Metakaolin based geopolymers to encapsulate nuclear waste

PhD thesis

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Abstract
This thesis investigates the potential use of geopolymers to encapsulate intermediate level waste (ILW), particularly Magnox swarf contaminated with Al metal and Cs/Sr-loaded clinoptilolite. Both wastes have different interactions with the encapsulation matrix. For Magnox swarf waste containing trace Al metal, the pH of the encapsulating matrix is a key factor that controls corrosion and release of hydrogen. Cs and Sr can leach from contaminated clinoptilolite into the encapsulating geopolymer and therefore the chemical interactions of these ions with the matrix have been investigated.

A fundamental understanding of the geopolymer system used for encapsulation was developed. This involved investigating the influence of different precursor on the mechanical properties. It was shown showed that metakaolin based geopolymers are unstable at room temperature when in contact with an atmosphere with a low relative humidity and excessive drying shrinkage occurs. This shrinkage can be reduced by adding inert fillers which have low impact on the mortar viscosity and mechanical strength.

Magnox waste and Al-metal have been encapsulated in metakaolin based geopolymers and surface interactions studied using SEM-EDX and XRD. In addition the corrosion rates were determined. Magnox swarf does not react with the geopolymers matrix, while Al-metal rapidly corrodes. However, by using a metakaolin with a low molar Si:Al ratio and controlling the molar Al:Na ratio in geopolymers the corrosion can be significantly reduced and allows encapsulation of this difficult waste stream.

Surface reactions of Cs/Sr-contaminated clinoptilolite and geopolymers were also studied. Simulated wastes containing Cs\(^{+}\) and Sr\(^{2+}\) salts were mixed with geopolymers and the influence of the cations on the geopolymer microstructure and leaching were investigated. Mixing Cs/Sr-contaminated clinoptilolite with activation solution causes surface dissolution of clinoptilolite with release of Cs and Sr ions into the matrix. Leaching of Cs contaminated geopolymers showed that Cs\(^{+}\) ions can be immobilised at concentrations up to 10 wt%. Sr\(^{2+}\) reacts with the activating solution and dissolved metakaolin and is build chemically into the structure.

The research has resulted in a number of key conclusions related to the stability of metakaolin derived geopolymers and their interactions with the selected wastes.
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Publications derived from the work in this thesis

Journal Papers


Conference Papers


Table of contents

Abstract 3

Acknowledgement 4

Publications derived from the work in this thesis 6

Table of contents 8

List of figures 12

List of tables 17

CHAPTER 1  Introduction 18

1.1 Nuclear waste 19

1.2 Classification of nuclear waste types 19

1.3 Immobilisation and encapsulation of hazardous/nuclear waste 20

1.3.1 S/S of HLW 22

1.3.2 S/S of ILW and LLW waste 22

1.4 Encapsulation of ILW and LLW in the UK 23

1.4.1 Magnox swarf and Al metal 24

1.4.2 Cs/Sr contaminated clinoptilolite 27

1.5 Summary 30

CHAPTER 2 Geopolymers for immobilisation and encapsulation of nuclear waste 32

2.1 Geopolymers 32

2.2 Influence of different parameters 35

2.2.1 Solid precursor 35

2.2.2 Si source and alkaline solution 38

2.2.3 Influence of pH on silicate and aluminate 40

2.2.4 Altering the molar ratio of Al:Si:Na:H₂O 41

2.2.5 pH alteration of the activation solution 44

2.2.6 Variation of the curing temperature 45

2.3 Summary 46

CHAPTER 3 Aims, objectives and experimental approach 47

3.1 Introduction 48

3.2 Research aim and objectives 48

3.3 Experimental approach 49

CHAPTER 4 Experimental methods and analytical techniques 52

4.1 Materials 53

4.2 Preparation of geopolymers 55

4.3 Particle size 55

4.4 Mechanical tests 56

4.4.1 Compressive strength 56
4.4.2 Flexural strength 56
4.4.3 Hardness 57

4.5 Density and porosity 58
4.5.1 Porosity 58
4.5.2 Theoretical density 59

4.6 Shrinkage/expansion 60

4.7 Micro-structural analysis 60
4.7.1 Crystalline phase analysis using X-ray diffraction (XRD) 61
4.7.2 Scanning Electron Microscopy (SEM) and energy dispersive X-ray analysis (EDX) 61

4.8 Heat stability 62
4.8.1 Thermogravimetry analysis (TGA)/Differential thermal analysis (DTA) 62
4.8.2 Dilatometer 62

4.9 Chemical tests 63
4.9.1 pH measurements 63
4.9.2 Inductively coupled plasma-optical emission spectrometer (ICP-OES) 63
4.9.3 Isothermal calorimeter 64

4.10 Results and error calculation 64
4.11 Conclusion 64

CHAPTER 5 Influence of different metakaolins on the mechanical properties of geopolymers 65
5.1 Introduction 66
5.2 Materials and Methods 67
5.3 Results 71
5.4 Discussion 82
5.5 Conclusion 83

CHAPTER 6 Drying shrinkage on geopolymer samples 84
6.1 Introduction 85
6.2 Materials and Methods 86
6.3 Results 88
6.4 Discussion 97
6.5 Conclusion 102

CHAPTER 7 Influence of inert and active filler on the mechanical properties of metakaolin geopolymers 103
7.1 Inert fillers in general 104
7.1.1 Materials and Methods 104
7.1.2 Results 108
7.1.3 Discussion 115
7.1.4 Conclusion 117
7.2 Influence of the size of inert fillers 118
  7.2.1 Materials and Methods 118
  7.2.2 Results 120
  7.2.3 Discussion 123
  7.2.4 Conclusion 125

7.3 Influence of reactive fillers 126
  7.3.1 Materials and Methods 127
  7.3.2 Results 128
  7.3.3 Discussion 137
  7.3.4 Conclusion 138

7.4 Overall conclusion 139

CHAPTER 8 Encapsulation of Magnox swarf and Al metal 140
  8.1 Introduction 141
  8.2 Materials and Methods 141
  8.3 Results 146
  8.4 Discussion 154
  8.5 Conclusion 157

CHAPTER 9 Encapsulation of Cs/Sr contaminated clinoptilolite 158
  9.1 Introduction 159
  9.2 Influence of high alkaline geopolymers on clinoptilolite 160
    9.2.1 Measuring of the stability of clinoptilolite in geopolymers 160
    9.2.2 Cs and Sr diffusing from clinoptilolite 162
    9.2.3 Discussion of the stability and diffusion experiments 164
    9.2.4 Conclusion of the stability and diffusion experiments 165
  9.3 Interactions of Cs with geopolymers 166
    9.3.1 Materials and Methods 166
    9.3.2 Results 167
    9.3.3 Discussion 171
    9.3.4 Conclusion 173
  9.4 Interactions of Sr with geopolymers 174
    9.4.1 Materials and Methods 174
    9.4.2 Results 175
    9.4.3 Discussion 182
    9.4.4 Conclusion 184

CHAPTER 10 Conclusion and future work 185
  10.1 Conclusion 186
  10.2 Further work 187
    10.2.1 Further characterisation of different formed geopolymer gels 187
    10.2.2 Modelling drying shrinkage 187
    10.2.3 Cs and Sr in geopolymers 188
10.2.4 Optimising geopolymers/clinoptilolite mixtures 188
10.2.5 Large scale experiments 188
10.2.6 Optimising inert/active filler geopolymers 189
10.2.7 Fire resistance 189

References 190

Appendix 205

<table>
<thead>
<tr>
<th>Appendix Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1 Dissolution of metakaolin in 1 wt% HF and 8 M NaOH solution over time</td>
<td>205</td>
</tr>
<tr>
<td>A-2 Size effects during drying</td>
<td>206</td>
</tr>
<tr>
<td>A-3 Accelerated ageing</td>
<td>206</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1-1: Storage of nuclear waste in a special pit. The containers are stored under water.......................... 20
Figure 1-2: a) Schematic Magnox fuel rod, modified from (Weaver, 2009) and b) Magnox alloy after storage in special pits. ........................................................................................................................................................................... 24
Figure 1-3: Pourbaix diagrams for Mg in water at 25°C, line a and b represent the stability of water. Below line a H2 is produced, above line b O2, modified from (Pourbaix, 1966). .................................................. 25
Figure 1-4: Pourbaix diagrams for Al in water at 25°C, modified from (Pourbaix, 1966). ............................. 26
Figure 1-5: Al metal rod encapsulated in a) mixture of PC/BFS with a mass ratio of 1:3 and w/s = 0.33 and b) novel MgO binder system containing 20% MgO, 5% MgCO3, 25% silica fume and 50% sand, w/s = 0.275. Samples were 28 days cured at room temperature (Zhang, 2012). ..... 27
Figure 1-6: Removal of Cs+ and Sr2+ radio-nuclides from contaminated water, modified from (Gordon, 2008)........................................................................................................................................................................... 28
Figure 1-7: Clinoptilolite Cs-exchanged, dehydrated Hexacamium tecto-hexaalumotriacontasilicate (Cs6Al6Si18O72), modified from (Johnson et al., 2003). ........................................................................................................................................................................... 29
Figure 2-1: Structure of kaolinite, modified from (White et al., 2009). .......................................................... 36
Figure 2-2: Solid state magic angle spinning 27Al-NMR spectrum of kaolin at different temperatures, modified from (Sanz et al., 1988). ........................................................................................................................................................................... 37
Figure 2-3: XRD spectra of kaolin during calcinations.................................................................................... 38
Figure 2-4: Stability of sodium silicate solutions and the phases which may precipitate during storage at 25 °C, modified from (Wills, 1950). ........................................................................................................................................................................... 39
Figure 2-5: Viscosity of different silicate solutions at 20 °C. The numbers above each line represent the mass ratio of SiO2/Na2O or SiO2/K2O, modified from (Weldes and Lange, 1961). a) viscosity of sodium silicate solutions, b) viscosity of potassium silicate solution. ................................................. 39
Figure 2-6: Variety of oligomeric silicate anions in alkaline solution, each point represents a SiO4 unit, modified from (Harris and Knight, 1983). ........................................................................................................................................................................... 41
Figure 2-7: Metakaolin-based geopolymers, the molar Al:Na:H2O ratio was 1:1:5.5 and the Si:Al has been altered between 1.15 and 2.15. Samples were cured 7 days, modified from (Duxson et al., 2007b). ........................................................................................................................................................................... 42
Figure 2-8: Compressive strength for different Si:Al and Na:Al ratios, modified from (Rowles and O’Conner, 2003). ........................................................................................................................................................................... 44
Figure 2-9: Solubility and development of compressive of metakaolin as a function of pH, modified from (Phair & van Deventer, 2001). ........................................................................................................................................................................... 45
Figure 2-10: Development of compressive strength of metakaolin-based geopolymers cured at different temperatures over time. Initial curing at 40 and 60 °C was carried out for 4 hours, modified from (Rovnanik, 2010). ........................................................................................................................................................................... 46
Figure 3-1: Layout of experimental approach, MK=metakaolin................................................................. 51
Figure 4-1: Crystalline phases of used metakaolins, a=quartz (SiO2). .......................................................... 53
Figure 4-2: Schematic picture of Vicker hardness measurement, modified from (Glinicki and Zielinski, 2004). ........................................................................................................................................................................... 57
Figure 4-3: Schematic curve of the “indentation size effect”, modified from (McColin, 1990). 58
Figure 4-4: Technical picture of a dilatometer (DIL 402 E), modified from (Netzsch, 2006). .................. 63
Figure 5-1: XRD of Agrical (as received) and residue after dissolution in HF, key: a = Quartz low (Ref. Code 00-005-0490), b = SiO2, (Ref. Code 01-080-2147), c = kaolinite (Ref. Code 00-006-0221). ........................................................................................................................................................................... 72
Figure 5-2: 27Al NMR results for each metakaolin ......................................................................................... 73
Figure 5-3: Setting time, measured by penetration ......................................................................................... 74
Figure 5-4: Calorimetric results during geopolymerisation, a) maximal heat output over time, b) total heat output.

Figure 5-5: Flexural strength for all geopolymer mixtures.

Figure 5-6: Defect pore size in geopolymers samples.

Figure 5-7: Defects due to remaining air bubbles in the geopolymer samples.

Figure 5-8: Compressive strength data for all geopolymers mixtures.

Figure 5-9: Plot to calculate the Weibull number m, linear fit shown for Agrical.

Figure 6-1: Negative of a photograph of cracking due to drying in 30 mm diameter metakaolin based Na-geopolymer disc samples prepared with a molar ratio Al:Si:Na:H$_2$O of 1:2:1:8.5 at ambient temperature: (a) as before drying and (b) after drying. The sample has been cured for 56 days.

Figure 6-2: Comparison of pure geopolymer sample placed at different relative humidity for 3 month at 20 °C. Molar ratio of Al:Si:Na:H$_2$O was 1:2:1:8, average of 5 measurements were taken.

Figure 6-3: Series of geopolymer samples during drying. The molar Al:Si:Na:H$_2$O ratio was 1:2:1:8. In photograph c the cracks were difficult to identify therefore they were white highlighted. The sample had a diameter of 30 mm.

Figure 6-4: Effect of water evaporation via ambient temperature drying on shrinkage of different metakaolin geopolymers containing different initial molar water ratios: a) absolute water losses and b) water loss normalised to a remaining molar water ratio. Data points were averages of 3 results.

Figure 6-5: Changes in flexural strengths upon drying of prismatic samples prepared with different molar water ratios. Data points were averages of 5 measurements. All data is for samples 8 mm x 8 mm x 40 mm in size.

Figure 6-6: DSC/TGA result for geopolymers with a molar ratio Al:Si:Na:H$_2$O of 1:2:1:8.

Figure 6-7: Dilatometric analysis up to 1000°C (10°C/min, He gas) of metakaolin pastes containing different mixing water molar ratios.

Figure 6-8: Effect of molar Si to Al ratio on maximum water loss before onset of drying shrinkage in an Al:Si:Na:H$_2$O system of 1:x:1:8 composition. Samples were cured for 56 days in sealed bags before being subject to a sequential drying procedure. Data points are averages of 3 measurements.

Figure 6-9: Dilatometer results of geopolymers heated up to 360 °C where the Si:Al ratio was altered. Measured after 56 days curing.

Figure 6-10: Effect of molar Na to Al ratio on maximum water loss before onset of drying shrinkage in an Al:Si:Na:H$_2$O system of 1:2:x:8 composition. Samples were cured for 56 days in sealed bags before being subject to a sequential drying procedure. Data points are averages of 3 measurements.

Figure 6-11: Effect of Na versus K on sensitivity to drying shrinkage of samples cured for 56 days in sealed plastic bags in an Al:Si:Na/K:H$_2$O system of composition 1:2:x:8. Data points are averages of 3 measurements.

Figure 6-12: Dilatometer results of geopolymers with an Si:Al ratio of 1.8:1 using Na$^+$ and K$^+$ ions to balance the negative aluminate charge. Measured after 56 days curing.

Figure 6-13: Schematic structure of geopolymers with a molar Al:Si ratio lower 1:2 (left) and a molar Al:Si ratio higher than 1:2 (right).

Figure 7-1: Particle size distribution of sand used in this study.

Figure 7-2: Schematic representation to describe viscosity.

Figure 7-3: Cone-plate system to measure viscosity, modified from (Gehm, 1998).
Figure 7-4: Viscosity over increasing/decreasing shear rate of geopolymers. The molar ratio of Al:Si:Na was 1:2:1, the molar water ratio was altered between 7.5 to 9.0. ...............................109

Figure 7-5: Viscosity of different geopolymer/sand mixtures at a shear rate of 70 s⁻¹. The molar ratio of Al:Si:Na was 1:2:1 and the water ratio was altered between 7.5 to 10.5. ...............................110

Figure 7-6: Compressive strength for geopolymer/sand mortars after 75 days curing. Specimens were not dried before measuring. The molar ratio of Al:Si:Na was 1:2:1 and the water ratio altered between 7.5 to 10.5. Results are the average of 5 measurements and the lines represent the calculated compressive strength using Equation 7-7. .........................................................111

Figure 7-7: Compressive strength load-deflection curves for a pure geopolymer sample, a geopolymer mortar and a schematic curve displaying the behaviour of a load curve when crack deflection takes place. Geopolymer samples were 75 days cured at ambient temperature and not dried before measuring and the molar ratio of Al:Si:Na:H₂O was 1:2:1:8.5.........................................................112

Figure 7-8: Vickers Hardness of geopolymer mortars with a molar ratio of Al:Si:Na:H₂O 1:2:1:8.5 before drying. Each point represents an average of 7 results. The line represents the calculated Vickers hardness using Equation 7-7.................................................................................113

Figure 7-9: Compressive strength of geopolymer/sand mortars after drying at 110 °C. The molar ratio of Al:Si:Na was 1:2:1 and the water ratio was altered between 7.5 to 10.5. Samples in the grey area could not be measured due to cracks. Data represent the average of 5 measurements. .................................................................................................................................114

Figure 7-10: Strain induced in geopolymer/sand samples when heated to 500 °C at a heating rate of 10 °C/min. Each point was measured using dilatometry and represents the maximum shrinkage observed. The molar ratio of Al:Si:Na:H₂O was 1:2:1:8. The grey line shows the theoretical shrinkage of geopolymer mortars, calculated using equation 7-8. ........................................115

Figure 7-11: Particle size distribution of sand used in this study. .........................................................119

Figure 7-12: a) Schematic of the disc and the dimensions, b) picture of the experimental test, c) possible fractures during a test, modified from (Ovri & Davies, 1987) ........................................120

Figure 7-13: Diametrical tensile strength of Na-based geopolymers mortars using different grades of sand, before drying. Curing time were 14 days; results are averages of 5 measurements. ..121

Figure 7-14: Diametrical tensile strength of Na-based geopolymers mortars using different grades of sand, after drying at 110 °C. Curing time were 14 days; results are averages of 5 measurements........................................................................................................122

Figure 7-15: Na-based geopolymers, all samples contain medium size sand, a) polished sample contains 20 wt% sand; b) polished sample contains 50 wt% sand; c) polished sample containing 50 wt.% sand; d) unpolished sample containing 50 wt% sand; the solid particle is a sand particle........................................................................................................................................123

Figure 7-16: Cracks at the interface between filler particles and matrix due to shrinkage, modified from (Grassl et al., 2010). ............................................................................................................124

Figure 7-17: Simplified surface reaction of sand particles with dissolved alumininate and silicate.125

Figure 7-18: Isothermal calorimetry results for geopolymers/filler mixtures, measured at 20 °C, a) geopolymer mixtures contain the maximum percentage; the graph is separated into a wetting zone (A) and the second exothermic signal, b) second exothermic signal for all geopolymers/filler mixtures........................................................................................................................130

Figure 7-19: Total heat output for geopolymer/filler samples in the first 30 hours at 20 °C. ........131

Figure 7-20: Influence of active filler on total porosity in geopolymers after 360 days curing at ambient temperature......................................................................................................................132

Figure 7-21: Compressive strength over time for all geopolymers/filler mixtures. ......................133
Figure 7-22: Dilatometry results to determine the extent of shrinkage due to the loss of “free” water on samples cured 360 days at ambient temperature, a) geopolymer mixtures contain the maximum percentage, b) overview for all geopolymers/filler mixtures, the dotted lines mark the trend line.

Figure 7-23: XRD spectra for four samples each containing the maximum possible amount of fillers after 360 days curing; key: a = SiO₂, b = un-reacted Ca(OH)₂, c = Tobermorite (crystalline CSH gel), d = calcium silicate (CSH gel), e = magnesium silicate (MSH gel), f = un-reacted MgO.

Figure 7-24: SEM pictures for four samples each containing the maximum possible amount of one of the fillers, containing, a) Ca(OH)₂, b) CEM 1, c) MgO, d) sand. Samples were cured 360 days at ambient temperature.

Figure 8-1: pH value for different Na₂SiO₃ solutions with varying molar Si:Na ratio and comparison of the expected pH value for activation solutions for metakaolins with a different Si:Al ratio (PQ, 2004).

Figure 8-2: a) Magnox alloy as received, b) XRD spectrum of white powder on Magnox surface, a = brucite (Mg(OH)₂).

Figure 8-3: Corrosion of metal as a function of shear stress in corrosive medium, modified from (Balbaud-Celerier and Barbier, 2001).

Figure 8-4: Schematic apparatus to measure the corrosion rate of Al-rod.

Figure 8-5: Corrosion of Al-rod in different buffer solution. The dotted lines point out the linear slope which has been used to calculate the amount of H₂ released.

Figure 8-6: Dissolution of Mg from Magnox chips in different buffer solutions. The dotted lines point out the linear slope which has been used to calculate the corrosion rate of Magnox at various pH values.

Figure 8-7: Corrosion kinetics of Magnox alloy at different pH values.

Figure 8-8: a) Backscattered SEM-EDX analysis of a MetaStar 501 based geopolymer and Magnox alloy. The molar Al:Si:Na:H₂O ratio was 1:2:1:8. The line indicates where the line scan was taken. b) EDX analysis of MetaMax based geopolymers, molar Al:Si:Na:H₂O ratio was 1:2:1:8 and control mixture PC/BFS.

Figure 8-9: Corrosion of Al metal after encapsulation in different matrices. The molar Al:Si:Na:H₂O ratio in all geopolymers was 1:2:x:8.

Figure 8-10: Backscattered SEM-EDX MetaMax samples and control mixture, the Al:Na ratio was altered in the geopolymers samples. a) molar Al:Na ratio of 1:0.9, b) molar Al:Na ratio of 1:1, c) control sample OPC/BFS 1:3 and d) shows the EDX results on the interlayer.

Figure 8-11: Crystalline analysis of the interlayer of MetaMax based geopolymers and Al metal. The molar Al:Si:Na:H₂O ratio was 1:2:0.9:8, Key = a = bayerite (α-Al(OH)₃), b = gibbsite (γ-Al(OH)₃), c = quartz.

Figure 8-12: Compressive strength over time after curing at ambient temperature.

Figure 8-13: Pourbaix diagram of amorphous Al(OH)₃, modelled using HSC Chemistry® 6.1.

Figure 9-1: Relative mass yields for fragments from U-235 thermal neutron induced fission, modified from (Schmitt et al., 1962).

Figure 9-2: Dissolution of clinoptilolite in buffer solutions.

Figure 9-3: SEM image of polished sample, A = clinoptilolite, B = interfacial reactio zone (IRZ), C = geopolymer matrix, b) EDX results of two independent measurements, the molar Al:Si:Na:H₂O ratio in the geopolymer mixture was 1:2:1:9.

Figure 9-4: Schematic experimental procedure to measure the interactions of waste and geopolymers.
Figure 9-5: SEM and SEM-EDX results for MetaStar 501 based Na geopolymers after mixing it with Cs/Sr contaminated clinoptilolite showing the diffusion of Cs and Sr into the matrix. The sample was cured for 14 days. a) SEM image showing the transition zone between geopolymers and clinoptilolite, b) diffusion of Na from geopolymers into clinoptilolite, c) diffusion of Sr into the geopolymer matrix, d) diffusion of Cs into geopolymers.

Figure 9-6: Geopolymer with a molar Al:Si:Na:H₂O ratio of 1:1.6:1:9, cured in sealed bags for 9 month, a) room temperature, b) 75 °C.

Figure 9-7: Leaching of Na and Cs of Na-based geopolymers, altering the molar Al:Si ratio, in all cases the Cs concentration was below the detection limit.

Figure 9-8: Leaching of Na and Cs of Na-based geopolymers, varying the molar Al:Na ratio, in all cases the Cs concentration was below the detection limit.

