0,730	0,554	0,452	0,362	0,143

Weathering Cell Test Leachability Results												
Leach (mg/l)		**Extraction Number**										
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Al	FA	2,05	1,70	0,24	0,29	1,33	2,43	1,21	0,00	4,60	0,00	0,00
	MA1	13,47	1,46	0,32	0,44	1,69	2,70	2,05	0,00	4,41	0,13	0,00
	MA2	26,48	6,08	0,41	0,39	2,50	2,81	1,31	0,00	4,21	0,00	3,69
	MA3	2,66	1,11	0,44	0,59	3,53	3,06	1,41	0,00	3,93	0,00	4,45
	CA	10,79	1,51	0,26	0,65	3,49	1,95	1,20	0,00	3,99	0,00	0,00
Pb	FA	0,054	0,118	0,043	0	0	0	0	0	0	0	0
	MA1	0,054	0,064	0,075	0	0	0	0	0	0	0	0
	MA2	0,064	0,075	0,043	0	0	0	0	0	0	0	0
	MA3	0,161	0,118	0,000	0	0	0	0	0	0	0	0
	CA	0,075	0,086	0,064	0	0	0	0	0	0	0	0
Na	FA	1032,1	765,3	384,1	275,0	245,9	22,7	63,5	13,0	12,2	29,9	4,1
	MA1	607,6	255,6	302,0	189,0	127,1	-0,4	44,9	14,3	12,1	11,4	15,9
	MA2	1187,3	681,1	434,1	513,4	157,0	1,7	55,2	27,9	63,0	0,0	5,5
	MA3	481,6	1704,6	121,2	31,8	24,7	7,1	1,6	0,7	0,0	58,0	-2,1
	CA	746,5	486,8	321,7	291,7	274,0	0,0	25,8	70,0	0,0	76,6	6,4
Mg	FA	0,32	28,78	14,40	47,22	27,49	6,17	39,24	26,82	21,10	21,53	20,29
	MA1	0,53	7,37	3,87	24,09	5,45	7,24	23,74	19,69	26,77	26,61	29,88
	MA2	0,49	5,86	27,33	38,66	14,09	7,39	16,97	15,95	23,15	0,00	13,14
	MA3	44,85	59,36	5,50	33,56	21,21	5,57	16,48	12,95	13,72	23,43	21,39
	CA	2,60	1,71	8,59	14,07	1,45	0,00	17,62	6,52	27,20	6,94	7,66
K	FA	8,47	17,31	65,18	45,17	4,10	6,61	19,88	16,61	13,95	36,59	7,10
	MA1	17,31	8,35	28,00	47,72	4,30	3,52	19,95	14,15	11,20	15,06	8,47
	MA2	17,31	8,37	37,26	11,94	4,07	4,26	15,10	2,59	10,50	5,76	2,60
	MA3	0,74	3,43	4,36	37,79	2,10	3,51	12,38	9,71	13,01	21,32	7,40
	CA	8,12	17,31	2,60	50,00	2,50	4,38	22,12	11,19	11,26	33,08	4,15
Ca	FA	1,88	14,08	95,42	186,24	94,52	20,10	186,28	81,98	90,20	58,08	83,38
	MA1	2,98	13,32	78,43	139,30	95,84	30,50	154,74	107,25	134,75	45,94	50,59
	MA2	1,06	6,68	66,95	98,91	75,21	18,49	50,96	39,09	71,00	0,00	24,59
	MA3	12,24	17,14	119,95	147,32	135,16	17,02	97,13	53,86	55,23	80,12	39,13
	CA	1,53	5,09	130,67	94,92	96,97	0,00	94,16	47,35	108,58	77,51	50,09
Fe	FA	0,11	0,10	0,34	0,05	0,17	0,24	0,34	0,27	0,06	0,13	0,30
	MA1	0,09	0,06	0,31	0,05	0,11	0,17	0,58	0,00	0,08	0,16	0,17
	MA2	0,15	0,01	0,32	0,05	0,12	0,20	0,35	0,12	0,16	0,00	0,10