Figure 9-9: Leaching of K and Cs out of K-based geopolymers, altering the molar Al:K ratio, the molar Al:Si ratio was 1:2.

Figure 9-10: FTIR spectra of MetaStar 501 Na-based pure geopolymer and mixed with 16 wt% Cs.

Figure 9-11: XRD of Na-based geopolymer loaded with Cs, Key a = silicon oxide (SiO₂).

Figure 9-12: FTIR results after Sr is incorporated into metakaolin based geopolymers with a molar Al:Si:Na:H₂O ratio of 1:2:1:9.

Figure 9-13: TGA results from geopolymers containing Sr(OH)₂, a) mass loss over temperature, b) calculated un-reacted Sr(OH)₂ based on TGA results using mass loss from de-hydroxylation.

Figure 9-14: DTA of geopolymers containing Sr(NO₃)₂.

Figure 9-15: Crystalline phase of geopolymers phases, a) Sr(OH)₂ in geopolymers, b) Sr(NO₃)₂ in geopolymers, key: a: un-reacted Sr(OH)₂, b: SrCO₃, c: strontium aluminate silicate, d: SiO₂ from metakaolin, e: NaNO₃, f: un-reacted Sr(NO₃)₂.

Figure 9-16: Leaching of Sr²⁺ and Na⁺ from Na based geopolymers, A*= expected Na leaching if Sr replaces Na as charge balancing cation, a) geopolymers mixed with Sr(OH)₂, b) geopolymers mixed with Sr(NO₃)₂.

Figure 9-17: Dissolution of Sr(NO₃)₂ in the activation solution and formation of a SrSiO₃ layer.

Figure 9-18: Potential influence of Sr into the geopolymers structure, left side: charge balancing cation, right side: integrated into the geopolymer gel based on results for tobermorite.

Figure A-1: Dissolution of metakaolin in 1wt% HF and 8 M NaOH solution over time.

Figure A-2: Changes in flexural strength upon drying of prismatic samples comparing different sizes. Small sample = 8 x 8 x 40 mm³, big sample = 25 x 25 x 80 mm³. The molar Al:Si:Na:H₂O ratio was 1:2:1:9.5 and data points were averages of 5 measurements.

Figure A-3: The effect of curing time, curing temperature and Si:Al ratio on the evolution of crystalline phases in Agrical MK based geopolymers. Where a = initial crystalline phase (SiO₂); b = Faujasite; c = sodium aluminium silicate; d = Zeolite P1.
List of Tables

Table 1.1: UK waste volumes in stock (for 2001) and predicted future arising (Mathieson et al., 2005). ...............................................................................................................................................................................................23
Table 1.2: Chemical composition of PC and BFS. ...............................................................................................................................................................................................................................................................23
Table 1.3: Different Cs radioisotopes and their half life (Pfennig et al., 2006). ...............................................................................................................................................................................................................................................................27
Table 1.4: Different Sr radioisotopes and their half life, h = hours, d = days, a = years (Pfennig et al., 2006). ...............................................................................................................................................................................................................................................................28
Table 2.1: Reaction energy for different condensation reaction (Catlow et al., 1996). .................................................................................................................................................................................................................................43
Table 4.1: Chemical composition (wt%) and mean particle size from used metakaolins according to XRF. ...............................................................................................................................................................................................................................................................53
Table 4.2: Silicate solutions (in wt%) and alkali hydroxides. .................................................................................................................................................................................................................................54
Table 4.3: Fillers used to improve mechanical properties. .................................................................................................................................................................................................................................54
Table 4.4: Materials used to study the waste/encapsulation interactions. .................................................................................................................................................................................................................................54
Table 4.5: Geopolymer mixtures with a molar ratio Al:Si:Na/K:H₂O ratio of 1:2:1:8 expressed in mass. ...............................................................................................................................................................................................................................................................55
Table 5.1: Un-dissolved residue after 20 hours dissolution in wt%. Results are the average of three measurements. ...............................................................................................................................................................................................................................................................71
Table 5.2: XRF analysis of Agrical before and after dissolution in wt%. ...............................................................................................................................................................................................................................................................73
Table 5.3: Content of different Al coordination using 27Al-NMR in wt%. ...............................................................................................................................................................................................................................................................73
Table 5.4: Fracture toughness of geopolymers. Result represents the averages of 6 measurements. ...............................................................................................................................................................................................................................................................77
Table 5.5: Weibull numbers for compressive and flexural strength, as well as average and median strength of metakaolin based geopolymers. ...............................................................................................................................................................................................................................................................81
Table 6.1: Molar compositions of samples. .................................................................................................................................................................................................................................................................................................87
Table 6.2: Comparison between Na and K (Migliore et al., 1988). .................................................................................................................................................................................................................................................................................................101
Table 7.1: Mixtures investigated in this study. The molar ratio of Al:Si:Na was in all mixtures the same 1:2:1, with the molar ratio of water added varied between 7.5 and 10.5. For all mixtures the w/s solid ratio and the volume percentage of added sand is shown in the table. .................................................................................................................................................................................................................................................................................................106
Table 7.2: Theoretical and calculated density to determine volume percentage of sand in geopolymers. Each sample value represents the average of 5 measurements. Calculated density was calculated using Equation 7-2. .................................................................................................................................................................................................................................................................................................109
Table 7.3: Mixtures investigated in this study. The molar ratio of Al:Si:Na:H₂O was in all mixtures the same 1:2:1:8. For all mixtures the w/s solid ratio and the volume percentage of added sand is shown in the table. .................................................................................................................................................................................................................................................................................................127
Table 8.1: Comparing of the activation solution for two metakaolins with a different molar Al:Si ratio. .................................................................................................................................................................................................................................................................................................142
Table 8.2: Prepared geopolymers samples and their molar ratios to study corrosion between encapsulation matrix and metal. .................................................................................................................................................................................................................................................................................................143
Table 9.1: Molar compositions of samples. .................................................................................................................................................................................................................................................................................................166
Table 9.2: Physical properties of different cations (Weast, 1987). .................................................................................................................................................................................................................................................................................................172
Table 9.3: FTIR vibration signals (Yunsheng et al., 2008). .................................................................................................................................................................................................................................................................................................173
Table 9.4: Concentration of Sr in the prepared geopolymer samples. .................................................................................................................................................................................................................................................................................................174
CHAPTER 1

INTRODUCTION
CHAPTER 1 INTRODUCTION

1.1 Nuclear waste

Nuclear waste arises during the production of electricity by nuclear power plants but is also generated at other facilities. In the UK 30 volume percent (vol%) of nuclear waste is produced by nuclear power plants, 9 vol% from research and development activities, ~2 vol% from military and the remainder comes from medical, industrial and fuel fabrication facilities (Mathieson et al., 2005). Due to the radiation emitted, nuclear waste is treated as hazardous waste. This does not only complicate the disposal but also the handling and storage. If nuclear waste leaches into the environment, it can become part of the food chain and over short or long time concentrates in human body cells. In the human body, the radiation can damage cells and soft tissue which can result in cancer. To avoid this problem, nuclear waste has to be encapsulated and immobilised. A safe encapsulation/immobilisation can be difficult because of the wide range of radioactive elements in the waste with different chemical characteristics.

In addition to a suitable nuclear waste form, a storage facility capable of safely holding the waste for a long time is required. It has to be ensured that the waste is not a threat to the environment over a long time period. Currently, research is ongoing to find appropriate waste forms and stable geological formations for the final storage of nuclear waste. Until then the waste is stored close to the facilities where it was produced.

1.2 Classification of nuclear waste types

To reduce the amount of hazardous nuclear waste, it is usually classified into two groups: contaminated and non-contaminated components. The non-contaminated waste can be disposed of with normal waste. The contaminated waste, based on the emitting radiation, is further classified according to both the amount and type of radiation emitted: high- (HLW), intermediate- (ILW), low- (LLW), very low-level- (VLLW), very short lived- (VSLW) and exempt wastes (EW) according to the risk they pose (Agency, 2009).

The different waste classifications are:

- HLW – waste which contains a large proportion of highly active materials and therefore releases heat or long lived radionuclides which need to be considered in the design of disposal facilities. It is expected that this waste will be disposed of in deep, stable geological formations often several hundred meters below the surface.
• ILW – waste with radioactivity levels over the boundaries for LLW which contains particularly long lived radionuclides. It needs only limited or no provision of cooling. However, disposal near the surface is not possible due to its high activity.

• LLW – waste which contains marginal amounts of radioactive material but does not exceed an average of 400Bq/g to 4000 Bq/g for individual packages of radiation. This type requires robust isolation for periods of up to a few hundred years.

• VLLW – waste which does not need a high level of containment and isolation. Disposal near surface landfill with limited regulatory is possible.

• VSLW – waste that include nuclides of very short half-life and with activity concentrations above the clearance levels. This kind can be stored until the activity has dropped below the levels for clearance and afterwards handled as conventional waste.

• EW - waste that contains such a small concentration of radio nuclides that it does not require provisions for radiation protection.

Currently, the different waste types are stored in special pits before encapsulation. These pits allow collection of enough waste so that a sufficient amount is available for encapsulation. Moreover, during storage radiation of the highly radioactive material reduces to lower levels by decay. Figure 1-1 shows an example of how this waste is stored at Sellafield (UK).

![Figure 1-1: Storage of nuclear waste in a special pit. The containers are stored under water.](image)

1.3 Immobilisation and encapsulation of hazardous/nuclear waste

Immobilisation and encapsulation of hazardous and especially radioactive waste is problematic. Not only is special treatment required to ensure that the waste is no longer a threat to the environment but also radiation which can slowly destroy the encapsulation matrix has to be considered. This treatment can be described as an immobilisation and encapsulation process. This can include a range of different procedures e.g. thermal/nonthermal destruction, chemical/physical
treatment or immobilisation. One of the major aims of these methods is to reduce the amount of waste and to produce acceptable final waste forms. These final matrices have to meet specific requirements to avoid the leaching of hazardous/nuclear material and have high durability, resistance to chemicals and radiation and have high temperature and mechanical stability. Another important property of the encapsulation matrix is the pH value. It should be in a range so that corrosion of the waste and the surrounding container is minimal, not only to avoid unwanted side reactions with the waste but also to avoid corrosion of the container, which represents the final “man made” barrier to the environment, followed by the geological location. In general, the necessary specifications require the retention of activity under normal and accident conditions. Additionally, each waste type has different special requirements depending on its physical and chemical properties e.g. heat release, aggregate state and surface reaction. If the waste releases heat, like HLW, cooling may be required. Solid ILW should not react with the encapsulation matrix and liquid ILW should be immobilised in the matrix. One of the main chemical reactions in solid wastes which has to be avoided is gas generation and the resulting durability issue. The problem with gas producing chemical reactions is the pressure which can build up between the encapsulation matrix and the waste. Over time, this pressure may cause the matrix to crack. When ground water comes in contact with the encapsulation matrix, it can travel through the crack to the waste, dissolve some hazardous particles and contaminate the environment.

Over the last 60 years, solidification/stabilisation (S/S) processes have been used to encapsulate and immobilise hazardous/nuclear waste (Conner, 1990). S/S is currently the proven technology for 57 hazardous waste streams (Chang, 2001).

Stabilisation or immobilisation means converting a waste stream into a less soluble form (Freeman, 1997). This can be done either by adding an absorbent such as an ion exchanger or by using a chemical treatment for example increasing the pH to precipitate heavy metals (Erdema et al., 2004, Smičiklas et al., 2007a). Normally, after this treatment the water containing the waste can be reused.

Solidification (encapsulation) refers to the use of additives and binders that transform the mixed waste from sludge into a solid form that holds its shape without the support of a container. Another aim of solidification is to convert the waste stream into a medium which is easier to handle and store. It also reduces the surface area of the waste minimising the risk of leaching (Freeman, 1997).

The best S/S solution for HLW is encapsulation in a glass or ceramic matrix (Lee et al., 2006). For ILW and LLW, Portland cement/blast furnace slag (PC/BFS) or bitumen matrices are often chosen (Flambard et al., 1986, Milestone, 2006).
1.3.1 S/S of HLW

S/S of HLW is even more complex compared to that of ILW and LLW due to the high radiation and the heat release generated during fission (Ewing et al., 1995). Vitrification has proved to be the most suitable technique to encapsulate HLW (Lee et al., 2006). During this process, the nuclear material is converted into a glassy form by mixing the waste with molten glass. The advantage of this method is that the chemical composition of glass can be altered over a wide range, so that different waste types can be tolerated. The production process is relatively simple and the final product has extremely high durability. However, the disadvantage of this process is that temperatures of ~1000 °C are required to melt the glass and mix the waste with the molten glass. At this high temperature, it is possible that elements or compounds could vaporise and contaminate the encapsulation facility.

1.3.2 S/S of ILW and LLW waste

The amounts of ILW and LLW produced and stored in the UK are much higher than the amount of HLW, as shown in Table 1.1. However, S/S of these types of waste is significantly less complex because the radiation is relatively low and the waste does not generate significant amounts of heat. A possible S/S technique, which is currently used in the UK, involves mixing the waste with a mixture of Portland cement (PC) and blast furnace slag (BFS) (Sharp et al., 2003b, Milestone, 2006).

The hydration reactions during setting and curing occur at a high pH which creates relatively insoluble radioactive metal hydroxides or oxides and therefore lowers the possibility of leaching. In addition, physical stabilisation takes place. Inorganic compounds such as carbonates and silicates can substitute potential metal ions in the waste into a mineral structure. Disadvantages of this technique are:

- The high pH of the hydration can cause corrosion of metals in the waste;
- The cement bonding mechanisms are limited in their retention or chemically absorption of radionuclides;
- Over time the pH reduces in cement systems due to further reactions (Mathieson et al., 2005, Glasser, 1992).
Table 1.1: UK waste volumes in stock (for 2001) and predicted future arising (Mathieson et al., 2005).

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Conditioned plus unconditioned volumes in stock [m$^3$]</th>
<th>Total future conditioned arisings [m$^3$]</th>
<th>Total conditioned volume [m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLW</td>
<td>14700</td>
<td>1490000</td>
<td>1510000</td>
</tr>
<tr>
<td>ILW</td>
<td>75400</td>
<td>163000</td>
<td>2370000</td>
</tr>
<tr>
<td>HLW</td>
<td>1960</td>
<td>0.75</td>
<td>1510</td>
</tr>
<tr>
<td>Total</td>
<td>92100</td>
<td>1660</td>
<td>1750000</td>
</tr>
</tbody>
</table>

1.4 Encapsulation of ILW and LLW in the UK

Since the early 1960s a mixture of PC and additives has been used to immobilise ILW (Stefanovsky et al., 2004). This is because PC has attractive properties such as wide availability, alkaline chemistry meaning low solubility of many radionuclides, it is non-flammable and a high compressive strength can be obtained. PC was first patented in 1824 and has been extensively characterised and its long term behaviour has been widely investigated (Francis, 1977). It is produced by heating a mixture of limestone, clay and additives at temperatures up to 1450°C. However, major drawbacks for PC are low chemical and radiation resistance and therefore it is not used for HLW. Other disadvantages are low freeze resistance and microbiological degradation. To overcome these issues, additives such as clay, sand, rutile, plasticizers, milled incinerator bottom ash, fly ash, blast furnace slag (BFS) and other waste products have to be added (Stefanovsky et al., 2004).

In the UK, research has been focused on a blend of PC with BFS for encapsulation of LLW and ILW (Sharp et al., 2003b, Tsaousoglou, 2007, Setiadi, 2007). The addition of BFS to PC improves compressive and flexural strength (Sivasundaram and Malhotra, 1992). BFS is a by-product of the steel industry and is produced by quenching molten iron slag from a blast furnace in water or steam. The product is then dried and ground to a fine powder (BS). The chemical composition of PC and BFS can be seen in Table 1.2 (Sharp et al., 2003a).

Table 1.2: Chemical composition of PC and BFS.

<table>
<thead>
<tr>
<th>mass [%]</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>67</td>
<td>22</td>
<td>6</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>BFS</td>
<td>43</td>
<td>34</td>
<td>16</td>
<td>0.5</td>
<td>5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Despite the improved mechanical properties resulting from the addition of BFS to PC, there are currently two waste streams in the UK for which this mixture is problematic due to the high pH and high Ca content in the cement mixture. These problematic waste streams are:

- Al contaminated Magnox swarf, from Magnox reactors, a legacy waste;
- Caesium and strontium (Cs and Sr) contaminated clinoptilolite.

### 1.4.1 Magnox swarf and Al metal

A mixture of Magnox swarf and Al metal is a legacy waste which has been generated from Magnox (Magnesium non-oxidising) reactors. These Generation I reactors were mainly used in the UK but also in Italy and Japan. This particular reactor type used a Mg/Al alloy (Magnox) with 0.8% Al as a fuel rod and Al metal from the holder. The fuel was placed in the tube which was sealed at both ends. A schematic image of a Magnox fuel rod is shown in Figure 1-2a (Weaver, 2009). At the end of its life the fuel is removed by stripping the alloy. Afterwards, it was cut into small pieces and stored in special pits. Aged Magnox waste is depicted in Figure 1-2b.

![Figure 1-2: a) Schematic Magnox fuel rod, modified from (Weaver, 2009) and b) Magnox alloy after storage in special pits.](image)

The problem with the Magnox alloy is that Mg corrodes at a pH value lower than ~11 and at such high pH, Al corrodes. This electrochemical behaviour can be clearly illustrated using Pourbaix diagrams, as shown in Figure 1-3 for Mg and in Figure 1-4 for Al.

Pourbaix diagrams show the electrochemical half potential of different reactions against pH value, as shown in Figure 1-3 and 1-4. They are separated into three different regions: immunity, corrosion and passivity. Immunity means that the metal is not attacked, while corrosion indicates
that general attack will occur. Passivity represents a surface reaction where the metal forms a stable coating of oxide or hydroxide on the surface of the metal, such as an oxide layer on Al which reduces the corrosion rate. Line a and b in the Pourbaix diagrams represent the stability of water in a reducing/oxidising environment and are usually plotted in these diagrams. Between line a and b water is stable, below line a, the decomposition of $\text{H}_2\text{O}$ into hydrogen is favoured:

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

Above line b water can be oxidised into $\text{O}_2$:

$$2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4H^+ + 4e^-$$

The Pourbaix diagram for Mg metal is plotted in Figure 1-3. It can be seen that Mg corrodes up to a pH value of ~11 and at higher pH values, passivation occurs. This is due to the fact that Mg forms a thin protective layer of hydroxide. From this figure it is clear that Mg is stable in high pH systems such as PC. However, Magnox waste streams not only contain pure Magnox alloy but also Al metals. The Pourbaix diagram of Al is more complex compared to that of Mg as depicted in Figure 1-4. It can be seen that Al has two corrosion zones and one passivation zone.
In this passivation area Al forms a thin Al oxide layer on the surface. The nature of this thin oxide layer is complex due to the different possible configurations of aluminium oxide which can be formed. These include diaspore (α-AlO(OH)), böhmite (γ-AlO(OH)), nordstrandite (triclinic Al(OH)₃), bayerite (β-Al(OH)₃), and gibbsite (γ-Al(OH)₃). Each Al oxide has different electrochemical behaviour. At pH values below 4 and above 9 corrosion of Al occurs and hydrogen gas (H₂) is released. The H₂ gas causes a pressure rise and as a result cracks appear in the matrix.

\[
pH < 4 \quad 2Al + 6H^+ \to 2Al^{3+} + 3H_2
\]

\[
pH > 9 \quad 2Al + 6H_2O + 2OH^- \to 2Al(OH)_4^- + 3H_2
\]

According to the Pourbaix diagrams for Mg and Al, the encapsulation matrix should have a pH of 9 for Al waste and 11 for Magnox swarf. This is not possible because one encapsulation matrix cannot have two pH values at the same time. However, previous research has already shown that when using an encapsulation matrix with a pH value between 10 and 11 promising results are obtained as, depicted in Figure 1-5 (Zhang, 2012a). In this picture Al metal was encapsulated in a conventional PC/BFS mixture (a) and a novel MgO based cement (b). It can be seen that the Al metal is highly corroded in Figure 1-5a whereas in Figure 1-5b no corrosion can be observed. The measured pH value of the PC/BFS mixture was 12.5 and from the novel MgO binder system ~10.8.
Figure 1-5: Al metal rod encapsulated in a) mixture of PC/BFS with a mass ratio of 1:3 and w/s = 0.33 and b) novel MgO binder system containing 20% MgO, 5% MgCO$_3$, 25% silica fume and 50% sand, w/s = 0.275. Samples were 28 days cured at room temperature (Zhang, 2012).

1.4.2 Cs/Sr contaminated clinoptilolite

Cs and Sr are produced during fission of heavy atoms. When a heavy atom (such as uranium) undergoes fission, it splits asymmetrically into two large fragments and neutrons. These two fragments have a mass number between 75 and 165 and some of these nuclides are Cs (atomic mass around 133 g mol$^{-1}$) and Sr (atomic mass around 90 g mol$^{-1}$).

There are 40 different Cs isotopes with an atomic mass ranging between 112 and 151 (Pfennig et al., 2006). Most of the 40 Cs isotopes have a half life shorter than 15 days and therefore are not a real problem because during storage most of them have already changed to a stable nuclide by undergoing $\beta^+$ decay. During a $\beta^+$ decay an electron ($e^-$) is formed, the atomic number ($Z$) increases and the neutron number ($N$) decreases.

$$\frac{A}{Z}^YN \rightarrow \frac{A}{Z+1}^{Y-N-1}N^- + e^- + E$$

However, three of them have a have a relative long stability, as shown in Table 1.3.

<table>
<thead>
<tr>
<th>isotope</th>
<th>year</th>
<th>decay mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs 134</td>
<td>2.1</td>
<td>beta plus</td>
</tr>
<tr>
<td>Cs 135</td>
<td>$2 \times 10^6$</td>
<td>beta minus</td>
</tr>
<tr>
<td>Cs 137</td>
<td>30.2</td>
<td>beta minus</td>
</tr>
</tbody>
</table>

From these three Cs isotopes only Cs 137 can be considered harmful. Cs 134 undergoes a beta plus decay but most of it has already formed a stable form during storage and the emitted radiation of Cs 135 is relatively low to be considered dangerous (Pfennig et al., 2006). In general Cs has
similar properties to potassium (K) and after intake into the body it is absorbed by the gastrointestinal tract and built into the muscle structure where it remains for approximately 110 days (Ringer, 1882, Rosoff and Cohn, 1963, Rundo, 1964).

Sr has 34 known isotopes with an atomic mass from 73 to 105 but only five of them have a half life longer than a day, as shown in Table 1.4 (Pfennig et al., 2006). Taking into account that the waste is usually stored for years, only Sr 90 has a half life which can be a threat to the environment and mankind (Pfennig et al., 2006). The physical and chemical properties of Sr are similar to those of calcium (Ca) (Kornberg, 1961). After exposure to Sr, it is absorbed by the intestine and built into the bone structure and teeth where it has a half life of 49 years (Spencer et al., 1957, Degteva and Kozheurov, 1994, Libby, 1956 June). After replacing Ca in the bone, it can cause bone tumor and leukemia. It is also believed that it can be absorbed by the parathyroid resulting in hyperparathyroidism.