	MA3	0,16	0,11	0,32	0,25	0,12	0,15	0,29	0,20	0,15	0,00	0,03
	CA	0,11	0,08	0,33	0,31	0,27	0,13	0,14	0,12	0,18	0,00	0,00
Ba	FA	0,05	0,68	0,81	0,68	0,91	0,48	0,55	1,08	0,68	0,00	1,95
	MA1	0,10	1,40	1,07	0,64	1,33	0,59	1,31	0,37	0,00	3,30	1,28
	MA2	1,02	0,49	0,42	0,69	0,65	0,39	0,60	0,00	0,00	0,28	0,00
	MA3	0,40	0,43	1,28	0,56	0,88	0,38	1,29	0,26	0,40	0,90	0,04
	CA	0,10	0,98	1,46	1,92	0,84	0,38	0,77	0,00	0,00	1,11	0,95

Appendix O: Acid Neutralization Capacity

	Na	**Mg**	**K**	**Fe**	**B**	**Al**	**Ca**	
pH	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	ANC (Mol H+/kg)
FA								
3	89,41	189,71	79,11	5,15	3,11	285,66	1873,58	3,31
4	95,79	165,91	76,77	8,96	2,93	122,03	1652,05	2,56
5	86,68	142,84	61,1	5,71	2,63	35,81	1423,79	1,98
6	82,77	113,4	70,89	2,42	2,3	3,26	1052,99	1,51
7	96,63	109,94	64,5	6,54	2,31	9,28	961,99	1,11
8	85,84	71,89	82,89	12,43	1,41	11,01	551,92	0,76
9	82,73	49,71	47,82	25,63	0,95	3,03	372,3	0,44
10	84,59	21,02	51,04	7,69	0,77	1,93	202	0,19
11	73,82	2,74	47,47	2,22	0,34	3,24	37,48	0,00
MA3								
3	44,67	144,49	76,35	14,64	2,06	95,75	1963,37	0,83
4	44,11	131,96	60,85	7,09	1,97	34,16	1839,31	0,60
5	45,58	120,11	75,01	17,54	1,93	25,17	1627,67	0,48
6	90,17	99,08	60,78	9,39	1,57	14,5	1295,2	0,38
7	43,13	96,31	62,32	45,71	1,44	58,62	1139,18	0,30
8	44,07	59,04	65,34	7,56	0,79	9,91	679,81	0,22
9	42,85	51,92	49,75	13,4	0,71	9,57	597,06	0,16
10	45,73	50,35	48,58	7,89	0,86	12,23	430,71	0,10
11	46,26	13,15	53,75	5,41	0,58	9,65	107,42	0,00
MA2								
3	257,66	99,18	15,65	18,88	2,09	135,97	561,34	0,50
4	323,2	127,11	22,76	4,72	2,77	142,89	759,65	0,35
5	320,96	104,48	20,19	12,78	2,6	26,93	667,82	0,23
6	225,53	48,49	12,94	9,94	1,54	3,15	287,58	0,15
7	296,22	50,32	10,44	1,1	1,92	4,66	291,38	0,07
8	298,13	61,92	10,97	3,25	2,01	41,49	345,94	0,05
9	304,63	17,34	7,98	2,42	1,47	2,64	112,39	0,00
CA								
3	240,73	133,91	34,34	66,27	1,35	250,93	1988,73	1,47
4	225,12	131,59	34,04	21,16	1,02	116,51	2058,06	1,15
5	232,48	122,46	30,72	4,73	0,89	24,09	1908,88	0,90
6	346,1	104,81	32,33	2,13	0,77	2,94	1502,76	0,70

7	287,29	98,6	28,02	10,76	0,75	1,2	1225,89	0,52
8	281,01	91,59	25,08	8,3	0,68	0,59	909,18	0,37
9	221,92	64,63	20,87	1,08	0,38	0,93	652,03	0,25
10	319,3	16,47	22,61	2,9	0,21	0,29	137,22	0,00
10	295,13	12,41	22,44	1,7	0,24	0,38	94,22	0,00
MA1								
3	95,06	170,25	71,01	4,65	2,83	95,6	2205,19	1,68
4	73,04	154,77	61,17	7,39	2,95	8,31	2155,09	1,30
5	70,92	137,48	53,63	1,26	2,93	2,63	1865,28	1,00
6	1869,1	783,46	398,86	0,99	16,26	181,04	10366	0,76
7	74,64	124,75	53,85	1,86	2,66	1,21	1595,23	0,56
8	63,28	13,84	52,33	3,93	0,56	0,45	277,13	0,38
9	69,19	37,04	55,13	3,76	1,05	0,95	482,38	0,23
10	62,74	5,83	51,28	1,95	0,37	1,7	112,88	0,08
11	64,56	6,25	55,56	29,17	0,47	1,99	181,59	0,00

	Cr	**Ni**	**As**	**Pb**
pH	**mg/l**	**mg/l**	**mg/l**	**mg/l**
FA				
3	0,305	0,364	0,018	0,036
4	0,305	0,277	0,050	0,033
5	0,241	0,184	0,020	0,012
6	0,237	0,067	0,014	0,014
7	0,267	0,060	0,047	0,027
8	0,220	0,036	0,051	0,032
9	0,180	0,023	0,022	0,015
10	0,147	0,023	0,016	0,013
11	0,141	0,020	0,025	0,009
MA3				
3	0,084	0,267	0,046	0,036
4	0,080	0,180	0,023	0,020
5	0,158	0,096	0,062	0,049
6	0,130	0,041	0,037	0,026
7	0,180	0,074	0,031	0,028
8	0,182	0,026	0,029	0,021
9	0,189	0,018	0,026	0,023
10	0,199	0,046	0,027	0,049
11	0,176	0,025	0,029	0,022
MA2				
3	0,354	0,177	0,087	0,016
4	0,309	0,233	0,079	0,017
5	0,048	0,182	0,028	0,011
6	0,119	0,033	0,097	0,011
7	0,196	0,027	0,110	0,006

8	0,243	0,071	0,044	0,011
9	0,190	0,016	0,038	0,005
CA				
3	0,383	0,269	0,079	0,048
4	0,142	0,250	0,035	0,020
5	0,034	0,183	0,016	0,012
6	0,031	0,119	0,012	0,007
7	0,079	0,067	0,010	0,007
8	0,135	0,018	0,010	0,006
9	0,135	0,009	0,009	0,004
10	0,151	0,005	0,007	0,005
10	0,146	0,005	0,009	0,007
MA1				
3	0,053	0,332	0,018	0,011
4	0,043	0,170	0,010	0,005
5	0,112	0,118	0,011	0,010
6	0,099	0,100	0,012	0,010
7	0,097	0,036	0,013	0,004
8	0,066	0,005	0,011	0,004
9	0,096	0,013	0,014	0,024
10	0,068	0,009	0,012	0,029
11	0,068	0,065	0,014	0,036

Appendix P: Unconfined Compressive Strength

14 Day Test					
Sample	Area (cm2)	Force (kN)	Force (N)	UCS (N/cm2)	UCS (MPa)
DuraPozz	100	5,00	5000	50,00	0,50
	100	5,60	5600	56,00	0,56
	100	5,40	5400	54,00	0,54
Average		5,33	5333	53,33	0,53
PozzFill	90	16,00	16000	177,78	1,78
	90	17,60	17600	195,56	1,96
	90	17,00	17000	188,89	1,89
Average		16,87	16867	187,41	1,87
MA3	87	1,20	1200	13,79	0,14
	83	1,60	1600	19,28	0,19
	85	1,80	1800	21,18	0,21
Average		1,53	1533	18,08	0,18
MA1	80	2,20	2200	27,50	0,28
	85	2,00	2000	23,53	0,24
	80	2,40	2400	30,00	0,30
Average		2,20	2200	27,01	0,27
FA	95	4,40	4400	46,32	0,46
	95	4,40	4400	46,32	0,46
	95	4,80	4800	50,53	0,51
Average		4,53	4533	47,72	0,48