<table>
<thead>
<tr>
<th>isotope</th>
<th>time</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr 82</td>
<td>25.3 d</td>
<td>beta plus</td>
</tr>
<tr>
<td>Sr 83</td>
<td>32.4 h</td>
<td>beta plus</td>
</tr>
<tr>
<td>Sr 85</td>
<td>64.9 d</td>
<td>beta plus</td>
</tr>
<tr>
<td>Sr 89</td>
<td>50.5 d</td>
<td>beta minus</td>
</tr>
<tr>
<td>Sr 90</td>
<td>28.6 a</td>
<td>beta minus</td>
</tr>
</tbody>
</table>

Cs and Sr ions are present in spent fuel and washed out when the fuel is stored under water in the special pits. Before this water can be discharged into the sea, the radioactive ions need to be removed. A schematic of the cleaning facility is shown in Figure 1-6 (Gordon, 2008)

**Figure 1-6**: Removal of Cs\(^+\) and Sr\(^{2+}\) radio-nuclides from contaminated water, modified from (Gordon, 2008).
The contaminated water is filtered using sand beds to remove any suspended solids. The pH of the solution is then reduced from 11.5 to 8.5 using CO2. This is necessary because a high pH would dissolve clinoptilolite (Cotton, 2008). When the radioactive water reaches the clinoptilolite beds, the Cs+ and Sr^{2+} ions are absorbed immediately from the clinoptilolite (Smičiklas et al., 2007b).

Clinoptilolite is a naturally occurring mineral which belongs to the group of zeolites. Zeolites consist of a crystalline, micro-porous aluminosilicate network made up of tetrahedral coordinated aluminate and silicate groups. Depending on the structure, the final zeolite can have uniform pores and/or channels in which substances or molecules can be retained. For this reason, these materials are used as molecular sieves which absorb molecules and elements of smaller diameter than to the pores. These pores or channels are conventionally defined by the ring size of the aluminate and silicates. In Figure 1-7 a “10-ring” zeolite is shown (Johnson et al., 2003).

![Figure 1-7: Clinoptilolite Cs-exchanged, dehydrated Hexacesium tecto-hexaalumotriacontasilicate (Cs_6Al_6Si_30O_72), modified from (Johnson et al., 2003).](image)

The aluminate has a negative charge and is balanced by a cation. These cations are loosely held and can be readily exchanged for others in the contact solution. Due to this property, zeolites have been considered for treatment of liquid radioactive waste, containing Cs+ and Sr^{2+} ions (Smičiklas et al., 2007a). The main focus has been on mordenite, erionite, chabazite and clinoptilolite with clinoptilolite receiving the most attention due to its widespread occurrence and high selectivity for Cs+ and Sr^{2+} ions.
After removing both elements from the water using clinoptilolite, an encapsulation matrix is required to ensure that radioactive Cs\(^+\) and Sr\(^{2+}\) do not leach. A proposed matrix is cement although it is unclear how zeolites interact with this system. Furthermore, it has been shown that the high pH of cement dissolves zeolites (Gordon et al., 2008). Additionally, the exchange of sodium (Na\(^+\)) and potassium (K\(^+\)) ions, which are already present in the cement matrix, with Cs ions in the zeolite has been observed (Jenni and Hyatt, 2010). In both cases, Cs and Sr can be released into the cement matrix during the encapsulation process. Researchers have demonstrated that cement does not retain Cs and Sr ions and in presence of water, leaching occurs (Komarneni and Roy, 1981). To lower the leaching of Cs\(^+\) and Sr\(^{2+}\) ions from cementitious pastes, research has investigated the influence of leaching after adding zeolite P to the cement (Poon et al., 1999).

The release of Cs and Sr ions into the cement matrix either due to dissolution or ion exchange would result in a precipitation of Sr as Sr(OH)\(_2\) due to the high pH of the matrix and Cs would remain as an ion which can easily diffuse through the matrix. Although Sr precipitates as Sr(OH)\(_2\), the solubility of Sr(OH)\(_2\) in water is relatively high with around 9 g l\(^{-1}\) which means it still can be a threat to the environment if the waste comes into contact with ground water. Furthermore, it has been shown that Cs has relatively high leaching rates when cement pastes are used and that the chemical binding of Cs has an insignificant effect on immobilisation (Bagosi and Csetenyi, 1998, Crawford et al., 1984, Atkinson and Nickerson, 1988, Holgersson et al., 1998).

### 1.5 Summary

In this chapter nuclear waste and its treatment has been discussed in general. It was shown that nuclear waste is classified into three main groups. The largest group contains ILW which also is the most difficult fraction to encapsulate/immobilise due to a wide range of different nuclides. Two difficult waste streams of ILW have been identified:

- Al containing Magnox swarf and
- Cs/Sr contaminated clinoptilolite.

In the next chapter a potential encapsulation matrix for these waste streams will be introduced.
CHAPTER 2  GEOPOLYMERS FOR IMMOBILISATION AND ENCAPSULATION OF NUCLEAR WASTE
CHAPTER 2 GEOPOLYMERS FOR IMMOBILISATION AND 
ENCAPSULATION OF NUCLEAR WASTE

Currently, nuclear waste is stored next to the facility where it is produced. In the near future this waste has to be immobilised and encapsulated therefore the nuclear industry has to solve the problem of the safe disposal of nuclear waste. New encapsulation systems are required to meet the requirement that current materials cannot deliver of (Flynn et al., 1992). For HLW, glass is considered to be the best solution for encapsulation. For ILW and LLW this would be far too expensive and cheaper systems based on cement are needed. In order to meet not just the cost objectives but also the performance requirements the development of a toolbox of materials that can be tailored to the waste materials has been suggested (Milestone, 2006). Geopolymers have been proposed as a potential material because of two main advantages over PC, faster strengthening and improved acid resistance (Milestone, 2006, Khalil and Merz, 1994, Comrie et al., 1988). Geopolymers can gain 70% of final strength within 4 hours of mixing, whereas PC undergoes a hydration reaction and the strength increases gradually over time (Palomo and Lopez de la Fuente, 2003, Silva et al., 2007, Davidovits, 1991, Hardjito et al., 2004). In acid solutions, a PC matrix will completely dissolve while only the surface of geopolymers undergoes attack (Davidovits, 1993, Wallah et al., 2005, Wallah and Rangan, 2006). Furthermore, long term experiments undertaken in different aggressive solutions using metakaolin based geopolymers showed no change in flexural strength (Palomo et al., 1999a). Geopolymers are resistant to fire and unaffected by microbial environment with no sign of attack after 4 weeks (Cheng and Chiu, 2003, Hermann et al., 1999). It has been shown that the workability even for low water/solid ratios is high, which is an important factor for waste encapsulation (Palomo et al., 1999b). Geopolymers have similar properties to zeolites which are known to absorb ions such as Cd, Pb, Ni, Co, Cs and Sr (Davidovits, 1988, Abd El-Rahman et al., 2006, Shi et al., 2009). Ongoing research is investigating the immobilisation of Cs, Sr and heavy metal ions in geopolymers which are the main ions in liquid ILW (Perera et al., 2006, Perera et al., 2007a, Perera et al., 2005, Hanzliceck et al., 2006).

2.1 Geopolymers

A new cementitious material has been introduced in the 1940s which was termed geopolymers in the 1970s by Davidovits (Davidovits, 1982, Berck, 1975, Davidovits, 1989). In recent years these materials have also been referred to as alkali activated cement, mineral polymers, inorganic polymers, inorganic polymer glasses, alkali-bonded ceramics, soil cements and
hydroceramics. However, the most common terms in the literature are geopolymers or inorganic polymers. The binding phase in these inorganic polymers is a tetrahedrally coordinated alkali-aluminosilicate gel. The polymerisation is a geosynthesis, a reaction that chemically integrates minerals, such as naturally occurring silico-aluminate (Swanepoel and Strydom, 2002, Xu and van Deventer, 2000). The reaction occurs at room temperature and is activated by a high alkaline solution, and forms, an amorphous polymer, which is chemically and structurally similar to natural rock (Hewayde et al., 2006). The final product can be considered as an amorphous equivalent of feldspars (KAlSi$_3$O$_8$, NaAlSi$_3$O$_8$, CaAl$_2$Si$_2$O$_8$) but the synthesis is similar to an organic condensation polymerisation. Therefore these materials have been termed geopolymers (Hos et al., 2002, Davidovits, 1991).

Geopolymers are not only an amorphous equivalent to alkali feldspar, they also can be considered as amorphous zeolites because all materials are built up of tetrahedrally interlinked aluminates and silicates. The laboratory synthesis of zeolites and geopolymers is a similar process involving a polycondensation reaction (van Jaarsveld et al., 1997, Breck, 1974). The difference between the formation of zeolite and geopolymers however lies in the concentration of precursors. The formation of zeolites requires higher amounts of water and occurs in closed hydrothermal systems. These systems crystallise from dilute aqueous solutions where the molecules have enough time to orientate into a crystal structure (Breck, 1974). In contrast, geopolymerisation reactions are fast and result in an amorphous structure. Despite the fast reaction, the formation of zeolite nanocrystallites within the geopolymer gel has been observed (Provis et al., 2005b, Bell et al., 2008b).

The geopolymerisation mechanism is not fully understood and varies depending on the precursors and activation solution. However, the general reaction can be separated into three different steps with overlapping phases (Provis and van Deventer, 2007b, Yao et al., 2009)

1. Deconstruction, dissolution of the solid state;
2. polymerisation;
3. stabilisation.
Geopolymers for immobilization and encapsulation of nuclear waste

Deconstruction

In an alkaline environment, aluminium oxide and silicium oxide are dissolved from the solid precursor and form aluminate ($\text{Al(OH)}_4^-$) and silicate ($[\text{SiO}_x(\text{OH})_y]^-$). The major silicate species are $[\text{SiO(OH)}_3]^-$ and $[\text{SiO}_2(\text{OH})_2]^2-$, with the concentration ratio of $[\text{SiO}_2(\text{OH})_2]^2-$ to $[\text{SiO(OH)}_3]^-$ increasing with pH (Weng et al., 2005, Panias et al., 2007).

Polymerisation

After dissolution of the solid species, aluminates and silicates are formed. The following condensation reaction between aluminate and silicate is a nucleophilic substitution reaction (Weng and Sagoe-Crentsil, 2007). An example of this reaction between $[\text{Al(OH)}_4^-]$ and $[\text{SiO(OH)}_3]^-$ is shown below.

Stabilisation

The oligomers undergo a further condensation reaction and release the water which was consumed during the hydrolysis. With this gelation, the system starts to rearrange and reorganise, resulting in a three dimensional aluminosilicate network that is relatively resistant to dissolution in water (Fernández-Jiménez et al., 2006, Provis and van Deventer, 2007a).
Geopolymers for immobilization and encapsulation of nuclear waste

2.2 Influence of different parameters

2.2.1 Solid precursor

Geopolymers can be produced from a variety of different precursors containing a high amount of aluminate. The main precursors which are currently used are metakaolin, pulverized fly ash (PFA) and slags (Kong et al., 2007, van Jaarsveld et al., 2002, Chindaprasirt et al., 2009). Each material has advantages and disadvantages such as price, availability and elemental consistency. However, the most important difference between metakaolin and PFA is the elemental consistency which cannot always be guaranteed for PFA (Fernández-Jiménez and Palomo, 2003). This is due to the difference in the production of PFA, which is a by-product of coal fire power stations, and the natural synthesis of metakaolin.

In this study, it was decided to use metakaolin as precursor for geopolymers due to the high elemental consistency. For the nuclear industry, it is more important to work with materials were the elemental composition is more important compared to the price. One of the key parameters for all encapsulation materials is that the availability of the precursors with a constant elemental composition should be guaranteed for approximately 50 years.

Pulverised fly ash (PFA)

Coal is formed when organic material is buried before decay has occurred. The overlying sediment area needs to be thick enough to protect the organic material from oxygen and sunlight. Over time the weight of sediment compresses the material, squeezing out water, eventually converting it to coal (Cook, 2003). This means that coal is a blend of organic matter mixed with sediments and consists of a complex mixture of organic and inorganic substances. When coal is burnt in coal fire power stations at temperatures up to 1600 °C, inorganic material embedded in the coal can melt or undergoes phase transitions (Hemmings and Berry, 1987). As the type and concentration of minerals in coal can vary the final particle size and shape of PFA can fluctuate (Diamond, 1986). Furthermore, to optimise the calorific value, coal is often blended with coal from other sources and the formed PFA can vary significantly.
Metakaolin

Metakaolin is produced by heating kaolinite to temperatures between 500 and 800 °C depending on purity and crystallinity (Keyte, 2009). The origin of kaolinite is complex and there are several formation theories (Drombrowski, 1993, Pickering and Murray, 1994, Hurst and Pickering, 1997, Elzea Kogel et al., 2000). The most accepted theory is lateritic weathering and intensive desilication of parent volcanic rocks under warm-temperate to subtropical, humid conditions (Mizota and Longstaffe, 1996, Bird and Chivas, 1988, Biscaye, 1965, Ollier, 1969). It is suggested that muddy rivers carried materials and deposits which then settled out in lagoons and ponds (Moll, 2001). The remaining organic material ensured a reducing environment, leading to development of pyrite and anaerobic bacterial action. Action of the sea, intense weathering and soils-formation cycles commenced, leading to re-crystallization of kaolinite (Moll, 2001). The final deposits contain well crystallised and highly pure kaolinite with a molar ratio of Si:Al of 1 to 1.5. A model of kaolinite can be seen in Figure 2-1 (White et al., 2009). In this figure kaolinite is represented as 1:1 layered aluminosilicate. Each layer contains a sheet of tetrahedrally coordinated SiO$_4$ which are connected to a sheet of octahedrally coordinated AlO$_6$ (Sato et al., 2005).

![Figure 2-1: Structure of kaolinite, modified from (White et al., 2009).](image)

After kaolinite is transformed into metakaolin the aluminium coordination number changes from 6 to a mixture of 4, 5 and 6 (Sanz et al., 1988). This change of the coordination number can be measured using solid state magic angle spinning Al-NMR, as shown in Figure 2-2 (Sanz et al., 1988). It can be seen that with increasing temperature the amount of Al with a
coordination number of 5 increases. The highest amount of Al(V) is reached after exposure to 850 °C and at 980 °C only Al(IV) and Al(VI) are present in the sample.

Figure 2-2: Solid state magic angle spinning $^{27}$Al-NMR spectrum of kaolin at different temperatures, modified from (Sanz et al., 1988).

The crystalline structure also changes during heating, as shown in Figure 2-3. Up to 600 °C two crystalline peaks from kaolinite at 15° and 28° 2θ can be seen. Both peaks disappear at higher temperatures and an amorphous hump is formed which remains until 980 °C. This amorphous hump is formed due to thermal de-hydroxylation. This de-hydroxylation is partially reversible when metakaolin is in contact with moisture (Lee et al., 2003, Wang et al., 2005, Rocha et al., 1990).
As explained, after the transformation of kaolinite into metakaolin, the Al coordination number can vary (MacKenzie et al., 1985, Rocha and Klinowski, 1990, Granizo and Blanco, 1998b, Badogiannis et al., 2005, Granizo et al., 2007). Currently, there is some speculation about the exact role of the different Al-coordination and there are two theories about the Al coordination numbers (Davidovits, 2008, MacKenzie et al., 2007). One states that Al(V) plays an important role in the properties of geopolymers such as setting time and strength whilst the other theory assumes that not only Al(V) is important but the strain in the bonding network induced by thermal dehydroxylation. Currently, both theories have not been further investigated.

2.2.2 Si source and alkaline solution

Sodium or potassium silicate (Na$_2$SiO$_3$ or K$_2$SiO$_3$) solution is used to provide a source of silicates and to act as binder, alkali activator and plasticiser. Due to the fact that in Na$_2$SiO$_3$ or K$_2$SiO$_3$ solution solid material is dissolved in water at certain Na$_2$O/K$_2$O:SiO$_2$ mass ratios precipitation occurs, as shown in Figure 2-4 for Na$_2$O:SiO$_2$ respectively. This figure shows only a small part of the ternary phase diagram which is not easy to determine because of the formation of meta stable aqueous silicate solutions which can slowly precipitate (Wills, 1950). Another problem apart from the chemical stability of silicate solutions is their viscosity. With
increasing mass content of SiO$_2$ and Na/K$_2$O the viscosity increases, as demonstrated for Na$_2$O/SiO$_2$ and K$_2$O/SiO$_2$ mixtures in Figure 2-5 (Weldes and Lange, 1961).

**Figure 2-4:** Stability of sodium silicate solutions and the phases which may precipitate during storage at 25 °C, modified from (Wills, 1950).

**Figure 2-5:** Viscosity of different silicate solutions at 20 °C. The numbers above each line represent the mass ratio of SiO$_2$/Na$_2$O or SiO$_2$/K$_2$O, modified from (Weldes and Lange, 1961). a) viscosity of sodium silicate solutions, b) viscosity of potassium silicate solution.
Furthermore, depending on the alkali cation (Na or K) used for geopolymerisation, not only the stability of the solution and viscosity, every stage of the chemical reaction is influenced, from setting, to mechanical and chemical properties. The use of K as opposed to Na ions, lowers the mixing viscosity, reduces setting time and results in higher compressive strengths. A disadvantage of using K is the reduced resistance to acid attack compared to Na based geopolymers (van Jaarsveld and van Deventer, 1999, Provis and van Deventer, 2007b, Duxson et al., 2007b). The alteration in the mechanical properties is a result of different chemical reactions caused by the difference in size, alkalinity and hydration sphere of the K⁺ cations. For example the larger hydration sphere of K⁺ can be more easily removed due to a lower charge density compared to Na⁺ and this allows a denser polycondensation reaction, which leads to a higher solution concentration and therefore faster setting and higher strength (Phair and van Deventer, 2002, Phair and van Deventer, 2001). In addition, the smaller Na⁺ causes the formation of smaller silicate monomers and oligomers whereas the larger K⁺ supports the formation of larger silicate oligomers. Therefore the addition of NaOH may increase the quantity of monomeric silicate whilst KOH increases the degree of polycondensation. These example show that the selection of a suitable hydroxide is of great importance to the reaction (Phair and van Deventer, 2002).

2.2.3 Influence of pH on silicate and aluminate

In section 2.1 it has been established that the dissolution of the solid precursor requires a high pH environment. Previous studies investigated the influence of high pH values on aluminates and silicates. By using the partial charge model (PCM) it has been shown that in an alkaline environment Al³⁺ ions have a tetrahedral coordination over the entire accessible pH range and the major Al species is [Al(OH)₄]⁻ while the major silicate species are [SiO(OH)₃]⁻ and [SiO₂(OH)₂]²⁻ (Weng et al., 2005, Weng and Sagoe-Crengsil, 2007, Rahier et al., 1997). In addition, in alkaline solution, Si(OH)₄ condensates and a wide variety of oligomeric silicate anions have been shown to exist, as presented in Figure 2-6 (Harris and Knight, 1983).
Geopolymers for immobilization and encapsulation of nuclear waste

Figure 2-6: Variety of oligomeric silicate anions in alkaline solution, each point represents a SiO$_4$ unit, modified from (Harris and Knight, 1983).

2.2.4 Altering the molar ratio of Al:Si:Na:H$_2$O

Geopolymers contain a certain amount of Al$_2$O$_3$, SiO$_2$, Na$_2$O/K$_2$O and H$_2$O. To express this chemical composition often molar ratio is used, e.g. a molar Al:Si:Na:H$_2$O ratio of 1:2:1:8 means that in the geopolymer mixture are 1 mol Al, 2 mols Si, 1 mol Na and 8 mol of H$_2$O. The alteration of any molar ratio Al:Si, Al:Na or Al:H$_2$O has an impact on the mechanical properties.

Variation of molar Si:Al ratio

The molar alteration of the molar Si:Al ratio influences the setting time, compressive strength and porosity. In Figure 2-7 only the influence on the compressive strength is shown (Duxson et al., 2007b). It can be seen that with increasing Si the mechanical properties improve. However, with an Si:Al ratio above 1.95 the strength decreases again. This effect had been explained by suggesting that at higher Si:Al ratio the gel becomes unstable (Duxson et al., 2007b). The lower strength at lower molar Si:Al ratios is probably due to the formation of a porous structure when little or no soluble silicate is present in the activation solution (Duxson et al., 2004).
Geopolymers for immobilization and encapsulation of nuclear waste

![Graph](image)

**Figure 2-7:** Metakaolin-based geopolymers, the molar Al:Na:H₂O ratio was 1:1:5.5 and the Si:Al has been altered between 1.15 and 2.15. Samples were cured 7 days, modified from (Duxson et al., 2007b).

Increasing the amount of silicate solution increases the compressive strength but decreases the setting time of the final product (Silva et al., 2007, Duxson et al., 2007b). The reason for this is that Al tends to dissolve faster than Si, and for systems with a low molar Si:Al ratio more \([\text{Al(OH}_4]\)^\text{−}\) is available for condensation and free \([\text{Al(OH}_4]\)^\text{−}\) can been measured (Weng and Sagoe-Crentsil, 2007). This suggests that during the dissolution process, not enough \([\text{SiO(OH}_3]\)^\text{−}\) and \([\text{SiO}_2(\text{OH})_2]\)^\text{2−}\) were present for the condensation reaction to occur and therefore a weak network is formed (Weng and Sagoe-Crentsil, 2007). With a decrease in Al:Si ratio no free \([\text{Al(OH}_4]\)^\text{−}\) can be detected which means that aluminate reacts immediately with silicate species, and because of the high amount of silicate, the aluminate will be saturated with four silicate molecules (Sagoe-Crentsil and Weng, 2007). The following condensation reaction can only occur between the silicate species located on the surface of the aluminate, which has been reported is relatively slow (Silva et al., 2007, Weng and Sagoe-Crentsil, 2007).

In addition, a geopolymer with a molar ratio of Al:Si>1 cannot be produced according to the Loewenstein avoidance principle (Loewenstein and Lowenstein, 1954). This principle can be explained by comparing the formation energies of aluminate silicates and di-aluminates, shown in Table 2.1 (Catlow et al., 1996). The formation of aluminate silicates is an exothermic reaction whereas the reaction between two aluminates is an endothermic process. This shows that Al can only occupy the centre of every other tetrahedrally coordinated molecule linked by
an oxygen bridge. Therefore for a lower Si content, network with high structural integrity cannot form.

Table 2.1: Reaction energy for different condensation reaction (Catlow et al., 1996).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Energy [kcal mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(OH)₄ + [Al(OH)₄]⁺</td>
<td>→ [SiOAl(OH)₆]⁻ + H₂O</td>
</tr>
<tr>
<td>2Si(OH)₄</td>
<td>→ [SiO(OH)₆] + H₂O</td>
</tr>
<tr>
<td>2[Al(OH)₄]⁻</td>
<td>→ [Al₂(OH)₆]⁻ + OH⁻</td>
</tr>
<tr>
<td>2[Al(OH)₄]⁺</td>
<td>→ [Al₂O(OH)₆]²⁻ + H₂O</td>
</tr>
<tr>
<td>2[Si₂O(OH)₆]⁻</td>
<td>→ [Si₄O₈(OH)₈]⁻ + H₂O</td>
</tr>
<tr>
<td>[Si₂O(OH)₆]⁻ + [SiOAl(OH)₆]⁻</td>
<td>→ [SiO₂AlO₄(OH)₆]⁻ + 2H₂O</td>
</tr>
</tbody>
</table>

Variation of the molar Al:Na ratio

Variation of the Al:Na ratio influences the compressive strength of geopolymers, as shown in Figure 2-8 (Rowles and O’Conner, 2003). This effect can be explained using information related to the production of zeolites. It was proposed that hydroxide is important for the dissolution step whereas the cation (Na⁺ or K⁺) contributes to crystallisation (Murayama et al., 2002). To produce inorganic polymers the amount of OH⁻ and cation are equal because NaOH/KOH is the only alkaline material which is present during the reaction. Samples with a low concentration of NaOH/KOH do not have enough OH⁻ to dissolve metakaolin, therefore some of material remains un-reacted and the compressive strength is reduced (Wang et al., 2005, Rowles and O’Conner, 2003). With increasing NaOH/KOH concentration, the mechanical properties such as strength and apparent density increase due to the enhanced dissolution of metakaolin (Wang et al., 2005).
Figure 2-8: Compressive strength for different Si:Al and Na:Al ratios, modified from (Rowles and O’Conner, 2003).

Variation of molar H$_2$O:Al ratio

An important factor is the molar H$_2$O:Al ratio. A low H$_2$O:Al ratio is necessary to provide a material with high mechanical strength but a reduction of the H$_2$O:Al ratio increases the mix viscosity. However, a low viscosity of the mixture is important so that the paste flows around the waste and the maximum of encapsulation can be ensured. Nevertheless, the amount of water in the encapsulation matrix should be as low as possible because after the dissolution and precipitation reaction the water forms pores. Between these pores not only an exchange of water can take place but also diffusion of radioactive ions is possible which can then migrate through the whole system (Monteilhet et al., 2006, Goto and Roy, 1981, Atkinson and Nickerson, 1984).

2.2.5 pH alteration of the activation solution

To dissolve sufficient amounts of Al and Si from a mineral or waste to form a geopolymer with good mechanical properties, a high pH is necessary. The high pH guarantees that enough [Al(OH)$_4$]$^-$ and [SiO(OH)$_3$]$^-$ is available for the geopolymerisation. Previous studies have been demonstrated that the solubility of metakaolin changes with pH and with higher solubility the
mechanical properties increase, as shown in Figure 2-9 (Phair and van Deventer, 2001). It can be seen that at pH values between 6 and 10.5 the solubility of Si and Al from metakaolin is low and only starts to increase at a pH value higher 11.5. However, a pH of 12 is required to produce a material with a minimum of compressive strength but with further increase of the pH the mechanical properties increase (Phair and van Deventer, 2001).

![Figure 2-9: Solubility and development of compressive of metakaolin as a function of pH, modified from (Phair & van Deventer, 2001).](image)

### 2.2.6 Variation of the curing temperature

Next to the molar ratio and pH value of the activation solution, the curing temperature and curing time influence the mechanical properties of metakaolin based geopolymers. It has been reported that higher temperature increases the speed of reaction and the geopolymer matrix sets within 4 hours. However, when curing temperatures are between 40 and 60 °C a decrease of the compressive strength has been observed, as shown in Figure 2-10 (Rovnaník, 2010). This effect is due to incomplete reactions and gel contraction (Cioffi et al., 2003, Rovnaník, 2010). The higher temperatures favour the dissolution of Al and Si which increases the reaction rate but results in incomplete dissolution of metakaolin. Furthermore, with prolonged curing time, the higher temperature causes dehydration and shrinkage of the gel (van Jaarsveld et al., 2002). By decreasing the curing temperature below 20 °C, a delay of the setting up to 4 days has been
observed. Of interest is that the setting of the mixture is delayed but the lower curing temperature had no effect on the mechanical properties (Rovnaník, 2010).

![Figure 2-10](image_url)

**Figure 2-10:** Development of compressive strength of metakaolin-based geopolymers cured at different temperatures over time. Initial curing at 40 and 60 °C was carried out for 4 hours, modified from (Rovnaník, 2010).

### 2.3 Summary

In this chapter geopolymers have been introduced as a potential encapsulation matrix. The influence of solid precursor, the molar ratio of Al:Si:Na/K:H₂O as well as the importance of the cation have been explained. It was shown that good mechanical properties can be achieved when geopolymers with a molar Si:Al ratio of ~2 are used. In addition, the differences of pulverised fly ash and metakaolin have been discussed. It was concluded that metakaolin has a better chemical consistency and should therefore be used as solid precursor.
CHAPTER 3 AIMS, OBJECTIVES AND EXPERIMENTAL APPROACH
CHAPTER 3 AIMS, OBJECTIVES AND EXPERIMENTAL APPROACH

3.1 Introduction
The previous chapters have provided a review of nuclear waste, especially Al contaminated Magnox swarf and Cs/Sr contaminated clinoptilolite and introduced geopolymers as a potential encapsulation matrix for both waste streams. Several areas have been identified regarding the optimisation of the geopolymer mix and investigating the interactions of geopolymers and waste.

The purpose of this chapter is to define the aims and objectives of the research presented in this thesis in some detail and to outline the experimental approach adopted to achieve these objectives.

3.2 Research aim and objectives
The research carried out has addressed one principle question:

- Can geopolymers be used to encapsulate Al containing Magnox swarf and Cs/Sr contaminated clinoptilolite as an alternative to PC/BFS mixtures?

Specific objectives of the research were:

- characterise the influence of different metakaolins on the mechanical properties of geopolymers;
- investigate drying shrinkage effects in metakaolin based geopolymers;
- assess the physical properties and shrinkage of geopolymer mortars;
- examine whether Magnox swarf and Al can be immobilised in a geopolymer matrix;
- study the interactions of geopolymers and clinoptilolite;
- evaluate the bonding of Cs and Sr in a geopolymer structure;

Each of these aspects contributes to existing knowledge or represents completely novel contributions to the literature.
3.3 Experimental approach

Figure 3-1 illustrates a schematic diagram of the experimental approach which has been adopted in order to achieve the research aim and objectives. The study was divided into the following six parts:

**Influence of different metakaolin precursor**

The nuclear industry requires a precursor material with consistent chemical composition. This means, the chemical composition should not change over a long time. Kaolinite is a relative pure mineral containing mainly Al$_2$O$_3$ and SiO$_2$ with only traces of other oxides. However, there are several sources for kaolinite and metakaolin and the molar ratio of Al:Si varies between sources. A change of the Al:Si ratio requires a variation of the activation solution containing different amounts of Na$_2$SiO$_3$ and NaOH which could influences the mechanical properties. A further problem is the production of metakaolin. Currently, there are no standards for producing metakaolin from kaolinite and therefore the amount of reactive Al can differ.

In order to investigate the influence of different metakaolins and reactive Al(V) in the precursor, three different metakaolins were used to prepare geopolymers and the mechanical properties determined.

**Shrinkage of metakaolin-based geopolymers**

During the above experiments it was observed that metakaolin-based geopolymers had a tendency to crack during storage at room temperature. This cracking is an issue when geopolymers are used for nuclear waste encapsulation and has to be understood. Therefore an extensive study has been performed on this behaviour to identify the cause of the shrinkage in metakaolin based geopolymers.

**Influence of inert and active fillers on the mechanical properties**

Shrinkage cannot be avoided in geopolymers but can be controlled by the relative humidity. However, the final geological formation to store nuclear waste is unknown and currently there are no regulations for the encapsulation matrix. This means the shrinkage of geopolymers can be an issue. A possible way to reduce the shrinkage and the resulting cracking can be to add fillers to the mixture. There are two different filler types which can be used, inert and active, and this chapter will discuss the influence of both filler types on the mechanical properties.
Encapsulation of Al metal and Magnox swarf
The interactions of Magnox swarf and Al-metal with geopolymers are investigated. Both waste streams were mixed separately with the encapsulation matrix and surface reactions studied.

Encapsulation of Cs/Sr contaminated clinoptilolite
Another problematic waste stream is Cs/Sr contaminated clinoptilolite. In this part of the research contaminated clinoptilolite was mixed with metakaolin and silicate solution and the interactions between zeolite and formed geopolymers studied. Researchers suggested a different chemical behaviour of Cs and Sr in geopolymers and therefore each ion was studied individually:

- Interactions of clinoptilolite in geopolymers
- Interactions between Cs and geopolymers
- Interactions between Sr and geopolymers
Aims, objectives and experimental approach

**Figure 3-1:** Layout of experimental approach, MK=metakaolin.
CHAPTER 4  EXPERIMENTAL METHODS AND ANALYTICAL TECHNIQUES
CHAPTER 4  EXPERIMENTAL METHODS AND ANALYTICAL TECHNIQUES

4.1 Materials

To determine whether geopolymers can be used as a nuclear waste encapsulation matrix, three different metakaolins have been studied. The chemical composition and mean particle sizes of each is presented in Table 4.1. MetaStar 501 and Agrical 1200 were from Imerys (UK) and MetaMax from BASF (Germany). It can be seen that the chemical composition of all metakaolin is fairly similar according to XRF.

Table 4.1: Chemical composition (wt%) and mean particle size from used metakaolins according to XRF.

<table>
<thead>
<tr>
<th>Metakaolin</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Other oxides</th>
<th>LOI</th>
<th>Mean particle size [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetaStar 501</td>
<td>56.0</td>
<td>38.1</td>
<td>3.3</td>
<td>0.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Agrical 1200</td>
<td>55.0</td>
<td>39.0</td>
<td>4.9</td>
<td>1.0</td>
<td>6.5</td>
</tr>
<tr>
<td>MetaMax</td>
<td>53.0</td>
<td>43.8</td>
<td>3.1</td>
<td>1.0</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Although the chemical composition is similar, the crystalline phases vary between each metakaolin, as shown in Figure 4-1. While all metakaolins show the characteristic amorphous hump between 18 and 35 2θ degree, Agrical 1200 contains a high content of crystalline quartz compared to MetaMax and MetaStar 501.

Figure 4-1: Crystalline phases of used metakaolins, a=quartz (SiO$_2$).
To prepare sodium and potassium based geopolymers, metakaolin had to be mixed with an activation solution. This solution was prepared using the chemicals reported in Table 4.2.

**Table 4.2**: Silicate solutions (in wt%) and alkali hydroxides.

<table>
<thead>
<tr>
<th>Name</th>
<th>Brand name/grade</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>potassium hydroxide</td>
<td>KOH general purpose grade</td>
<td>Fisher Scientific, (NH*, USA)</td>
</tr>
<tr>
<td>potassium silicate</td>
<td>K$_2$SiO$_3$ 26.9% SiO$_2$/13.2 K$_2$O/59.9% H$_2$O</td>
<td>PQ Corporation</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>NaOH general purpose grade</td>
<td>VWR (Pennsylvania, USA)</td>
</tr>
<tr>
<td>sodium silicate</td>
<td>Na$_2$SiO$_3$ 26.0% SiO$_2$/8.0%Na$_2$O/66.0% H$_2$O</td>
<td>VWR (Pennsylvania, USA)</td>
</tr>
</tbody>
</table>

* = New Hampshire

To improve the mechanical properties of geopolymers different fillers were used, as presented in Table 4.3.

**Table 4.3**: Fillers used to improve mechanical properties.

<table>
<thead>
<tr>
<th>Name</th>
<th>Brand name/grade</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcium hydroxide</td>
<td>Ca(OH)$_2$ general purpose grade</td>
<td>Fisher Scientific (New Hampshire, USA)</td>
</tr>
<tr>
<td>magnesium oxide</td>
<td>MgO Baymag 40/reactive MgO</td>
<td>Baymag, Canada</td>
</tr>
<tr>
<td>Portland cement</td>
<td>PC CEM 1</td>
<td>NNL* (Hanson Cement Ltd, UK)</td>
</tr>
<tr>
<td>sand</td>
<td>Redhill 110</td>
<td>Sibelco, UK</td>
</tr>
</tbody>
</table>

* = National Nuclear Laboratory, UK (NNL)

To investigate the interaction of waste and geopolymers, geopolymers had to be mixed with the different wastes. A list of materials used can be found in Table 4.4.

**Table 4.4**: Materials used to study the waste/encapsulation interactions.

<table>
<thead>
<tr>
<th>Name</th>
<th>Brandname/grade</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminium rod</td>
<td>Al 100%</td>
<td>Goodfellow (UK)</td>
</tr>
<tr>
<td>blast furnace slag</td>
<td>BFS</td>
<td>NNL (Hanson Cement Ltd, UK)</td>
</tr>
<tr>
<td>caesium nitrate</td>
<td>CsNO$_3$ 99+%</td>
<td>Acros organics (Belgium)</td>
</tr>
<tr>
<td>caesium hydroxide clinoptilolite</td>
<td>CsOH 99.5%</td>
<td>Acros organics (Belgium)</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>HCl 37.5% Agristar</td>
<td>BDH (UK)</td>
</tr>
<tr>
<td>hydrofluoric acid</td>
<td>HF 40%</td>
<td>Fisher (New Hampshire, USA)</td>
</tr>
<tr>
<td>Magnox swarf</td>
<td></td>
<td>NNL (UK)</td>
</tr>
<tr>
<td>nitric acid</td>
<td>HNO$_3$ 69% AnalR</td>
<td>BDH (UK)</td>
</tr>
<tr>
<td>strontium nitrate</td>
<td>Sr(NO$_3$)$_2$ 99+%</td>
<td>Acros organics (Belgium)</td>
</tr>
<tr>
<td>strontium hydroxide</td>
<td>Sr(OH)$_2$*8H$_2$O general purpose grade</td>
<td>Acros organics (Belgium)</td>
</tr>
<tr>
<td>Universal buffer</td>
<td></td>
<td>BDH (UK)</td>
</tr>
</tbody>
</table>
4.2 Preparation of geopolymers

The activation solution was prepared by mixing either Na$_2$SiO$_3$ or K$_2$SiO$_3$ solution, deionised water and NaOH or KOH. This mixture was stirred for 24 hours to reach equilibrium. The activation solution was then mixed with metakaolin either by hand or using an automatic mixer (65-L0006/AM, Controls, Italy) for 3 minutes. The paste was then either cast into sealed polyethylene bags, 8 mm x 8 mm x 50 mm plastic (ABS) or 10 mm x 10 mm x 60 mm stainless steel moulds. A vibrating table was used during casting to remove air bubbles from samples which were then placed in sealed polyethylene bags and cured at ambient temperature (22 ± 3 °C). Samples in plastic/steel moulds were de-moulded after curing for 2 days, covered with cling film to avoid water evaporation and allowed to continue curing at ambient temperature (22 ± 3 °C).

To express the chemical composition of geopolymers, the molar formulation of Al, Si, cation and water is given. For example Al:Si:Na:H$_2$O = 1:2:1:8 means that the geopolymer sample contains 1 mol Al, 2 mols Si, 1 mol Na and 8 mol H$_2$O. However, by using molar ratio it is difficult to determine the water to solid ratio of each mixture. Therefore in Table 4.5 example mixtures for each metakaolin with a molar Al:Si:Na/K:H$_2$O ratio of 1:2:1:8 based on the XRF results from Table 4.1 but expressed in mass.

| Table 4.5: Geopolymer mixtures with a molar ratio Al:Si:Na/K:H$_2$O ratio of 1:2:1:8 expressed in mass. |
|-------|-------|-------|-------|-------|-------|-------|-------|
| metakaolin | metakaolin | Na$_2$SiO$_3$ solution [g] | NaOH [g] | H$_2$O [g] | K$_2$SiO$_3$ solution [g] | KOH [g] | H$_2$O [g] |
| MetaStar 501 | 10 | 12.9 | 1.7 | 3.3 | | | |
| Agrical M1200 | 10 | 14.2 | 1.6 | 1.3 | | | |
| MetaMax | 10 | 18.2 | 1.6 | 0 | | | |
| MetaStar 501 | 10 | | | | 12.6 | 2.2 | 2.9 |
| Agrical M1200 | 10 | | | | 13.7 | 2.1 | 2.5 |
| MetaMax | 10 | | | | 18.7 | 1.9 | 0.9 |

4.3 Particle size

In previous studies it has been reported that the particle size of metakaolin can have an influence on the mechanical properties. It has been shown that an increase of the surface area from 16 to 26 m$^2$g$^{-1}$ increases the compressive strength by approximately 34% (Weng et al., 2005). This means, before mechanical strength data of geopolymers produced by different metakaolins can be compared, the surface area of metakaolin has to be determined. However, the surface area of a non porous material is in direct relationship with the particle size.
Therefore, the particle size can be used as indirect measurement of the surface area. Particle size was measured by laser diffraction and is based on the principle that larger particles scatter light at lower angles compared to smaller ones. In this study a Beckman Coulter LS100 (California, USA) was used which covers a range from 0.4 to 900 µm. Results were analysed using the Fraunhofer model. Dry samples were added directly to the water medium, the suspension was sonicated for 60 seconds and measured.

4.4 Mechanical tests

Mechanical strength describes the ability of a material to withstand an applied stress without failure. The applied stress can be either tensile, compressive, or shear. Although mechanical properties are not key parameters because after encapsulation the waste is stored in drums and later underground, with those data an easy comparison between each mixture is possible. Furthermore, due to the simplicity of these measurements, a large amount of different samples can be produced and compared. In this study the compressive and flexural strength as well as hardness were measured.

4.4.1 Compressive strength

Compressive strength is measured by applying a force to opposite sides of a sample and measuring the force at which the specimen fails. The two sides where the force is applied must be parallel in order to obtain accurate data. In this study compressive strength was determined using cubic samples with an edge length of either 8 mm or 10 mm using a Zwick/Roell Z010 (Germany) machine with a 10 KN load cell. The crosshead speed was set to 0.2 mm/min and the edges of the samples were polished beforehand using sand paper.

Compressive strength ($\sigma$) was then calculated using the following equation (4-1):

$$\sigma = \frac{F}{A} \quad 4-1$$

with $F$ the maximum applied load and $A$ the cross-sectional area.

4.4.2 Flexural strength

The flexural strength was determined via a three point bending test. During this test the specimen is placed on two points and a force is applied to the middle of the bar.
A Zwick/Roell Z2.5 (Germany) machine was used with a 2 KN load cell. The crosshead speed was set up to 0.5 mm/min and the support span had a length of 40 mm. The dimensions of the rectangular samples were 60 mm x 10 mm x 10 mm. Before measuring the flexural strength the edges of each sample were polished. The flexural strength ($\sigma_f$) was calculated using Equation 4-2.

$$\sigma_f = \frac{3Fl}{2bd^2}$$  \hspace{1cm} 4-2

where $F$ is the maximum force measured, $l$ is the distance between the support points, $b$ the width and $d$ the thickness of test beam.

### 4.4.3 Hardness

Hardness expresses the resistance of a solid material to penetration. A Zwick/Roell Indentec ZHV (Germany) instrument was used to measure Vickers hardness (HV) of geopolymers.

HV is measured using a diamond pyramid indenter with a point angle of 136º. The indenter is placed on the sample surface orthogonally. A load ($F$) is then gradually applied for a set of amount of time. A negative copy of the pyramid indenter can be seen, as presented in Figure 4-2 (Glinicki and Zielinski, 2004). HV is the quotient of the test force divided by surface area of the indentation.

$$HV = \frac{2Fs\sin^{136}}{d^2}$$  \hspace{1cm} 4-3

where $d =$ average of the length of $d_1$ and $d_2$ in Figure 4-2.

![Figure 4-2: Schematic picture of Vicker hardness measurement, modified from (Glinicki and Zielinski, 2004).](image)
The hardness can be dependent on the applied load and the penetration time. For most materials it decreases with an increase in load, as shown in Figure 4-3 (McColin, 1990). This means that a variation of the load can be a valuable tool to provide sensitive information about the microstructure of the material (Igarashi et al., 1996). To reduce these microstructure effects a load of 1000 g was held for 10 seconds on the sample.

![Figure 4-3: Schematic curve of the “indentation size effect”, modified from (McColin, 1990).](image)

4.5 **Density and porosity**

Porosity, especially open porosity of the encapsulation matrix is a key parameter because it provides an overview of the possibility that ground water reaches the encapsulated waste after the final storage. Porosity ($P$) describes the volume fraction of empty (void) spaces ($V_v$) over total volume ($V_t$) (Equation 4-4) (DIN, 1984).

$$ P = \frac{V_v}{V_t} \quad 4-4 $$

4.5.1 **Porosity**

Different types of pores need to be considered: open pores and closed pores. All pores together give the total porosity ($P_{total}$), which relates the pore volume ($V_v$) and total volume ($V_t$). $V_v$ is the sum of the volume of the open pores ($V_{open}$) and the volume of the closed pores ($V_{closed}$) (BS, 1995). The volume $V_{solid}$ is equal to volume of the whole sample excluding all pores (Equation 4-5):
The open and closed porosity can be determined using the Archimedes principle. This is based on the principle that a porous material becomes heavier after saturation of the pores with a liquid. In addition, the buoyancy of the body changes with theoretical density when closed pores are present. The buoyancy is related to the elevated mass \((m_{\text{elevated}})\) which represents the lift of a body in a liquid.

To calculate the porosity the dry mass \((m_{\text{dry}})\), the elevated mass and the soaked mass \((m_{\text{soaked}})\) have to be determined and Equation 4-6 applied:

\[
P_{\text{open}} = \frac{V_{\text{open}}}{V_t} = \frac{m_{\text{soaked}} - m_{\text{dry}}}{\rho_{\text{fluid}} V_t}\]

The total porosity can be calculated using Equation 4-7 and by calculating \(V_{\text{total}}\) using the density of the fluid \((\rho_{\text{fluid}})\) in which the body is placed and \(m_{\text{lift}}\) and \(m_{\text{soaked}}\).

\[
P_{\text{total}} = 1 - \rho_{\text{rel}} = 1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{th}}} = 1 - \frac{m_{\text{dry}}}{V_{\text{total}}} = 1 - \frac{\rho_{\text{fluid}} m_{\text{dry}}}{\rho_{\text{th}} m_{\text{soaked}} - m_{\text{elevated}}}
\]

### 4.5.2 Theoretical density

To calculate the total porosity the theoretical density \((\rho_{\text{th}})\) has to be known. A common way to determine the theoretical density of a substance is by measuring the volume \((V_s)\) and later using the mass \((m_{\text{dry}})\) to calculate the density. \(V_s\) can be determined using a Helium gas expansion pycnometer. It consists of two chambers, one with a removable lid in which the sample is placed \((V_r)\) and a second chamber with a fixed volume \(V_c\). Both chambers are connected via a pathway. Before the measurement the second chamber is filled with gas up to a constant known pressure \(P_1\) while the other is evacuated. After the removable lid is removed from the second chamber He flows into the chamber containing the sample and the new pressure \(P_2\) in the system is measured (see Equation 4-8).

\[
V_s = V_c + \frac{V_c \rho}{1 - \rho_{\text{th}}}
\]

From \(V_s\) the theoretical density \(\rho_{\text{th}}\) can be calculated using Equation 4-9.

\[
\rho_{\text{th}} = \frac{m_{\text{dry}}}{V_s}
\]

For this research, a helium gas pycnometer, Micromeritics, AccuPyc II 1340 (Georgia, USA), was used to determine the theoretical density.
4.6 Shrinkage/expansion

To ensure that the encapsulation matrix is stable over a long time, shrinkage/expansion measurements can be used. Shrinkage/expansion describes the behaviour of a material during setting. For cements, there are four different types of shrinkage/expansion reported (Holt, 2001):

- Thermal shrinkage: occurs when concrete undergoes temperature fluctuation and is due to resulting volume changes (Kosmatka et al., 2002, Hedlund, 1996)
- Carbonation: an expansion which occurs when cement paste in the hardened concrete reacts with moisture and carbon dioxide in the air, and the cement paste (Johannesson and Utgenannt, 2001)
- Drying shrinkage: refers to the reduction in concrete volume resulting from a loss of water from the cement paste which can happen during curing or in the hard paste as a result of capillary pressure (Mindess and Young, 1981, Bazant and Raftshol, 1982, Hwang and Young, 1984)
- Autogenous shrinkage: a macroscopic volume change occurring with no moisture transfer to the exterior surrounding environment. It can be described as chemical shrinkage affiliated with the hydration of cement particles (Tazawa, 1999, Lynam, 1934).