28 Day Test					
Sample	Area (cm2)	Force (kN)	Force (N)	UCS (N/cm2)	UCS (MPa)
DuraPozz	96	9,20	9200	95,83	0,96
	98	9,20	9200	93,88	0,94
	100	9,20	9200	92,00	0,92
Average		9,20	9200	93,90	0,94
PozzFill	93	20,60	20600	221,51	2,22
	93	22,00	22000	236,56	2,37
	81	15,60	15600	193,79	1,94
Average		19,40	19400	217,28	2,17
MA3	80	2,60	2600	32,50	0,33
	82	2,60	2600	31,71	0,32
	81	2,00	2000	24,84	0,25
Average		2,40	2400	29,68	0,30
MA1	78	4,40	4400	56,41	0,56
	75	4,40	4400	58,67	0,59
	75	2,20	2200	29,33	0,29
Average		3,67	3667	48,14	0,48
FA	85	4,20	4200	49,41	0,49
	78	4,40	4400	56,41	0,56
	97	6,00	6000	61,86	0,62
Average		4,87	4867	55,89	0,56

56 Day Test					
Sample	Area (cm2)	Force (kN)	Force (N)	UCS (N/cm2)	UCS (MPa)
DuraPozz	100	10,40	10400	104,00	1,04
	100	10,40	10400	104,00	1,04
	100	10,40	10400	104,00	1,04
Average		10,40	10400	104,00	1,04
PozzFill	90	22,80	22800	253,33	2,53
	90	23,60	23600	262,22	2,62
	90	24,80	24800	275,56	2,76
Average		23,73	23733	263,70	2,64
MA3	80	2,00	2000	25,00	0,25
	80	2,00	2000	25,00	0,25
	77	4,80	4800	62,34	0,62
Average		2,93	2933	37,45	0,37
MA1	70	3,60	3600	51,43	0,51
	46	3,80	3800	82,61	0,83
	75	3,40	3400	45,33	0,45
Average		3,60	3600	59,79	0,60
FA	80	11,20	11200	140,00	1,40
	95	8,40	8400	88,42	0,88
	80	5,90	5900	73,75	0,74
Average		8,50	8500	100,72	1,01

Appendix Q: SEM EDS Spot Analysis

	FA1	FA2	FA3	FA4	CA	FA1 - 1	FA1 - 2	MA1	MA2	MA3	MA3
	1	2	3	4	5	6	7	8	9	10	11
Element	Weight%										
O	50,97	52,63	48,55	47,95	43,71	-		26	27,56	48,06	55,68
NS	0,74	0,76	0,96	-				0,66		0,35	0,57
Al	11,43	11,16	9	12,71	13,88	21,19	31,44	5,02	14,45	10,58	13,84
Si	25,05	26,13	25,2	26,05	35,02	28,82	39,04	11,1	30,16	23,35	25,71
Ca	1,49	0,36	1,78	-		21,98	8,28	1,68	9,8	20,61	6,28
Ti	2,46	3,94	8,71	8,45		16,29					
Fe	7,87	5,03	5,81	4,84	2,38	11,71	21,23	56,49	18,03		
Mg								0,95			
Cl								0,22			
Totals	100,01	100,01	100,01	100	94,99	99,99	99,99	100,95	100	102,95	102,08

Appendix R: Leaching Test Comparison

Element	CPB Mixture	**WCT** (mg/kg)	TLT (mg/kg)	Ash Concentration (mg/kg)	Concentration and Brine **(mg/kg)**	Brine **(mg/kg)**	Leached (mg/kg)
Al	FA	9,89	8,07	141095,65	141097,12	1,47	50,23
	MA1	19,04	10,68				
	MA3	15,13	9,45				
Pb	FA	0,15	0,14	50,51	50,52	0,007	0,49
	MA1	0,14	0,14				
	MA3	0,2	0,13				
Na	FA	2034,22	283,87	445,11	3433,10	2987,99	241,89
	MA1	1128,27	89,25				
	MA3	1391,26	185,83				
Mg	FA	180,97	17,34	5125,73	5234,51	108,78	49,77
	MA1	125,17	15,06				
	MA3	184,31	23,75				
K	FA	172,13	68,34	6475,11	6483,79	8,68	73,99
	MA1	127,17	27,91				
	MA3	119,08	47,76				
Ca	FA	651,55	40,9	19940,94	20046,41	105,47	3504,51
	MA1	609,75	72,01				
	MA3	553,07	95,36				
Fe	FA	1,5	0,92	25703,60	25710,61	7,01	0,28
	MA1	1,27	1,18				
	MA3	1,27	1,09				
Ba	FA	5,61	1,23	1136,85	1136,94	0,09	176,49
	MA1	8,13	0,98				
	MA3	4,86	1,04				