The first type of shrinkage has not to be considered because geopolymers are cured at a constant low temperature. Expansion due to carbonation of un-reacted NaOH/KOH is possible but most unlikely. The matrix and waste are mixed and cured in metal drums. After a short time of curing, the drum is closed and a penetration of CO₂ through the lid of the drum is most likely too slow as to be regarded as an issue. This means only drying and autogenous shrinkage have to be investigated.

Drying shrinkage was determined either by measuring the change in the original length of 30 mm long cylindrical samples using a manual extensometer (Instron, UK) or dilatometry, as explained in section 4.8.2.

4.7 Micro-structural analysis

To visualise the pore structure of materials as well as to obtain information about the arrangement of atoms micro-structural analysis can be used. The micro-structure describes the microscopic properties of a material, including fine structure and microstructure but also the arrangement of atoms. For example amorphous solids usually have a structural short-range
order in the field of neighbouring atoms but no long range order whereas, crystalline solids have an ordered lattice structure of long range order.

4.7.1 Crystalline phase analysis using X-ray diffraction (XRD)

X-ray diffraction can be used to identify crystalline phases in a solid material by measuring the angles and intensities of a diffracted X-ray beam. X-rays are used because their wave length is similar to the distance between atoms. Atoms in a crystalline structure are arranged in structural units and constructive interference between crystals and x-rays is only possible for defined angles. The relationship is described by the Bragg equation (4-10):

\[ n \lambda = 2d \sin \theta \]

where: \( \lambda \) = wave length (Cu K\( \alpha \) 0.15418 nm), \( d \) = distance between the crystal planes, \( \theta \) = angle to the grate plane in which the x-ray hits the sample, \( n \) = grade of the measured maximum counted from the middle.

The XRD analysis was carried out on dry samples milled to a fineness <150μm to determine major crystalline phases in samples. XRD powder diffractions were collected on a PANalytical X-Pert Pro MPD diffractometer from Phillips (Netherlands). The crystalline phase were then analysed using the computer program HighScorePlus.

4.7.2 Scanning Electron Microscopy (SEM) and energy dispersive X-ray analysis (EDX)

Scanning electron microscopy involves moving an electron beam over the surface of the analysed object. The resulting electron interactions are used to produce an image of the surface of the object therefore the surface has to be conductive. When materials are used without a conductive surface gold or carbon coating can be used. In this work a JOEL-5610LV microscope (Massachusetts, USA) was used and samples were coated with a gold layer.

To characterize the elemental composition of small sample areas, SEM can be combined with X-ray analysis. Electrons hit the sample and remove electrons close to the core. This gap is immediately filled by an energetic electron from a higher orbital with the release of energy (X-rays) characteristic to each element. The most common method is SEM combined with energy dispersive X-ray analysis (EDX).

For this work a JEOL JSM6480LV SEM from Oxford instruments with EDX was used (Massachusetts, USA).
4.8 Heat stability

An important parameter for an encapsulation matrix is heat stability. The heat stability describes the property of a material to resist heat. This resistance includes the resistance to heat related chemical reactions such as oxidation; physical property changes for instance phase transitions and mechanical properties like expansion.

4.8.1 Thermogravimetry analysis (TGA)/Differential thermal analysis (DTA)

Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) can be used to investigate the chemical and physical properties of materials during heating. The difference between the two systems is that a DTA measures the heat flow between an empty and filled crucible whereas TGA measures mass loss of the samples. In this study measurements were carried out using an STA (simultaneous thermogravimetry analysis) 449 F1 from Netzsch (Germany). The system has a holder for two crucibles, a reference and a sample crucible, which are connected to a balance. To measure the heat exchange between them, the two crucibles are linked by two conducting plates with thermocouples. The detector and working chamber were made of Al₂O₃ and operate up to temperatures of 1600 ºC. The whole holder system is inserted into a furnace which is heated by an electrical resistance element.

4.8.2 Dilatometer

Dilatometry is a thermo analytical technique used to determine the expansion or shrinkage of a material during controlled heating. The material is placed in a sample holder and a pushrod is pushing with 20 cN against the sample to detect the length change. The sample holder and pushrod are made of Al₂O₃. The maximum operating temperature for this assembly was 1680ºC. To provide an accurate temperature reading, the thermocouple is less than 10 mm away from the sample which provides an accurate temperature reading. In this study a Netzsch 402 E dilatometer from Germany was used, and this is shown schematically in Figure 4-4 (Netzsch, 2006).
4.9 Chemical tests

4.9.1 pH measurements

To adjust the pH values of buffer solutions used in Chapter 8 and 9 and to measure the pH value of the leachate a pH meter was used. The pH was measured using a Fisherbrand Hydrus 500 pH-meter (New Hampshire, USA) with an Inlab Routine Pro electrode from Mettler Toledo (Switzerland). The pH-meter was calibrated using three pH buffer solutions, of pH 4, 7 and 10.

4.9.2 Inductively coupled plasma-optical emission spectrometer (ICP-OES)

The atomic emission spectrometry (AES), also called optical emission spectrometry (OES), is used for the quantitative and qualitative analysis of solid, liquid and gaseous samples and has been used to quantify the amount of metal and clinoptilolite which went into solution during dissolution experiments. The method is based on the fact that excited atoms emit electromagnetic radiation which is characteristic for each element and this provides information on the composition of the sample. Atoms can be excited via external energy such as a flame, spark or inductively coupled plasma (ICP).

In this study an Optima 7300 DV ICP-OES from Perkin Elmer (Massachusetts, USA) was used. For all samples and standards, 1M HCl was used as matrix.
4.9.3 Isothermal calorimeter

In cement research a common instrument to characterise the different stages of reaction is isothermal calorimeter. An isothermal calorimeter determines the amount of heat that is released or absorbed during a chemical reaction at a constant temperature. In this study an isothermal JAF Conduction Calorimeter from Wexham Developments Limited (UK) was used to investigate the hydrolysis and polycondensation reactions during geopolymerisation. The temperature was set to \(20.0 \pm 0.1\) °C.

20 g of sample were prepared and mixed for 3 minutes by hand outside of the calorimeter. To avoid the formation of agglomerates, during mixing the paste was placed on a vibration table. Afterwards the sample was loaded into the instrument and the measurement started.

4.10 Results and error calculation

The results of the measurements are calculated using the arithmetic mean \(\bar{x}\) of all measured samples. This can be calculated using Equation 4.11:

\[
\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i = \frac{1}{n} (x_1 + \ldots + x_n)
\]

with \(n = \text{number of measurements}\) and \(x = \text{result of each experiment}\).

To calculate the error, the standard deviation \(\sigma\) was used. The standard deviation shows a statistical population or a probability distribution of a set of data. It shows the variation from the arithmetic mean. A low standard deviation indicates that the measured data points were close to the mean, whereas high standard deviation shows that the data are widely spread over a large range of values. It is calculated using the following equation (4.12).

\[
\sigma = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^2} = \sqrt{\frac{x_1^2 + x_2^2 + \ldots + x_n^2}{n}}
\]

4.11 Conclusion

This chapter has described all of the experimental/laboratory techniques employed for this research project. The following chapters display and discuss the results obtained from the application of these methods to investigate the use of geopolymers to encapsulate nuclear waste.
CHAPTER 5  INFLUENCE OF DIFFERENT METAKAOLINS ON THE MECHANICAL PROPERTIES OF GEOPOLYMERS
CHAPTER 5 INFLUENCE OF DIFFERENT METAKAOLINS ON THE MECHANICAL PROPERTIES OF GEOPOLYMERS

5.1 Introduction

Before geopolymers can be used for nuclear waste encapsulation key processing variables need to be optimised. These include the influence of curing temperature, influence of molar ratios, influence of charge balancing cations, and also the influence of different types of metakaolin precursors. All of these variables have been addressed in the past but surprisingly little attention has been given to the effect of different types of metakaolin on the final mechanical properties. Although metakaolin has a reliable chemical consistency, the activation process can vary between each plant. There is no standard to produce metakaolin from kaolin and therefore the concentration of reactive material can vary between different metakaolins due to differences in the manufacturing conditions (Sanz et al., 1988, Barbosa, 1999). An important factor, which has been used in the past to describe reactive material, is the coordination number of aluminium in the precursor (Davidovits, 2008, Cordi-Geopolymere, 2003). This is done because it has been widely reported that the aluminium coordination number in metakaolin influences the final mechanical properties of the formed geopolymer (Sagoe-Crentsil and Weng, 2007). However, there is little data available discussing the importance of Al(V). Furthermore, the proposed influence of Al(V) predates the introduction of new dissolution techniques to measure the amount of reactive material in a precursor (Ruiz-Santaquiteria et al., 2011).

Another significant technique which has not been used in the geopolymers research is statistical mechanics although most of the applications for geopolymers lie in the construction industry. Due to this compressive strength tests are common and widely accepted in the characterisation of geopolymers although it is difficult to compare the results with other works (Provis et al., 2005b). This is mainly due to a wide variety of sample sizes, geometries, strength testing apparatus, and procedures used by different authors (Rowles and O’Conner, 2003, Cheng and Chiu, 2003, Duxson et al., 2007b). In addition, strength results can not only vary between different research groups, even between different authors in a single research group (Provis et al., 2005b).

In research, the most commonly used approach for comparing results between different brittle materials is Weibull statistics (Edirisinghe and Evans, 1986, Petrovic, 2003). With Weibull statistics it is not only possible to estimate the behaviour of material under an applied force but also to determine the exact probability of failure under an applied load. There has been several studies to determine the minimum number of samples that are required for statistical analyses.
It has been shown that between 20 to 30 samples is sufficient for one experiment (Khalili and Kromp, 1991). Furthermore, by using Weibull statistics and measuring fracture toughness it is possible to model the critical defect size in a material. This can be important because failure of a brittle material occurs from the largest defect in a material.

Due to the fact that Weibull statistics can be used for brittle materials, it is proposed that this model can be applied for geopolymers. Therefore, this chapter characterises the influence of different commercially available types of metakaolin on the mechanical properties using Weibull statistics. In addition, before the preparation of geopolymer samples, all metakaolins are fully characterised by using Al NMR and measuring the reactivity.

5.2 Materials and Methods

$^{27}Al\text{ NMR}$

Nuclear magnetic resonance spectroscopy (NMR) is a spectroscopic method to investigate the electronic environment of individual atoms and interactions with neighboring atoms. This allows the elucidation of the structure and dynamics of molecules and concentration determinations. Particles and atoms that possess a nuclear spin have a magnetic moment. This magnetic moment can only occupy certain orientations in an external magnetic field. Without an external magnetic field all energy states are the same. After applying an external magnetic field different energy states can be observed (Zeeman effect) and can be expressed using Equation 5-1. $\Delta E$ is proportional to the strength of the external magnetic field $B_0$, the gyromagnetic ratio $\gamma$ of the nucleus and the reduced Planck constant $\hbar=1.0546*10^{-34}\text{Js}$.

$$\Delta E = \hbar \gamma B_0 = \hbar \omega_0$$  

To determine the coordination number of Al in metakaolin an Avance 600 solid state NMR from Bruker (Germany) was used.

In this study the solid state Al NMR measurements were conducted by Rob Law from the Department of Chemistry, Imperial College London (UK).

To determine the amount of Al with a coordination number of 4, 5 and 6, the spectra were analysed using the computer program dmfit and a Gaussian model (Massiot et al., 2002).

**Crystalline phase analysis**

The crystalline phase was measured as described in section 4.7.1.
Reactivity of metakaolin

To measure the reactive Al and Si content of metakaolin, a dissolution technique has been proposed (Ruiz-Santaquiteria et al., 2011, Arjunan et al., 1997, Fernández-Jimenez et al., 2006). By dissolving reactive material in either 1% HF or 8 M NaOH, filtering and analysing the residue, the amount of reactive Al can be determined (Ruiz-Santaquiteria et al., 2011). In this study, 1 g metakaolin was mixed either with 100 ml 8 M NaOH or 100 ml 1 wt% HF, stirred for 20 hours at ambient temperature and filtered. Preliminary work has shown that 20 hours are enough to dissolve the reactive metakaolin (see appendix, Table A.1). The filter paper was washed until pH neutral using deionised water and either calcined at 1000 °C for 1 hour prior to cooling to measure the residual mass or dried at 110 °C to determine the crystalline phases, as described in section 4.7.1.

Preparation of metakaolin geopolymers

All three metakaolin geopolymers were prepared with a molar Al:Si:Na ratio of 1:2:1 based on the dissolution experiments and XRF results. This ratio has been most frequently used in previous research and therefore the most data are available (Duxson et al., 2007a, Duxson et al., 2005b, Duxson et al., 2007b). The molar H$_2$O:Al ratio was set to 8 to obtain a low mixing viscosity. Previous studies varied the molar H$_2$O:Al ratio between 5.5 and 12 (Duxson et al., 2007a, Duxson et al., 2005b, De Silva et al., 2007, Rowles and O’Conner, 2003, Fletcher et al., 2005, Poulesquen et al., 2011). In these studies using a H$_2$O:Al ratio of 5.5 the mixing viscosity was never a concern but recent nuclear waste encapsulation studies using metakaolin-based geopolymers used a molar H$_2$O:Al ratio of 7.2 (Latella et al., 2008, Perera et al., 2006, Blackford et al., 2007). Samples were denoted according to the metakaolin used, MetaStar, MetaMax and Agrical. Additionally, Agrical samples were separated into Agrical and Agrical*. The difference between them is that Agrical was prepared by calculating the Al:Si using the chemical composition as received and for Agrical* the chemical composition after measuring the reactivity, as shown in Table 5.2. Samples were mixed as explained in section 4.2 and cured for 56 days.
Setting time

Setting time was measured using a Vicatronic Automatic Single Station Vicat Needle Apparatus from Qualitest (Florida, USA) following BS EN 196-3 (Standard, 2008). Approximately 400 g of paste are placed in a circular mould (radius 50 mm, depth 40 mm) and a 300 g needle is placed vertical above the paste. Each reading is taken 30 seconds after release of the needle. The initial setting is reached when the distance between the base plate is 4±1 mm and the final setting when the needle penetrates only 0.5 mm into the paste. To avoid water evaporation from the paste, the sample is stored under water during the measurement. However, the geopolymerisation reaction occurs in water and therefore the paste is water soluble before precipitation of larger polymer units. To avoid dissolution effects with the surrounding water; oil was used instead of water.

XRF

XRF was carried out by Castle Claysoils Ltd to determine the major elements present in metakaolin after dissolution in HF or NaOH. In this study a Spectro 2000 X-Ray Fluorescence Analyser (Germany) has been used and results are expressed as % total sample weight as oxides.

Isothermal calorimetry

Isothermal calorimetry has been determined as discussed in section 4.9.4.

Mechanical test

Compressive and flexural strength have been measured as described in section 4.4.1 and 4.4.2.

Fracture toughness

Toughness describes the ability of a material to resist the propagation of cracks. The difference between strength and toughness is that strength can be highly dependent on the size of the defects in the sample whereas toughness is independent of the defect size. The fracture toughness is calculated from the stress intensity factor (K) at which a thin crack starts using Equation 5-2 (Rooke and Cartwright, 1976):

$$K_{1c} = \frac{3P \Psi}{2bW^2} \overline{a_0}$$

5-2
Influence of different metakaolins on the mechanical properties

With: \( P = \text{force}, \ L = \text{span length}, \ a_0 = \text{notch length}, \ b = \text{sample width}, \ W = \text{sample height} \) and \( \Psi \) is given by the following equation (Srawley, 1976):

\[
\Psi = \frac{1.99 - \frac{a}{w} - \frac{1}{w} + 2.15 - \frac{3.9a^2}{w^2} + 2.7 \frac{a^2}{w^3/2}}{1 + 2\frac{1}{w} - \frac{a}{w}^{3/2}} \tag{5-3}
\]

**Weibull distribution**

The mechanical strength depends on the defect size in each material and is therefore quite variable. By measuring the mechanical strength of a large array of specimens it is possible to probe the defect size distribution. The statistical behaviour of strength data can be calculated using the Weibull function (Weibull, 1951). Weibull showed that the possibility of failure \( P_f \), for a number of tests can be described using the following equation:

\[
P_f = 1 - \exp \left( - \frac{\sigma}{\sigma_0} \right)^m \tag{5-4}
\]

Where the Weibull modulus, \( m \), indicates the scatter of strength values during a test, \( \sigma_0 \) is the reference strength and \( \sigma \) the nominally applied stress (Lawn and Wilshaw, 1975). This equation contains two unknown values, \( m \) and \( \sigma_0 \) and is therefore difficult to solve. To determine \( P_f \), Lawn suggested using the mean rank (Lawn and Wilshaw, 1975). However, Bergman compared the mean rank with three other possible estimators and concluded for tests limited to 50 samples Equation 5-5 should be used (Bergman, 1984, Masson and Bourgain, 1992):

\[
P_f = \frac{i - 0.5}{N} \tag{5-5}
\]

where \( N \) represents the total number of samples and \( i \) the rate of each individual sample. By combining and rearranging Equation 5-4 and 5-5, the Weibull parameter can be calculated:

\[
\ln \left( \ln \frac{1}{1 - P_f} \right) = m \ln \sigma - m \ln \sigma_0 \tag{5-6}
\]

when plotting \( \ln \left( \ln \frac{1}{1 - P_f} \right) \) against \( \ln \sigma_0 \) a straight line should be obtained.
**Calculation of the defect size using fracture toughness**

The defect size directly influences mechanical strength results and therefore plays an important role in the characterisation the final material and can be calculated using Equation 5-7 (Clegg et al., 1990):

\[
\sigma_f = \frac{K_{le}}{0.555 \cdot \alpha \pi}
\]

with: \(\sigma_f\) = flexural strength and \(a\) = defect size

### 5.3 Results

**Characterisation of metakaolin**

The XRD pattern for all used metakaolins in this study can be seen in Figure 4-1. All metakaolins show the characteristic amorphous hump between 20 and 30° 2θ and weak crystalline signals from SiO\(_2\).

By dissolving metakaolin in HF or NaOH, it was proposed that the reactive content can be measured. The remaining un-dissolved residue is shown in Table 5.1. It can be seen that all three metakaolin samples possessed high proportions of reactive material, although Agrical metakaolin clearly contained the lowest reactive content (78.3 wt%). In addition, after dissolving metakaolin in HF all samples have a lower mass compared to dissolution experiments in NaOH. The XRD analysis of the un-dissolved residue showed that during the dissolution process the whole amorphous phase dissolves and the remaining residue was purely crystalline, as shown in Figure 5-1. In Figure 5-1 only the XRD results after dissolving Agrical in HF are shown but a similar spectrum was measured after dissolution in 8M NaOH. It can be seen that after dissolution of the reactive material the amorphous hump completely disappears and only crystalline SiO\(_2\) and kaolinite remains.

| Table 5.1: Un-dissolved residue after 20 hours dissolution in wt%. Results are the average of three measurements. |
|-----------------|-----------------|-----------------|
|                 | MetaStar | Agrical | MetaMax |
| HF (1wt%)       | 2.5      | 14.7    | 3.8     |
| NaOH (8M)       | 5.1      | 21.7    | 6.4     |
The XRF analysis of the Agrical residue is shown in Table 5.2. It can be seen that after dissolving metakaolin in HF less SiO$_2$ can be measured in the residue. This indicates that during the dissolution in HF not only reactive metakaolin dissolves but also quartz. This would also explain the slightly higher masses in Table 5.1. This means that to measure the reactive amount of metakaolin, a solution of 8M NaOH should be used. Based on the dissolution results using 8M NaOH the reactive amount of metakaolin in Agrical was calculated, as shown in Table 5.2.

The different Al coordination numbers were measured using $^{27}$Al-NMR and the results are depicted in Figure 5-2. From these results the different Al coordination numbers were calculated using dmfit. The red line shows the total fit after the calculation. The results after the calculation can be found in Table 5-3. It can be seen that the amount of Al with a coordination number of five is varying between ~40 to 85 %. It can be seen that for all metakaolins the intensity of Al coordinated 4, 5 or 6 varies between each sample. Furthermore, the metakaolin Agrical shows two signals for Al(VI). The second peak indicates a crystalline phase of Al in metakaolin. This signal is most likely from kaolinite which has been measured in the crystalline phase.
Table 5.2: XRF analysis of Agrical before and after dissolution in wt%.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O+K₂O</th>
<th>CaO+MgO</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agrical</td>
<td>55</td>
<td>39</td>
<td>1</td>
<td>0.6</td>
<td>1.5</td>
<td>1.8</td>
<td>1</td>
</tr>
<tr>
<td>residue Agrical</td>
<td>60.3</td>
<td>20.2</td>
<td>4.5</td>
<td>0.2</td>
<td>7.9</td>
<td>1.6</td>
<td>2.9</td>
</tr>
<tr>
<td>residue Agrical</td>
<td>55.7</td>
<td>19.5</td>
<td>3.6</td>
<td>0.4</td>
<td>8.5</td>
<td>1.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Agrical* (reactive based on NaOH results)</td>
<td>42</td>
<td>35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.2: $^{27}$Al NMR results for each metakaolin.

Table 5.3: Content of different Al coordination using $^{27}$Al-NMR in wt%.

<table>
<thead>
<tr>
<th></th>
<th>Al(IV)</th>
<th>Al(V)</th>
<th>Al(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetaStar</td>
<td>20.1</td>
<td>43.7</td>
<td>36.2</td>
</tr>
<tr>
<td>Agrical</td>
<td>17.4</td>
<td>70.4</td>
<td>1.9</td>
</tr>
<tr>
<td>MetaMax</td>
<td>10.8</td>
<td>86.0</td>
<td>3.2</td>
</tr>
</tbody>
</table>
By taking into account Table 5.1 the Al:Si ratio for Agrical samples was not 1:2 because approximately 20 wt% remained undissolved. Using the XRF results from Table 5.2 the true Al:Si:Na:H₂O ratio would be 1:1.9:1.2:8.9. Therefore new samples were prepared, donated Agrical* with a molar Al:Si:Na:H₂O ratio of 1:2:1:8 based on the XRF results and dissolution experiments.

**Setting time and calorimetry data**

The initial and final setting times for all geopolymer mixtures are shown in Figure 5-3. To compare the setting times of different mixtures it has to be assumed that the viscosity in all mixtures is similar. This can be done because the water to solid (w/s) ratio for all geopolymers is similar with around 0.70 for MetaStar, MetaMax and Agrical. Agrical* has a w/s of 0.62 because it contains approximately 20 % of un-reactive filler. The w/s ratio was calculated as explained in section 7.1.1.

The fastest setting metakaolin source was Agrical and Agrical*, both sets within ~900 minutes. The difference in setting time between different Agrical mixtures is probably due to the difference in initial viscosity. Agrical has a lower viscosity and shows therefore a delayed setting. The longest setting time was around 2500 minutes for metakaolin samples using MetaMax. It has to be noted that the differences in setting time do not correlate to the measured Al(V) content.

![Figure 5-3: Setting time, measured by penetration.](image-url)
Figure 5-4a and b shows the calorimetric data collected during setting at 20 °C. The heat release is the highest for both Agrical samples followed by MetaStar and MetaMax. From the heat release results it can be assumed that samples with a higher total heat release set earlier due to a faster reaction. By comparing setting time and heat output both results correlate well. The heat release results can be separated into three main exothermic signals which have been characterised by other researchers (Buchwald et al., 2009, Yao et al., 2009, Granizo and Blanco, 1998a). At the beginning an exothermic signal (A) can be attributed to the wetting of solid surface with the activation solution (Buchwald et al., 2009, Yao et al., 2009). During this process, metakaolin is dissolved and Si-O and Al-O bonds on the surface are broken down in combination with the formation of alumina/silica-hydroxy species and oligomers, such as OSi(OH)₃⁻, Al(OH)₄⁻ and (OH)₂-Si-O-Al-(OH)₃ (Rahier et al., 2007, De Silva et al., 2007). After the exothermic signal and a characteristic minimum period of heat output, a second asymmetric exothermic signal (B) can be observed. This indicates the polymerisation step in which the oligomers form a larger network (Yao et al., 2009). On the downward slope of the second peak, a third exothermic event is represented by a shoulder (C) which has been observed by other researchers (Zhang et al., 2012). This shoulder can be seen for all samples except Agrical and indicates the stabilisation process. After that the reaction goes into a thermally steady stage process.
Influence of different metakaolins on the mechanical properties

Figure 5.4: Calorimetric results during geopolymerisation, a) maximal heat output over time, b) total heat output.
The total heat release during the reaction is shown in Figure 5-4b. Geopolymers using MetaMax, MetaStar and Agrical* as metakaolin source showed a similar total heat release after 7 days reaction of ~140 kJ/kg, suggesting that the quantity of gel formed is similar in each paste. The heat output for the sample using Agrical was ~20 kJ/kg lower due to the higher water content and different Al:Si:Na ratio. A change of the molar Al:Si:Na:H₂O ratio influences the heat output because a different geopolymer gel is formed. This would be in agreement with previous isothermal calorimetry studies in which the molar Al:H₂O and Al:Na ratios was varied (Granizo and Blanco, 1998a, Granzio et al., 2000).

**Influence of different metakaolin on mechanical properties**

Although all prepared geopolymers had the same molar Al:H₂O ratio and therefore prepared with a similar w/s ratio, it is difficult to compare the influence of different metakaolins on the mechanical properties such as compressive strength or flexural strength because these properties are highly dependent on the defects present in the sample. Previous research has suggested that defects play an important role in geopolymers but no previous work has been carried out to measure the size effect and to compare them with strength results (Latella et al., 2008). Therefore before strength values of each geopolymer can be compared, the defect size in the samples was determined. This was achieved by measuring the fracture toughness, which is a material property independent the defect size, and by calculating the defect size using the three point bending test results and Equation 5-7.

The fracture toughness results are given in Table 5.4 and the flexural strength for all geopolymers is depicted in Figure 5-5.

<table>
<thead>
<tr>
<th>geopolymer</th>
<th>K̄c [MPa/m²] average</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetaStar</td>
<td>0.22</td>
<td>0.03</td>
</tr>
<tr>
<td>MetaMax</td>
<td>0.2</td>
<td>0.01</td>
</tr>
<tr>
<td>Agrical</td>
<td>0.24</td>
<td>0.02</td>
</tr>
<tr>
<td>Agrical*</td>
<td>0.24</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Currently, there is little information in the literature about the fracture toughness in geopolymers. Latella measured $K_{IC}$ for pure geopolymers using a molar Al:Si:Na:H$_2$O ratio of 1:2:1:7.2 of 0.56±0.02 MPa/m$^2$ and De Silva measured a value of approximately 0.33 MPa/m$^2$ using a molar Al:Si:K:H$_2$O ratio of 1:3:1:6 (Latella et al., 2008, De Silva and Thaumaturgo, 2003). The latter results is fairly similar to the measured value in this study. The higher result obtained by Latella are probably due to different sample preparation. In their study, samples were cured only 2 hours at ambient temperature before placing them in a 60 °C oven for 24 hours. It is interesting to note that the data in Table 5.4 do not vary between the different precursors and that the results are similar to cement and cement pastes which have a fracture toughness of around 0.3 MPa/m$^2$ (Hillemeier and Hilsdorf, 1977, Brown and Pomeroy, 1973, Nallathambi et al., 1984).

From Figure 5-5, it can be seen that the flexural strength varies between 3 and 12 MPa and is similar for all mixtures with average strength of between 7 and 8 MPa. Slightly higher flexural strength values have been reported in previous studies but those used a much lower H$_2$O to Al ratio (Rovnaník, 2010). The similar flexural strength results already indicate that all samples
have a similar defect size which causes the failure. The calculated defect size can be seen in Figure 5-6. It is interesting that for all samples the main range of critical defects lies in a range between 0.5 and ~2 mm which shows that the defects are not on an atomic level and are due to remaining air bubbles in the system. Exemplary two defects are shown in Figure 5-7. It can be seen that the amount of remaining air bubbles in the samples are low.

**Figure 5-6:** Defect pore size in geopolymers samples.

**Figure 5-7:** Defects due to remaining air bubbles in the geopolymer samples.
Due to the fact that for all geopolymer mixtures the critical defect size is in a similar range, a comparison of the compressive strength is possible, as shown in Figure 5-8. It has to be noted that all samples have a threshold compressive strength of around 35 MPa and a median compressive strength of around 47 MPa except Agrical samples with a median strength of 41 MPa due to the higher water content, displayed in Table 5.5.

![Graph showing compressive strength data for all geopolymer mixtures.](image)

**Figure 5-8:** Compressive strength data for all geopolymers mixtures.

Based on these strength results, the Weibull number $m$ can be calculated which gives an indication of the variability of the results. The higher $m$, the more consisted the data, and conclusively less samples have to be measured to obtain reliable mean results. An example of the experimental compressive strength data and the linear regression fit for MetaStar is provided in Figure 5-9.
Influence of different metakaolins on the mechanical properties

Figure 5.9: Plot to calculate the Weibull number $m$, linear fit shown for Agrical.

The statistical summaries for all mixtures are given in Table 5.5. The Weibull numbers for compressive strength are similar to those of concrete and granite whereas for flexural strength are close to ceramics (Tumidajski et al., 2006, Kittl et al., 1990, Prewo, 1986, Nallathambi et al., 1984).

Table 5.5: Weibull numbers for compressive and flexural strength, as well as average and median strength of metakaolin based geopolymers.

<table>
<thead>
<tr>
<th>metakaolin</th>
<th>MetaMax</th>
<th>MetaStar</th>
<th>Agrical*</th>
<th>Agrical</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compressive strength [MPa]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weibull modulus ($m$)</td>
<td>13.1</td>
<td>10.5</td>
<td>12.3</td>
<td>12.2</td>
</tr>
<tr>
<td>characteristic strength ($\sigma_0$)</td>
<td>53.4</td>
<td>50.7</td>
<td>48.4</td>
<td>44.1</td>
</tr>
<tr>
<td>Average strength</td>
<td>51.4</td>
<td>47.5</td>
<td>46.5</td>
<td>42.3</td>
</tr>
<tr>
<td>STDEV</td>
<td>4.7</td>
<td>5.4</td>
<td>4.6</td>
<td>4.2</td>
</tr>
<tr>
<td>median</td>
<td>50.7</td>
<td>48.3</td>
<td>46</td>
<td>41.7</td>
</tr>
<tr>
<td><strong>Flexural strength [MPa]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weibull modulus ($m$)</td>
<td>3.7</td>
<td>4.2</td>
<td>5.4</td>
<td>5.6</td>
</tr>
<tr>
<td>characteristic strength ($\sigma_0$)</td>
<td>8.8</td>
<td>7.9</td>
<td>8.8</td>
<td>8.3</td>
</tr>
<tr>
<td>Average strength</td>
<td>8.0</td>
<td>7.3</td>
<td>8.1</td>
<td>7.6</td>
</tr>
<tr>
<td>STDEV</td>
<td>2.1</td>
<td>1.6</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>median</td>
<td>8.0</td>
<td>7.1</td>
<td>8.2</td>
<td>7.4</td>
</tr>
</tbody>
</table>
5.4 Discussion

XRD analysis of different metakaolin showed the typical amorphous hump which usually appears during the de-hydroxylation of kaolinite at temperature above 700 °C as shown in Figure 2-3. Furthermore, the dissolution experiments showed that independent of the Al coordination number, metakaolin dissolves almost completely in alkaline solution and only the crystalline phases of SiO$_2$, Al$_2$O$_3$ and other oxides remain un-dissolved. This indicates that the coordination number of Al(V) does not play an important role during dissolution and only a disordering of the amorphous structure is important.

One major piece of evidence supporting the argument that the coordination number of Al does not have a significant effect on the geopolymer reactions can be seen from the isothermal calorimetry results. In this study, all metakaolins showed the same total heat release of ~140 kJ/kg after 7 days which indicates that independent on the Al coordination number a similar chemical reaction occurs. However, the heat output and setting time seems to be influenced by the Al coordination number. A higher Al(V) coordination indicated that more Al is disordered and therefore the strains between the bonds are higher, and this suggests that those materials will react faster. This is only true for two metakaolins, Agrical and MetaStar. Agrical contains a higher amount of Al(V) compared to MetaStar, it sets faster and gave the highest heat output. From this conclusion, it would be expected that MetaMax sets fastest due to the highest Al(V) content but it has the slowest heat output and longest setting time. The fast setting for both Agrical samples is probably due to the high amount of crystalline material in the metakaolin. These un-dissolved crystals act as seeds, support the gelation process and therefore a higher heat release is observed (Bronić and Subotić, 1995, Rees et al., 2008). The difference in setting between MetaStar and MetaMax is probably due to the difference in molar Si/Al ratio in the precursor. MetaStar has got a molar SiAl ratio of 1.25 whereas MetaMax has a ratio of 1.03. Consequently, in order to obtain a Si/Al ratio of 2 in MetaMax a different sodium silicate solution with a different Si:Na ratio has to be added. Research has shown that the Si:Na ratio directly influences the pH value of the silicate solution and with increasing of the molar Si:Na the pH value decreases (PQ, 2004). This means that the pH value of the activation solution used for MetaStar samples was higher compared to the pH value of the activation solution used for MetaMax samples. This change of the pH value is most likely so significant that the dissolution rate of metakaolin is influenced and therefore the setting for MetaMax based geopolymers is delayed. Although the setting is delayed due to a reduced pH value the mechanical properties for all samples are similar. Therefore, it can be concluded that the pH value and the coordination number of Al in metakaolin are not so important.
All geopolymer mixes have a similar critical defect size and this assures that a comparison is reasonable. The flexural strength results for all samples vary between 3.5 and 13 MPa which makes it more difficult for comparison. This wide spread of the results can also be seen from the low Weibull modulus. This shows that a large amount of samples have to be measured to obtain reliable results, in contrast to compressive strength. The Weibull modulus for compressive strength is relatively high which means that even by measuring small amounts of samples relatively good results can be obtained. Furthermore, it can clearly be seen that the critical defects in the samples have a key role. Although, in this study care was taken to reduce the amount of trapped air in the sample by choosing a higher water ratio to keep the viscosity as low as possible and placing the sample for a long time on a vibration table the smallest critical defect size which has been achieved was 0.25 mm.

5.5 Conclusion

This initial study investigated the influence of Al(V) in metakaolin on the mechanical properties of sodium based geopolymers using Weibull statistics. Although, it has been widely accepted that the Al(V) content in metakaolin has an effect on the mechanical properties after activation, it has been shown that the Al(V) content had no direct relationship with any of the properties measured (strength, setting time, heat evolution and reactive content). The setting time is influenced by the molar Si:Al ratio present in the precursor and the presence of insoluble residue. The molar Si:Al content in metakaolin has a direct influence on the molar Si:Na ratio in the activation solution and therefore on the pH value of this solution. The higher the molar Si:Al ratio in metakaolin, the higher the pH value of the activation solution. Furthermore, un-dissolved material can act as seeds and increase the gelation process. In addition, it has been shown that before geopolymers are produced it is useful to determine and characterise the insoluble residue in metakaolin to control the chemical composition. This can be achieved using 8M NaOH solution because in HF solution quartz, present in metakaolin dissolves which influences the results.
CHAPTER 6  DRYING SHRINKAGE ON GEOPOLYMER SAMPLES
CHAPTER 6  DRYING SHRINKAGE ON GEOPOLYMER SAMPLES

6.1 Introduction

During the course of the work it was observed that geopolymers samples had the tendency to crack when allowed to dry during curing. Figure 6-1 shows that room temperature drying can cause extensive cracking of metakaolin based geopolymers. The left image (a) shows a 30 mm diameter metakaolin based Na-geopolymer sample immediately after de-moulding, and the right image (b) shows the same sample after drying at ambient temperature in a desiccator.

This cracking is probably due to drying shrinkage which has been observed in cementitious materials. For example, in Portland cement drying shrinkage is initiated by water removal from the micro-pore network resulting in crack propagation in the microstructure (Bell and Kriven, 2008, Perera et al., 2007b, Hwang and Young, 1984, Bazant and Raftshol, 1982). Attempts to avoid this drying shrinkage and crack propagation have focused in modifying the pore structure to minimise capillary porosity and by controlling water loss during curing (Perera et al., 2007b, Bell and Kriven, 2008).

Drying shrinkage in geopolymers at ambient temperature has been reported previously but has received little attention (Zuhua et al., 2009). Due to the high surface area and plate-like particles of metakaolin powder, a considerable excess of water is required to achieve sufficient flow for
good mixing and placement of metakaolin geopolymer pastes. In addition, unlike Portland cement, water is not incorporated directly into the final reaction products and only a small percentage of the mixing water remains as interstitial water in the geopolymer network (Perera et al., 2007b). Therefore a large excess of unbound or free water remains, which can evaporate from the hardened paste under low relative humidity conditions at ambient temperature (Duxson et al., 2007a).

Furthermore, very little attention has been given to the effect of molar geopolymer composition on ambient temperature drying shrinkage. The aim of the research presented in this chapter is to investigate the shrinkage of geopolymers during drying and in particular to evaluate the effect of metakaolin geopolymer composition on drying shrinkage and cracking at ambient temperature. Specifically the effect of the Si:Al and Na:Al ratios and the water content have been studied.

6.2 Materials and Methods

Composition studied

Metakaolin (MetaStar 501) geopolymer pastes were prepared with the molar Al:Si:Na/K:H₂O ratios shown in Table 6.1. In the first set of samples (1-4), the Al:Si:Na ratios were kept constant and the water content was varied. In the second set of samples (5-9) the Al:Si ratio was varied while the Al:Na ratio and water content was kept constant. In the third set of samples (10-13) the Al to Na ratio was varied while keeping the Al:Si ratio and water content constant. In the final set (14-17) the influence of the cation type (Na or K) was investigated. In all cases samples were prepared as described in section 4.2 and cured for 56 days before testing.
Table 6.1: Molar compositions of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>2</td>
<td>1</td>
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<td>10.5</td>
</tr>
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<td>8</td>
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<tr>
<td>6</td>
<td>1</td>
<td>1.8</td>
<td>1</td>
<td>-</td>
<td>8</td>
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<td>7</td>
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<td>12</td>
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<td>1.15</td>
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<td>1.3</td>
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<td>1</td>
<td>2.2</td>
<td>-</td>
<td>1</td>
<td>8</td>
</tr>
</tbody>
</table>

**Drying procedure**

Two different methods were used to dry the samples.

One set of samples were placed in sealed containers with constant relative humidity (RH) at 20 °C and allowed to equilibrate for 3 month. The RH was varied between 0 and ~95 % in 20 % steps. The RH in the chambers was controlled using different salt water mixtures (Weast, 1987). Water evaporation was monitored by measuring the mass at regular time intervals until equilibrium was reached when the flexural strength was measured. This was done to investigate the influence of RH on geopolymers.

A second set of samples were subjected to slow incremental drying. This involved storing the samples at ambient temperature and 45 ± 5 % RH, and then placing them in a fume cupboard for up to 2 days. When no further weight loss was recorded the samples were placed in a sealed desiccator containing silica gel. During the drying procedure the sample weight loss, shrinkage and flexural strength were measured.

**Mechanical tests**

Compressive and flexural strength have been measured as described in section 4.4.1 and 4.4.2.
**Heat stability**

TGA/DSC and dilatometry measurements have been carried out as explained in section 4.8.1 and 4.8.2.

**Shrinkage**

Shrinkage has been determined as discussed in section 4.6 and 4.8.1.

### 6.3 Results

The effect of water evaporation at different RH can be seen in Figure 6-2. Geopolymer samples lose around 22% of their mass water between 100 and 80% RH. After this step the trend continued linearly until ~30% mass loss at 0% RH. The flexural strength on the other hand did not change between 100% and 80% RH, increased between a RH of 80 and 40% RH to a maximum strength of ~13.5 MPa followed by a decrease at lower RH.

![Graph showing mass loss and flexural strength vs. relative humidity](image)

**Figure 6-2:** Comparison of pure geopolymer sample placed at different relative humidity for 3 month at 20 °C. Molar ratio of Al:Si:Na:H₂O was 1:2:1:8, average of 5 measurements were taken.

During drying it was observed that geopolymers samples start to crack from the edges first and over time the cracks grow to the middle of a specimen, as shown in Figure 6-3. This effect has
been reported for samples undergoing non-uniform drying, which leads to a moisture gradient (Bažant and Raftshol, 1982, Hwang and Young, 1984). The surface dries faster and therefore starts to shrink earlier which results in cracking.

![Series of geopolymer samples during drying](image1)

**Figure 6-3:** Series of geopolymer samples during drying. The molar Al:Si:Na:H$_2$O ratio was 1:2:1:8. In photograph c the cracks were difficult to identify therefore they were white highlighted. The sample had a diameter of 30 mm.

The effect of drying on samples (30 mm by 15 mm diameter cylinders) as a function of mix water molar ratio is depicted in Figure 6-4a and b. The data in Figure 6-4a indicate that a higher initial water content allows more water to be removed before shrinkage starts. Figure 6-4b shows the same data as in Figure 6-4a, but the water losses are normalised to calculate the effective molar ratio remaining in each sample as drying progresses. This normalisation offers a useful way of identifying the critical point at which samples undergo drying shrinkage. Changes in the effective sample molar water ratio were calculated using the following equation:

\[
New_{mwr} = Original_{mwr} \times \left( \frac{Total_{H2O} - Lost_{H2O}}{Total_{H2O}} \right)
\]

where:

- \(Original_{mwr}\) = the mixture design molar water ratio (i.e. 7.5, 8, 8.5, 9.5 or 10.5).
- \(Total_{H2O}\) = the total H$_2$O content as determined by TGA analysis expressed as % of sample mass.
- \(Lost_{H2O}\) = the sample mass loss during the drying period expressed as % of sample mass.

Due to the fact that after normalisation all data fell on the same line, it was necessary, for clarity, to offset each data series by 1 % shrinkage on the y-axis. In all samples no shrinkage occurs until the molar water to Al ratio falls below 3. To record these data an extensometer were used. The disadvantage of this instrument is that the total shrinkage could not be measured due to the formation of cracks.
Drying shrinkage on geopolymer samples

**Figure 6-4:** Effect of water evaporation via ambient temperature drying on shrinkage of different metakaolin geopolymers containing different initial molar water ratios: a) absolute water losses and b) water loss normalised to a remaining molar water ratio. Data points were averages of 3 results.
Drying shrinkage on geopolymer samples

The change in flexural strength of the geopolymer samples with decreasing molar water content is shown in Figure 6-5. A similar trend can be seen in Figure 6-4b, as a sudden change in flexural strength occurs when samples reach a molar water to Al ratio of 3. This is independent of the initial mixing water content. As observed in the other series, when the samples shrink, they initially strengthen but as drying proceeds the strength eventually decreases.

![Figure 6-5: Changes in flexural strengths upon drying of prismatic samples prepared with different molar water ratios. Data points were averages of 5 measurements. All data is for samples 8 mm x 8 mm x 40 mm in size.](image)

Representative DSC/TGA results for a geopolymer sample can be seen in Figure 6-6. The DSC signal shows an endothermic peak between 20 and 100 °C, which stabilises prior to a small exothermic hump at ~850 °C. The sample mass loss represented by the TGA data increases up to ~40% at 150 °C and then remains approximately constant.
Drying shrinkage on geopolymer samples

To compare the effect of drying on shrinkage with length changes during heating, shrinkage during heating was measured and the results are shown in Figure 6-7. The data is split into 4 sections as in Duxson et al, 2007 (Duxson et al., 2007a). A disadvantage of measuring the length change during heating is that it suggests that samples have to be heated up to ~150 °C before shrinkage occurs. This is due to the high heating rate. In this study a heating rate of 10 °C min⁻¹ was used, which does not permit the free water to evaporate completely before a temperature of 150 to 200 °C has been reached. At this point, the first two shrinkage events have already occurred: 1) shrinkage attributed to capillary pressure in the sample and 2) loss of free water (Rahier et al., 1996, Duxson et al., 2007a). However, the advantage of dilatometry is that the total drying shrinkage can be detected which is difficult using an extensometer because the extent of cracks in the samples were too high to measure shrinkage above 3 %, as shown in Figure 6-4b.

At temperatures around 800 °C geopolymers start to densify. This densification provokes a significantly higher degree of shrinkage in the sample with an initial water content of 10.5 mol compared to an initial water content of 8.5 mol due to the higher porosity.
Figure 6-7: Dilatometric analysis up to 1000°C (10°C/min, He gas) of metakaolin pastes containing different mixing water molar ratios.

The influence of the Si:Al ratio on the critical amount of water that can be removed before initial shrinkage is demonstrated in Figure 6-8. In contrast to the effect of the initial water content, altering the Si:Al ratio influences how much water can be removed without shrinkage and how much water is part of the geopolymer structure.
Drying shrinkage on geopolymer samples

Applying arbitrary distinctions of “free water”, “interstitial water” and “hydroxyl water” as water lost at <150 °C, 150 – 300 °C and 300 – 600 °C respectively (Duxson et al., 2007a), it is possible to see some clear differences in the response of samples with different Si:Al ratios, as shown in Figure 6-9. The data shows that samples with a lower Si:Al ratio are more resistant to shrinkage following the loss of “free water”. This is in agreement with the results shown in Figure 6-8. However, this did not translate to improved resistance to thermal shrinkage following the loss of “interstitial and some hydroxyl water”, where the opposite effect of Si:Al ratio was noted.

Figure 6-8: Effect of molar Si to Al ratio on maximum water loss before onset of drying shrinkage in an Al:Si:Na:H₂O system of 1:x:1:8 composition. Samples were cured for 56 days in sealed bags before being subject to a sequential drying procedure. Data points are averages of 3 measurements.
Drying shrinkage on geopolymer samples

Figure 6-9: Dilatometer results of geopolymers heated up to 360 °C where the Si:Al ratio was altered. Measured after 56 days curing.

Figure 6-10: Effect of molar Na to Al ratio on maximum water loss before onset of drying shrinkage in an Al:Si:Na:H₂O system of 1:2:x:8 composition. Samples were cured for 56 days in sealed bags before being subject to a sequential drying procedure. Data points are averages of 3 measurements.
Figure 6-10 shows that the amount of water incorporated in the geopolymer structure increases as the Na to Al ratio increases. Replacing Na with K as the charge balancing cation leads to a lower water content before the onset of drying shrinkage, as shown in Figure 6-11.

![Graph showing calculated molar water content remaining in sample at onset of drying shrinkage versus ratio Si:Al (mol)](image)

**Figure 6-11**: Effect of Na versus K on sensitivity to drying shrinkage of samples cured for 56 days in sealed plastic bags in an Al:Si:Na/K:H₂O system of composition 1:2:x:8. Data points are averages of 3 measurements.

In agreement to the higher water loss before shrinkage starts when Na is replaced with K, dilatometry results also show that the degree of shrinkage following the loss of “free water”, “interstitial water” and “hydroxyl water” is reduced as shown in Figure 6-12. Densification began at higher temperatures with K based geopolymers and caused a larger shrinkage, indicating that K samples had a more porous microstructure. This final observation is in contrast to that reported by Duxson et al. (Duxson et al., 2007c), although the fact that their samples were cured at 40 °C for 20 hours whereas these were cured at ambient temperature may be important.
Drying shrinkage on geopolymer samples

![Figure 6-12: Dilatometer results of geopolymers with an Si:Al ratio of 1.8:1 using Na⁺ and K⁺ ions to balance the negative aluminate charge. Measured after 56 days curing.](image)

6.4 Discussion

Figure 6-2 shows that the geopolymer samples already lose ~50 % of “free water” at a RH of 80 % without influencing the flexural strength. Between 80 and 60 % RH geopolymers lose only a minor additional amount of water but the flexural strength increases from 8 to 12 MPa. This indicates that between 80 and 60 % RH a critical amount of water has been removed and samples possible start to shrink. This drying shrinkage is independent of the initial molar water ratio as shown in Figure 6-4 and 6-5. The only difference between the initial water content and drying shrinkage is that for samples containing higher water content, more water can be removed before shrinkage starts. However, all samples showed shrinkage when the molar H₂O:Al ratio was around 3. This suggests that the drying shrinkage mechanism is relatively independent of total sample porosity and geopolymer gel density, since the initial molar water ratio significantly affects these properties. It also suggests that a fixed amount, tentatively be termed “structural” water, is present in all samples and it is the loss of this water which brings about the onset of shrinkage. The precise quantity of this “structural” water required is more likely to be a function of gel structure, which in turn is affected directly by the Si:Al and Na:Al molar ratios. The water lost before drying shrinkage occurs is arbitrarily referred to as “free water”. Since this water is
Drying shrinkage on geopolymer samples

not chemically bound, it can simply be removed from the open macro-pore network without creating any noticeable strain in the micro-pore network. However, removing more than the free water induces shrinkage. Furthermore, the data in Figure 6-5 shows a strong correlation between drying shrinkage and change in mechanical properties. The point at which the drying shrinkage occurs correlates to a sudden change in the mechanical properties.

It is noted that the increase of flexural strength was only observed using small samples (8 x 8 x 50 mm³). Flexural strength using larger specimens (25 x 25 x 80 mm³ – see appendix, Figure A-1) did not show an increase of the flexural strength. This indicates that there is an additional size effect, allowing for a uniform, crack-free, shrinkage in small samples but not in larger ones. However, the flexural strength tests at different RH show that when the sample moisture content falls below a characteristic minimum, drying shrinkage occurs.

During drying, “free water” leaves the structure without generating significant capillary pressure in the micro-pore network and this does not cause a change in dimensions. This free water is most likely to be present in larger pores which empty first. However, the capillary tension is smaller for larger pores and therefore no stress cracking occurs (Scherer, 1990). At the onset of drying shrinkage the flexural strength increases but as shrinkage continues, the flexural strength decreases. It is suggested that the decrease in strength is caused by the onset of sample cracking.

The results from Figure 6-4 and 6-5 show that first all “free water” evaporates before shrinkage occurs. After that, tensile stress is built up in the structure and cracks growing into the sample can be observed.

The length change of metakaolin-based geopolymers during heating occurs in different stages as shown in Figure 6-8 and this has been already explained (Duxson et al., 2007a). Stage A ranges from ambient temperature up to around 150 °C when negligible shrinkage occurs. This appears contradictory to the significant shrinkage noted at ambient temperature, but can be explained by the fact that the time in stage A in the dilatometer was limited to about 30 minutes compared to the sample drying process at ambient temperature which lasted several days. It is proposed that the onset of shrinkage observed at around 150 °C corresponds to the same mass loss as the onset of shrinkage in the ambient temperature drying process after 2 days. However, it was not possible to measure sample mass loss in the dilatometer. In moist samples up to 100 °C, the sample will remain cooler than the surrounding atmosphere as water evaporation consumes radiant heat on the sample surface. Although water is continually being lost from the samples during stage A, sufficient structural water remains to prevent significant gel contraction. By
Drying shrinkage on geopolymer samples

comparing the mass loss using TGA it can be shown that most of the mass in geopolymers is lost at ~ 150 °C which corresponds to “free water”.

In stage B, between 150 and 300 °C, all samples show shrinkage of around 5 % due to a loss of critical water. The sample with the higher mixing water ratio begins to shrink earlier, probably because these are more porous and consequently the gel structure less dense, allowing critical water to evaporate more easily.

In stage C, between 300 and 750 °C, samples are relatively stable, showing only slight shrinkage. At this point the samples are completely dry and although the samples would be significantly cracked, no further shrinkage occurs due to water loss. The slight increases in shrinkage noted has been attributed to loss of hydroxyl groups (Duxson et al., 2007a). Above 750 °C samples show rapid and massive shrinkage due to the onset of densification. This was confirmed by porosity and strength measurements (Kuenzel et al., 2012). The degree of shrinkage at this stage is significantly greater in specimens with higher mixing water. These samples had increased total porosity and shrink more during densification.

Figure 6-9 shows that as the Si:Al ratio increases the onset of shrinkage corresponds to a reduced water loss. More specifically, the critical minimum water content, or “structural” water, necessary to prevent drying shrinkage, increases linearly with increasing Si content. This suggests that more water is incorporated into the geopolymer structure as the Si to Al ratio increases. Previous work has shown that increasing the Si to Al ratio yields a micro-structure with fewer macro pores and more micro-pores (Duxson et al., 2005b). The formation of the different microstructure and the difference of onset shrinkage can be explained by comparing the formation of geopolymers at different Si:Al ratios. $^{27}$Al-NMR showed that when the molar Si:Al ratio is lower than 1.4 not all dissolved aluminate is incorporated into the geopolymers structure. At molar Si:Al ratios higher than 1.65 no unincorporated aluminate was found (Duxson et al., 2005a). To ensure that poor AlO$_4^-$ incorporation into the gel would not be a major issue, the Si:Al ratio was only varied between 1.6 and 2.4 in this study.

The results indicate that the Al content is likely to affect the geopolymer structure. Using a lower Si:Al content can indicate that on an atomic level a denser structure is formed and that less space for “structural” water is available, as a result of increased Na density, as illustrated in Figure 6-13. This means that more “free” water is available to form larger pores which would be in agreement with results obtained by other researchers (Duxson et al., 2005b). This interpretation would imply that the spheres of hydration of Na$^+$ cations could be a significant part of the “structural” water considered here. Other work has shown that increasing the Si:Al ratio from
Drying shrinkage on geopolymer samples

1.15 to 2.15 caused $^2$H NMR spectra to broaden progressively, possibly indicating that the contents of “structural” water increase with increasing Si:Al ratio (Duxson et al., 2005a). This would support the observations noted in this study.

![Figure 6-13: Schematic structure of geopolymers with a molar Al:Si ratio lower 1:2 (left) and a molar Al:Si ratio higher than 1:2 (right).](image)

By changing the Na:Al ratio a linear increase in the remaining critical water in the geopolymers sample can be observed (Figure 6-10). The original role of Na$^+$ ions is to facilitate a highly alkaline medium in which the metakoalin can dissolve. It is widely accepted that these ions act as charge balancing cations on negatively charged tetrahedral AlO$_4^-$ groups formed in the cementitious gel. These ions are not considered to be chemically bound but can be leached and potentially replaced by other ions (Aly et al., 2008).

Stoichiometrically and experimentally, a Na:Al molar ratio of 1 is generally considered to be ideal. An excess of Na, when added as NaOH, as was the case in these experiments to maintain a constant Si:Al ratio, would increase the alkalinity of the paste, which is important for the initial dissolution stage. However, with Na:Al ratios >1, theoretically there is little obvious benefit in the presence of excess Na$^+$ ions in hardened pastes from a chemical point of view.

The excess Na$^+$ ions clearly have a negative effect on the resistance to ambient temperature drying shrinkage as shown in Figure 6-9. Perhaps unexpectedly, there is no optimum resistance to drying shrinkage around Na:Al ratio of 1. Instead, a directly proportional relationship exists between the Na:Al ratio and the minimum molar water ratio permitted in pastes to avoid drying.
shrinkage over the range of 0.7-1.3 studied. From the slope of the trendline in Figure 6-10 an increase in Na:Al molar ratio of 1 would increase the “structural” water content by 6.0 moles, perhaps being linked with the typical sphere of hydration of hydrated Na\textsuperscript{+} cations which contains 6 molecules of H\textsubscript{2}O per Na\textsuperscript{+} ion (Waizumi et al., 1993).

The fact that this relationship is linear, despite the myriad of differences to samples that could be caused by more or less alkaline mix compositions, suggests that the total Na content is a highly significant factor in determining the important “structural” water content. Following this argument, again the data implies that a significant fraction of this calculated “structural” water could be due to spheres of hydration for alkali cations to maintain low ionic charge densities in the pore network solutions.

It is suggested that this occurs because equilibrium is established between Na\textsuperscript{+} ions in the aqueous phase in the large pores, and Na\textsuperscript{+} ions incorporated in the geopolymer structure. When the Na\textsuperscript{+} sphere of hydration is lost, the distribution of electrostatic charges in the structure becomes unstable as Na\textsuperscript{+} ions compete for the reduced water remaining in the structure. This creates pressure that leads to contraction of the gel structure.

Taking into account the hydration sphere of cations would also explain the reduced drying shrinkage of K-based metakaolin geopolymers, shown in Figure 6-11. Water is more easily removed from hydration spheres of K\textsuperscript{+} compared to Na\textsuperscript{+} and this might lead to less structural water, as shown in Table 6.2 (Migliore et al., 1988, MacPhee and Garcia-Lodeiro, 2011).

| Table 6.2: Comparison between Na and K (Migliore et al., 1988). |
|-----------------|-------|-------|
|                | Na\textsuperscript{+} | K\textsuperscript{+} |
| Radius, Å       | 0.97  | 1.33  |
| charge density [Z/r] | 1     | 0.75  |
| Hydration Energy [kcal mol\textsuperscript{-1}] | \(~95\) | \(~75\) |

Dilatometry measurements show that the maximum shrinkage due to water loss is smaller for K based geopolymers but the densification shrinkage is higher. This shows that the hydration sphere of K\textsuperscript{+} is smaller and therefore shrinkage due to water loss is reduced. This means less meso- and micro-pores collapse when water is removed. Furthermore, more water is placed in pores and therefore during densification the shrinkage is increased.
6.5 Conclusion

The effect of drying metakaolin-based geopolymers at ambient temperatures on shrinkage and strength has been investigated. It was found that drying shrinkage occurs between 60 and 80 % RH. The first water ("free water") to be lost during drying causes no shrinkage and no change in strength. Shrinkage and cracking only occur when a critical water loss is reached during drying ("structural water"). This critical amount of water should not be removed if shrinkage is to be avoided. It is suggested that structural water is present within the colloidal/polymeric geopolymer network as spheres of hydration surrounding the charge balancing cations (Na$^+$ or K$^+$). Consistent with this suggestion is that the amount of water incorporated within the nanostructure of the geopolymer only slightly depends on the amount of water used to prepare the pastes, but increases as the Si to Al ratio increases, increases as the Na to Al ratio increases and is higher for Na than for K based geopolymers.
CHAPTER 7 INFLUENCE OF INERT AND ACTIVE FILLER ON THE MECHANICAL PROPERTIES OF METAKAOLIN GEOPOLYMERS
CHAPTER 7  INFLUENCE OF INERT AND ACTIVE FILLER ON THE MECHANICAL PROPERTIES

The previous chapter has shown that it is difficult to avoid drying shrinkage and cracking of metakaolin based geopolymers. When the relative humidity is between 60 and 80 %, geopolymers start to lose hydration sphere water and cracking can occur. This drying can be an issue for the encapsulation matrix. A potential way to solve the shrinkage problem is by the addition of fillers. Fillers can be classified as inert or active fillers. Inert fillers, such as sand do not significantly react with the matrix. Previous studies have already used sand as a filler material in metakaolin-based geopolymers (Palomo et al., 1999a, Yunsheng et al., 2007, Yang et al., 2009, Yunsheng et al., 2008). Reactive fillers react partially or fully with the compounds of the matrix. For example, it has been reported that cement phases can be observed in metakaolin based geopolymers when mixed with blast furnace slag (Yip and Van Deventer, 2003).

This chapter reports on research that has been investigated the influence of inert and reactive fillers on the mechanical properties of metakaolin based geopolymers before and after water removal.

7.1  Inert fillers in general

7.1.1  Materials and Methods

Materials

Silica sand obtained from Sibelco (UK) was too coarse to be used as a filler. Therefore it was milled using a disc mill to give the particle size distribution shown in Figure 7-1.
In the previous chapter it was shown that the water content does not influence the shrinkage due to loss of the hydration sphere but it was recognised that a higher water content improves the workability. In this study the molar water ratio was varied between 7.5 and 10.5 and the Al:Si:Na ratio was kept constant at 1:2:1 because a significant amount of data is available for this mixture (Duxson et al., 2007a, Duxson et al., 2005b, Duxson et al., 2007b). Geopolymer samples were prepared as described in section 4.2. However, before adding the activation solution, sand was hand mixed with metakaolin (MetaStar 501). All prepared samples are shown in Table 7.1. In this table two different expressions were used to describe the prepared mortars: water/solid (w/s) ratio and volume percent (vol%) of added sand. w/s is often used in cement research and describes the ratio of water added to cement or cement/sand mixes. The disadvantage in using this term for geopolymer research is that theoretical all dissolved salts in the activation solution, here Na$_2$SiO$_3$ and NaOH, should be considered as liquid and a better expression would be liquid/solid ratio. However, due to the fact that Na$_2$SiO$_3$ and NaOH take part in the chemical reaction, it was proposed to consider these salts as a solid (Rangan, 2008). The following equation was used to calculate the w/s ratio:

$$ W = \frac{m_{H_2O} + \frac{m_{Na_2SiO_3 \text{ liquid}} \times \text{concentration}_{H_2O}}{100} + \frac{m_{NaOH} \times m_{H_2O}}{2 \times m_{NaOH}}}{m_{\text{metakaolin}} + \frac{m_{Na_2SiO_3 \text{ liquid}} \times \text{concentration}_{Na_2SiO_3 \text{ solid}}}{100} + \frac{m_{NaOH} \times m_{Na_2SiO_3}}{2 \times m_{NaOH}}} \quad 7-1 $$
with \(m = \text{mass}\), concentration = \textit{concentration} of either \(H_2O\) or \(Na_2SiO_3\) in \(Na_2SiO_3\) solution in \% and \(M = \text{molecular mass}\).

Another possibility is the replacement of geopolymers with sand is volume percentage. The volume percentage can be calculated using the linear rule of mixtures, as shown in Equation 7-2:

\[
\text{sand vol\%} = \frac{m_{\text{sand}}}{\rho_{\text{sand}}} = \frac{m_{\text{water}}}{\rho_{\text{water}}} \times \frac{m_{\text{geopolymer}}}{\rho_{\text{geopolymer}}} \times \frac{m_{\text{sand}}}{\rho_{\text{sand}}} \tag{7-2}
\]

With \(m = \text{mass}\) and \(\rho = \text{density}\)

To use equation 7-2, the density of geopolymers and sand has to be known. These values were measured using a He pycnometer.

\[\text{Table 7.1: Mixtures investigated in this study. The molar ratio of Al:Si:Na was in all mixtures the same 1:2:1, with the molar ratio of water added varied between 7.5 and 10.5. For all mixtures the w/s solid ratio and the volume percentage of added sand is shown in the table.}\]

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Viscosity measurements

Viscosity $[\eta]$ describes the internal friction of a liquid. The internal friction is caused by the attractive forces between the molecules of the fluid (cohesion). In general, the effect of internal friction can be described by two overlapping, interlocked molecular layers. During flow, the molecules pass each other which require a certain force, as shown in Figure 7-2.

Figure 7-2: Schematic representation to describe viscosity.

Viscosity, describes the relationship between this force and the properties of this fluid, as shown in equation 7-3:

$$\eta = \frac{\tau}{\gamma}$$  \hspace{1cm} 7-3

with $\tau$ = shear stress and $\gamma$ = shear rate.

To calculate $\tau$ and $\gamma$ for a cone/plate system, shown in Figure 7-3, following equations can be used (Equation 7-4 and 7-5) (Gehm, 1998):

$$\tau = \frac{3}{2\pi R^3} * M$$  \hspace{1cm} 7-4

$$\gamma = \frac{\pi}{30\beta} * n$$  \hspace{1cm} 7-5

where $R$ = radius of the cone, $M$ = torque, $\beta$ = cone angle, $n$ = number of revolutions.

The advantage of this system is that only small amounts of a substance are required so that sample loading and cleaning of the system is easy. In this work, viscosity was measured using a Paar Physica UDS200 rheometer from Anton Paar (Germany).
An advantage in using a rheometer is that the shear rate can be altered and the viscosity at different forces measured. Furthermore, an increasing/decreasing shear rate allows the measuring of thixotropic behaviour which describes the effect of remaining liquid over a fixed time after removing shear force.

In this study the viscosity was measured at 20 °C and the shear rate was increased/decreased from 0.1 to 75 s⁻¹.

**Mechanical tests**

Compressive strength and Vickers hardness was measured as explained in section 4.4.1 and 4.4.3.

**Heat stability**

The shrinkage during the loss of hydration sphere water was detected using a dilatometer, according to the method described in section 4.8.2.

### 7.1.2 Results

To use Equation 7-1 the density of the geopolymer and sand has been measured using He-pycnometry. The results are shown in Table 7.2. Additionally, the density of geopolymer/sand mixtures was measured and compared with density values calculated based on pure geopolymer and sand samples. The density of each mixture can be calculated using Equation 7-6.

\[
\rho_{total} = \rho_{geopolymer}(1 - f_{sand}) + f_{sand}\rho_{sand}
\]

with \( f = \) volume fraction and \( \rho = \) density

Table 7.2 shows that the calculated and measured densities are almost identical.
Table 7.2: Theoretical and calculated density to determine volume percentage of sand in geopolymers. Each sample value represents the average of 5 measurements. Calculated density was calculated using Equation 7-2.

<table>
<thead>
<tr>
<th>material</th>
<th>density measured [g/cm³]</th>
<th>stdev</th>
<th>calculated density [g/cm³]</th>
<th>stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>geopolymer (dry)</td>
<td>2.31</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sand</td>
<td>2.66</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>geopolymer (dry) +10 wt% sand</td>
<td>2.40</td>
<td>0.02</td>
<td>2.35</td>
<td>0.02</td>
</tr>
<tr>
<td>geopolymer (dry) +30 wt% sand</td>
<td>2.47</td>
<td>0.01</td>
<td>2.44</td>
<td>0.03</td>
</tr>
<tr>
<td>geopolymer (dry) + 60 wt% sand</td>
<td>2.57</td>
<td>0.02</td>
<td>2.55</td>
<td>0.02</td>
</tr>
</tbody>
</table>

To measure viscosity of geopolymers without sand and the thixotropic behaviour the shear rate was increased and decreased, as shown in Figure 7-4. Immediately after applying a shear force to geopolymer mixes the viscosity decreases. When this force is reduced the viscosity increases immediately, except for water ratios below 8.5, and follows the results obtained with increasing shear rate. For molar water ratios lower than 8.5 this increase of the viscosity with decreasing shear force is slightly delayed. Furthermore, an almost constant viscosity is measured at shear rates greater than 15 s⁻¹.

Figure 7-4: Viscosity over increasing/decreasing shear rate of geopolymers. The molar ratio of Al:Si:Na was 1:2:1, the molar water ratio was altered between 7.5 to 9.0.
After sand is added to the geopolymer pastes higher shear rates have to be applied to obtain a stable viscosity. At shear rates between 60 to 70 s\(^{-1}\) an almost constant viscosity for all mixtures was observed. The viscosity values taken from this point are given in Figure 7-5, with greater sand additions corresponding to higher final viscosity.

![Figure 7-5: Viscosity of different geopolymer/sand mixtures at a shear rate of 70 s\(^{-1}\). The molar ratio of Al:Si:Na was 1:2:1 and the water ratio was altered between 7.5 to 10.5.](image)

Figure 7-6 shows compressive strength data for geopolymer mortar samples. Although the viscosity is immediately influenced by sand addition the compressive strength does not change until approximately 25 vol% sand is added. This strengthening behaviour can be calculated using the rule of mixture (Equation 7-7):

\[
\text{compressive strength} = \frac{1-f_{\text{sand}}}{\text{strength}_{\text{geopolymer}}} + \frac{f_{\text{sand}}}{\text{strength}_{\text{sand}}}^{-1}
\]

where \(f\) represents the volume fraction of sand with a strength of 1100 MPa for quartz (fused) (CES, 2011).
Figure 7-6: Compressive strength for geopolymer/sand mortars after 75 days curing. Specimens were not dried before measuring. The molar ratio of Al:Si:Na was 1:2:1 and the water ratio altered between 7.5 to 10.5. Results are the average of 5 measurements and the lines represent the calculated compressive strength using Equation 7-7.

The calculated compressive strength is similar to the measured compressive strength. This strength increase may be influenced by a crack deflection mechanism (Kourtì et al., 2010, Kourtì et al., 2011). However, the typical loading curves for two geopolymer samples and a schematic crack-deflection curve are plotted in Figure 7-7. It can be seen that geopolymers fail completely after reaching their maximum strength unlike samples which show crack deflection which can be highly cracked but still able to withstand some load (Toutanji, 1996). For all lines, at the beginning an almost linear response can be observed up to first cracking, termed either as “bend over point-BOP” or “limit of proportionality-LOP”. When crack deflection takes place, the stress/strain curve becomes un-linear until the “modulus of rupture-MOP” is reached (Naaman, 2003). In all measured geopolymer mortars a sudden reduction in compressive strength occurred.
Influence of inert and active filler on the mechanical properties

Figure 7-7: Compressive strength load-deflection curves for a pure geopolymer sample, a geopolymer mortar and a schematic curve displaying the behaviour of a load curve when crack deflection takes place. Geopolymer samples were 75 days cured at ambient temperature and not dried before measuring and the molar ratio of Al:Si:Na:OH was 1:2:1:8.5.

Similar to the compressive strength are the results for the Vickers hardness (HV), depicted in Figure 7-8. To calculate the HV behaviour, Equation 7-7 has been used and for sand a HV of 1000 has been assumed (CES, 2011). The calculated results agree for water contents between 7.5 to 9.5 but predict slightly lower values at higher water additions.
Influence of inert and active filler on the mechanical properties

Figure 7-8: Vickers Hardness of geopolymer mortars with a molar ratio of Al:Si:Na:H$_2$O 1:2:1:8.5 before drying. Each point represents an average of 7 results. The line represents the calculated Vickers hardness using Equation 7-7.

After drying geopolymers mortars at 110 °C for one day, the compressive strength could only be measured for specimens containing more than 10 vol% sand, as presented in Figure 7-9. Furthermore, after drying, the compressive strength of all samples was approximately doubled compared to the results before drying. Samples containing less than 10 vol% of sand could not be measured due to extensive cracking.
Influence of inert and active filler on the mechanical properties

Figure 7-9: Compressive strength of geopolymer/sand mortars after drying at 110 °C. The molar ratio of Al:Si:Na was 1:2:1 and the water ratio was altered between 7.5 to 10.5. Samples in the grey area could not be measured due to cracks. Data represent the average of 5 measurements.

Figure 7-10 shows the influence of sand on shrinkage for a molar Al:H₂O ratio of 1:8.5, respectively. In Chapter 6 it was already shown that the molar water content does not influence the extent of shrinkage. It can be seen that shrinkage was reduced to less than 1 % after ~35 vol% of sand was added. The theoretical shrinkage was calculated by assuming a linear correlation between added volume percentage sand in the geopolymer mixture according to Equation 7-8:

\[
\text{shrinkage of GP mortar} = 1 - f_{\text{sand}} \cdot \text{shrinkage}_{\text{GP}} - f_{\text{sand}} \cdot \text{length change}_{\text{sand}}
\]

Equation 7-8

The length change of sand can be neglected due to the low temperatures and the large shrinkage of geopolymers during drying.
Influence of inert and active filler on the mechanical properties

Figure 7-10: Strain induced in geopolymer/sand samples when heated to 500 °C at a heating rate of 10 °C/min. Each point was measured using dilatometry and represents the maximum shrinkage observed. The molar ratio of Al:Si:Na:H$_2$O was 1:2:1:8. The grey line shows the theoretical shrinkage of geopolymer mortars, calculated using equation 7-8.

7.1.3 Discussion

Viscosity measurements show that metakaolin based geopolymers behave as a non-Newtonian liquid. The viscosity decreases with increasing of shear rate and after passing a shear rate of 20 s$^{-1}$ the viscosity is almost constant. This characteristic behaviour is often observed in suspensions containing high amounts of particles (Bingham, 1916, Bingham and Green, 1919). As the shear rate increases the particles start to orientate in the direction of rotation and the viscosity decreases (Nuntiya and Prasanphan, 2006). The sinusoidal wave between shear rates of 5 and 20 s$^{-1}$ can be described as a transient effect caused by the metakaolin particles. However, with increasing shear rate a steady-state viscosity is obtained. When less water is used, the viscosity increases and mixtures become difficult to cast (Panias et al., 2007).

Several researchers have reported thixotropic behaviour of geopolymer mixes associated with degradation and rebuilding of the structure (Steinmetz et al., 2006, Krivenko and Kovalchuck, 2007, Nuntiya and Prasanphan, 2006). These degradation/rebuilding-cycles are completely
reversible and time-dependent and can be measured using increasing and decreasing shear rate. According to the definition of a thixotropic liquid, not only the start/end viscosity of substances is different but also the viscosity between increasing and decreasing shear rate. This difference of the viscosity between increasing/decreasing shear rates can only be seen for samples with a molar water content lower 8.5 but the start and end viscosity is almost the same. This means that metakaolin based geopolymers with a molar water content between 7.5 and 10.5 do not behave as a thixotropic liquid. The difference in the viscosity at lower w/s ratios is probably due to the high amount of particles which are moving in the same direction.

It was not unexpected that with increasing sand content the viscosity increases due to the lower w/s ratio in the system. At a w/s ratio below 0.2 the water content is so low that a dry crumbly mortar formed which was extremely difficult to cast. Nevertheless, down to a w/s rate of 0.26 geopolymer mortars are highly workable and have good flow with the aid of a vibration table.

The mechanical strength is directly influenced by the molar water content and decreases with increasing water content due to higher porosity in the system (Panias et al., 2007). In geopolymers the water is only required to provide a medium for the dissolution and polycondensation reaction but afterwards it is present in pores as discussed in Chapter 6. The higher the initial water content, the higher the resulting porosity and the lower the mechanical strength.

Another important point is that although the viscosity is affected for even small changes in the w/s ratio, the mechanical strength does not show a change until ~25 vol% of geopolymer is replaced with sand. It has been suggested that this strengthening is due to crack deflection (Kourtí et al., 2011, Kourtí et al., 2010). However, by comparing the compressive strength loading curves with the expected deflection curve a different mechanism is suggested which results in strengthening of geopolymer mortars. At low sand concentrations the compressive strength is mostly dominated by the strength of the geopolymer. However, with increasing amount of filler in the sample during compression test the filler is compressed against each other and carry load.

This support of sand particles can not only be seen by measuring compressive strength but also HV. The results show that between 20 and 30 vol% of sand the HV increases. This is the same region in which the compressive strength starts to increase. This shows that the sand particles increase the mechanical properties of geopolymers because sand particles stack together and can carry load. This increase of the strength can be calculated by using the rule of mixture although, the HV results of geopolymers with molar water content higher than 9.5 deviate and are slightly higher compared with the calculated results. This is probably due to water evaporation on the
surface of geopolymers and the resulting shrinkage. Geopolymers with higher water content have a higher porosity and therefore a greater surface from which water can evaporate. In Chapter 6, it was shown that geopolymer shrink when water from the hydration sphere of charge balancing cations is lost. It is possible that the surface had already lost hydration sphere water and shrinkage has started. This means the measured hardness will be slightly higher compared to the calculated.

After drying at 110 °C, all geopolymer mortars with a volume percentage of filler less than 10 wt% fragment during the drying process due to extensive shrinkage. However, when more geopolymer matrix is replaced with sand the compressive strength of all samples almost doubles although the error in the compressive strength results is relatively high. This indicates that all samples have micro cracks which influence the compressive strength results. These micro-cracks are formed at the interfacial transition zone (ITZ), which refers to the region surrounding each aggregate particle where the microstructure is perturbed by the presence of aggregates (Scrivener et al., 2004). At the ITZ non-shrinkaging particles are in contact with a matrix which can shrink. During shrinkage strain increases and is released by the formation of micro-cracks.

Although, geopolymer-mortars samples have micro-cracks after drying, a survival after drying can be guaranteed when more than 10 vol% of filler are present. This is due to the fact that sand particles limit the shrinkage of the geopolymer network by forming a supportive matrix with a fixed void volume.

7.1.4 Conclusion

In this section the influence of sand on the mechanical properties of metakaolin-based geopolymers was investigated. Replacing geopolymer paste with sand almost immediately increases paste viscosity. Nevertheless, the mechanical strength increases with volume ratios higher than ~25%. This change can be calculated by using the rule of mixture equation. After heating the samples to 110 °C geopolymers mortars can survive the shrinkage because the sand particles significantly reduce shrinkage during heating. This is as a result of the sand particles limiting shrinkage by forming a supportive matrix with a fixed void volume. However, more than 10 vol% of geopolymers have to be replaced with sand that a survival can be guaranteed. At higher volume percentages the compressive strength of the mortars doubles which is due to cracks in the matrix.
7.2 Influence of the size of inert fillers

In Chapter 6 it was shown that principal mechanism behind shrinkage is the contraction of the geopolymer gel. Furthermore, the results in Chapter 7.1 indicate that the addition of filler can improve the mechanical properties and reduce the relative quantity of geopolymer gel present and therefore reduce the sensitivity to drying shrinkage. However, further important aspects such as filler particle size distribution and the quantity of added filler have to be considered. The study reported in this section presents a series of experiments designed to investigate the effect of different size fractions and additions of silica sand filler on the physical properties, particularly drying shrinkage, of metakaolin-based geopolymer samples.

7.2.1 Materials and Methods

The metakaolin (MetaStar 501) and activator solution used have been described in section 4.2. Geopolymer mixtures were prepared with 10 to 50 wt% of sand filler. Three different size fractions of sand were used; fine (< 75 μm), medium (75 – 150 μm) and coarse (150 – 212 μm), as shown in Figure 7-11. The molar ratio of the geopolymer paste was 1:2:1:8 Al:Si:Na:H2O for each mixture. Sand and metakaolin were premixed, added to the appropriate quantity of activator solution, mixed and cast into cylindrical moulds of 31 mm diameter with the aid of a vibrating table. Moulds were covered with cling film and placed in a relative humidity chamber maintained at >95% relative humidity and 23°C±2°C. After 48 hours, the samples were demoulded and individually wrapped in cling film.

After 14 days curing, one group of the samples were unwrapped and the tensile strength immediately measured (wet batch). A second group of samples were also unwrapped, but then dried at 110 °C for 24 hours (dry batch). The dry batch samples were then cooled in a desiccator before testing.
Influence of inert and active filler on the mechanical properties

Figure 7-11: Particle size distribution of sand used in this study.

Tensile strength measured using diametrical test (Brazilian test)

To investigate the development of micro cracks in samples either flexural or tensile strength can be measured. In this study, it was decided to measure the tensile strength by using the diametrical test. This test has been chosen due to its simplicity and the possibility of preparing a large number of specimens. A series of disc samples of 31 mm diameter and 5 mm height were subjected to the diametric compression test.

The diametrical test or Brazilian test, sometimes called the splitting tension test, is performed by compression of a disc specimen. This test is widely used to determine indirect the tensile strength of cements, rocks and ceramics (Wang et al., 2004, Wright, 1955, Jaeger and Hoskins, 1966). It is based on the fact that tensile stresses develop when a circular disc is compressed between two diametrically opposed forces. The maximum tensile stresses grow perpendicularly to the loading direction and are proportional to the applied load (Fahad, 1996). A schematic of the procedure is shown in Figure 7-12a and b with \( F = \text{force}, r = \text{radius of the disc} \). During the test the disc breaks in the middle into two almost equal pieces (normal tensile fracture mode) as shown in Figure 7-12c or split into three or four main pieces (triple-cleft fracture mode) along the load, as depicted in Figure 7-12d (Ovri and Davies, 1987).
Influence of inert and active filler on the mechanical properties

The tensile stress ($\sigma_x$) can be calculated using the following equation with $D =$ diameter and $t =$ thickness:

$$\sigma_x = \frac{2F}{\pi Dt} \quad 7-9$$

Micro-structural analysis

SEM has been used to analyse the sand distribution in geopolymers, as explained in 4.7.2. Before analyses samples were polished.

7.2.2 Results

Figure 7-13 shows the test results for wet samples. Regardless of the filler particle size the tensile strength increases slightly with increasing filler content which is in agreement with the results obtained in section 7.1 and this effect is more dominant for smaller filler particles.
Figure 7-13: Diametrical tensile strength of Na-based geopolymers mortars using different grades of sand, before drying. Curing time were 14 days; results are averages of 5 measurements.

However, after drying of the samples at 110 °C, all samples containing less than 20 wt% filler showed significant cracking and could not be measured, as shown in Figure 7-14. For samples containing fine fillers between 20 and 30 wt% had to be added to survive drying shrinkage. These results show that the coarse size fraction was more effective at reducing the drying cracks than the medium or fine size fraction. By comparing the standard deviation from Figure 7-13 and 7-14 for each measurement it can be seen that it is much larger after drying. This indicates that despite the fact that drying shrinkage is reduced there are still micro-defects in the sample which is in agreement with the results obtained in section 7.1.
The micro-structure of the geopolymer-sand mortars is shown in Figure 7-15. The filler particles are homogeneously distributed in the whole sample, as demonstrated in Figure 14a and b. From Figure 15a it is evident that there is a high degree of cracking in the matrix with lower sand content. However, this cracking is reduced with increasing filler which shows that the sand acts as reinforcements (Figure 7-15b). From the Figure 7-15c and d it can be seen that the sand particles are embedded in the geopolymer matrix.

**Figure 7-14:** Diametrical tensile strength of Na-based geopolymers mortars using different grades of sand, after drying at 110 °C. Curing time were 14 days; results are averages of 5 measurements.
Influence of inert and active filler on the mechanical properties

Figure 7-15: Na-based geopolymers, all samples contain medium size sand, a) polished sample contains 20 wt% sand; b) polished sample contains 50 wt% sand; c) polished sample containing 50 wt.% sand; d) unpolished sample containing 50 wt% sand; the solid particle is a sand particle.

7.2.3 Discussion

The results show that in wet samples not only the amount of filler but also the filler size influences the final mechanical strength. As discussed earlier the higher strength for finer filler particles is probably due to stacking of filler particles and their ability to carry a load. This theory is supported by SEM images which show that sand particles are widely distributed over the whole sample. At low concentrations the strength of pure geopolymers dominates but with increasing sand content the sand particles are able to support the matrix. However, after drying the development of micro-cracks in the material can be seen and this crack development is dependent on the filler size.

Chapter 6 showed that drying shrinkage is caused by a contraction of the gel structure when water loss exceeds a certain critical threshold. The sand particles are unaffected by water loss and are inert during the geopolymerisation process. Therefore, by substituting metakaolin by sand, the net quantity of gel in a given volume of specimen is effectively reduced. Although this
Influence of inert and active filler on the mechanical properties

is rather simple, it does support the fact that increasing the filler addition improves the resistance to drying shrinkage.

With regards to the differences between fine and coarse fillers, the effects are purely due to the physical size and associated surface areas. When hydration water is removed the structure of the geopolymer contracts and shrinks. However, the inert filler does not shrink and therefore tensions arise at filler-gel interfaces. At a certain point the geopolymer matrix cannot compensate these tensions and the material cracks, either within the gel or at the sand-gel interface or both. The gel-sand tensions are higher with fine sand filler because a greater surface area of the sand-gel interface is created.

The beneficial effect of coarser sand filler can be explained by Figure 7-17. In this image, it is evident that cracks in the gel terminate when they run into a sand particle. The largest cracks noted were in the pure gel sections. Larger filler particles present more effective obstacles to crack propagation than smaller filler particles, as shown by Grassl (Grassl et al., 2010).

![Figure 7-16: Cracks at the interface between filler particles and matrix due to shrinkage, modified from (Grassl et al., 2010).](image)

From the SEM image 7-15d it can be suggested that the surface of the sand particles interacts chemically with the geopolymer matrix which means improved bonding between filler particles and the geopolymer system. In previous work the solubility of quartz at different pH has been investigated. In these studies, it was shown that quartz can dissolve over a wide pH range (Knauss and Wolery, 1988, Bennet et al., 1988, Brady and Walther, 1990). Due to the fact that
dissolution rates are very low it can be assumed that the calculated molar Al:Si will not be affected. More important compared to the dissolution of quartz particles is the partly dissolution and hence the formation of a reactive surface. The high pH value of the activation solution can cause the formation of reactive SiO-groups on the surface which can interact with the dissolved aluminate and silicate and result in a chemical bonding between quartz surface and geopolymer, as shown in the Figure 7-17. These bonds would not only support the structure during shrinkage but also affect the strength of the system.

Figure 7-17: Simplified surface reaction of sand particles with dissolved aluminate and silicate.

7.2.4 Conclusion

From these results presented the following conclusions can be drawn:

- the problem of ambient temperature drying shrinkage in metakaolin-based geopolymers can be significantly reduced by adding sand as an inert filler;
- increasing the addition of filler in the range of 0 to 50 wt% causes a continual improvement in the tensile strengths in wet samples due to chemical bonding on the surface and a stacking effect;
for a given filler addition and within the particle size range of 0-250 µm, the resistance to
drying shrinkage improves as the grain size of sand filler increases;

- the reason for the better performance of the coarser sand filler is considered to be due to
the improved ability to restrict crack propagation within the gel.

7.3 **Influence of reactive fillers**

In Chapter 6 it has been shown that a drawback for metakaolin based geopolymers can be
sensitivity to drying shrinkage at ambient temperature. Another problem with these type of
geopolymers are the higher water demand due to the plate like structure of metakaolin particles.
However, in section 7.1 and 7.2 it was concluded that by adding inert filler the drying shrinkage
can be reduced which means only the high water demand can be an issue. The water is only
required during mixing and as a medium for the chemical reaction. Due to the fact that it does
not actually take part in any reactions, it remains as pore water and weakens the structure.
Removing this excess water before setting is difficult due to resulting shrinkage of the paste. A
possible way to remove the excess water could be by adding re-active filler. These filler can
either build into the geopolymers structure or interact with the dissolved silicate and water to
form reaction products which can fill the pores previously occupied by the water. In previous
studies, it has been shown that when BFS is present in metakaolin based geopolymers calcium
silicate gel (CSH) or calcium aluminate-silicate gel (CASH) gel is formed (Yip et al., 2005,
García-Lodeiro et al., 2010, García-Lodeiro et al., 2011, Yip and Van Deventer, 2003). CSH and
CASH gels are the main products of the hydration of cement and they are primarily responsible
for the strength in cement based materials.

However, the influence of active fillers on the mechanical properties of metakaolin-based
geopolymers has not previously been been discussed in detail, although it has been suggested
that the addition of CaO increases the strength by forming a CSH gel (Komnitsas and Zaharaki,
2007). In contrast, research has been conducted into the addition of up to 25 % metakaolin to
Portland cement in order to increase mechanical strength, durability, resistance to acid attack,
and to reduce permeability, shrinkage due to particle packing and potential for efflorescence
(Siddique and Klaus, 2009). Research was limited to this percentage as values higher than this
adversely affected the workability of the cement (Frías and Cabrera, 2000, Poon et al., 2006,
Sabir et al., 2001). However, little research has been reported regarding the addition of
percentages of Portland cement or other materials to metakaolin based geopolymers, which could
interact with the geopolymers structure thus minimising excess water. In this study, the use of
several active fillers, MgO, CaO in the form of Ca(OH)₂ and PC (CEM 1), were investigated in
order to limit the drying shrinkage, reduce porosity and therefore increase mechanical strength of metakaolin based geopolymers. Those filler have been used because they were easily available and they are relatively cheap.

### 7.3.1 Materials and Methods

**Materials**

In this study the MetaStar 501 metakaolin was used to prepare the geopolymers. As reactive fillers, Ca(OH)$_2$ powder, MgO powder and as PC CEM 1 have been used, as described in section 4.1. As control samples, geopolymer/sand mortars have been prepared. To obtain fine sand, sand was milled beforehand using a disc mill and sieving it through a 50 μm sieve.

**Preparation of geopolymer mortar samples**

Samples were prepared as explained in section 4.2. The Al:Si:Na molar ratio in the geopolymer binder was kept constant at 1:2:1. The molar water to Al ratio was set to 8. The geopolymer mortar samples prepared are given in Table 7.3. The w/s ratio was calculated as explained in the section 7.1 using Equation 7-1. The filler was added in 5 wt% intervals until the mixture was no longer workable. The maximum amount of filler added was therefore dependent on its type and much more sand could be added than reactive fillers. The amount of reactive filler decreased in the order MgO, CEM 1 and Ca(OH)$_2$.

**Table 7.3:** Mixtures investigated in this study. The molar ratio of Al:Si:Na:H$_2$O was in all mixtures the same 1:2:1:8. For all mixtures the w/s solid ratio and the volume percentage of added sand is shown in the table.

<table>
<thead>
<tr>
<th>wt% filler</th>
<th>w/s</th>
<th>sand</th>
<th>MgO</th>
<th>Ca(OH)$_2$</th>
<th>CEM 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.71</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>0.65</td>
<td>2.9</td>
<td>2.2</td>
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<td>2.4</td>
</tr>
<tr>
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<td>0.62</td>
<td>-</td>
<td>-</td>
<td>5.4</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>0.59</td>
<td>5.9</td>
<td>4.5</td>
<td>7.0</td>
<td>5.0</td>
</tr>
<tr>
<td>15</td>
<td>0.54</td>
<td>9.1</td>
<td>6.9</td>
<td>10.7</td>
<td>7.7</td>
</tr>
<tr>
<td>20</td>
<td>0.49</td>
<td>12.5</td>
<td>9.6</td>
<td>-</td>
<td>10.6</td>
</tr>
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<td>12.4</td>
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<td>15.4</td>
<td>-</td>
<td>-</td>
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<td>35</td>
<td>0.37</td>
<td>23.5</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>40</td>
<td>0.33</td>
<td>27.6</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>theor. density [g/cm$^3$]</td>
<td>2.66</td>
<td>3.58</td>
<td>3.34</td>
<td>3.19</td>
<td></td>
</tr>
</tbody>
</table>

127
Isothermal calorimetry

Isothermal calorimetry was measured as explained in section 4.9.4.

Porosity and density

Porosity results have been obtained using Archimedes' principle, as described in section 4.5.2. The theoretical density has been measured using a He pycnometer, as explained in section 4.5.1.

Mechanical properties

Compressive strength results were determined according to section 4.4.1.

Drying shrinkage

To measure drying shrinkage, a dilatometer was used, as described in section 4.8.2.

Micro-structural analysis

To measure the influence of reactive fillers in geopolymers, SEM and XRD were used. Both methods are explained in detail in section 4.7.

7.3.2 Results

Isothermal calorimetry – heat output

Figures 7-18a and b show the isothermal calorimetry results at 20 °C for samples made with fillers of Ca(OH)\textsubscript{2}, CEM 1, MgO and sand. Figure 7-16a presents the calorimetry results for the maximum percentage volume possible when taking into account sample viscosity and Figure 7-16b presents an overview for all mixes.

The maximum volume percentages of filler used were 10.6%, 10.7%, 15.4% and 27.6% for CEM 1, Ca(OH)\textsubscript{2}, MgO and sand respectively and were used in order to be able to observe any additional reactions that may occur. The sample containing sand as filler can be considered as a control sample as it is assumed that crystalline silica does not react with the geopolymer so any reaction detected is purely due to the geopolymeric reaction. For all samples an exothermic signal can be identified (A) which has been reported to be the wetting of the solid surface with
the activation solution (Buchwald et al., 2009, Yao et al., 2009). As all mixtures were initially prepared outside of the calorimeter the fast exothermic wetting peak could not be fully recorded. After the exothermic signal reaches a minimum, a second exothermic signal (B) can be observed. Previous studies using pure metakaolin mixtures reported a shoulder within the second exothermic peak (Zhang et al., 2012, Granizo and Blanco, 1998a). However, this cannot be seen, probably due to the relatively fast reaction. From the control mixture, it can be seen that the geopolymerisation starts within 2.5 hour, peaking at around 8 hours. After the addition of active fillers the heat output can either shift to the left as for Ca(OH)\textsubscript{2} or to the right as for MgO and CEM 1. With a shift to later times the second exothermic signal becomes much smaller and broader. However, this type of shift suggests that the presence of these fillers, MgO and CEM 1 delays the geopolymerisation reaction. The results for the CEM 1 containing mixture are in agreement with studies by previous researchers (De Schutter and Taerwe, 1995). From the results in Figure 7-18a it is difficult to determine the influence of active filler on the heat output because different volume percentages of filler are shown. In Figure 7-16b the second exothermic signal for all four filler types and volume percentage is plotted. The overall general trend observed is that increasing the percentage of filler causes a decrease in heat output rate and total heat release. This trend is expected as increasing filler content essentially reduces the percentage of geopolymer and less geopolymer reactants means lower heat output rates as the total amount of geopolymerisation will be reduced. For the heat output this trend is most pronounced for the MgO containing samples and much less for the Ca(OH)\textsubscript{2} and CEM 1 samples which show trends very similar to that of the control samples with sand.
Figure 7-18: Isothermal calorimetry results for geopolymers/filler mixtures, measured at 20 °C. a) geopolymer mixtures contain the maximum percentage; the graph is separated into a wetting zone (A) and the second exothermic signal, b) second exothermic signal for all geopolymers/filler mixtures.
Influence of inert and active filler on the mechanical properties

Isothermal calorimetry – total heat

It is difficult to draw any conclusions about any additional side reactions that occur just by comparing the peak height and shape. A further tool which can be used is by comparing the total heat output during a reaction, as presented in Figure 7-19. With increasing filler content the total heat output decreases linearly. Similar results have been observed for the maximum rate. It can be seen that the slope representing the MgO and Ca(OH)$_2$ filler samples is significantly steeper than that of the sand and CEM 1 samples, suggesting that the presence of MgO and Ca(OH)$_2$ somehow influences the geopolymerisation reaction. The line for the CEM 1 sample is similar to that of the sand samples indicating that the total heat output is not influenced in the first 30 hours.

![Figure 7-19: Total heat output for geopolymer/filler samples in the first 30 hours at 20 °C.](image)

Mechanical properties

An aim of this study was to investigate the influence of active filler on the porosity, which can be seen in Figure 7-20. From this figure it can be seen that the behaviour of active and inert filler in geopolymers is different. The addition of active filler lowers the total porosity compared to inert filler. Of interest is that the influence of active filler on the porosity is independent of the nature of the filler.
Influence of inert and active filler on the mechanical properties

Figure 7-20: Influence of active filler on total porosity in geopolymers after 360 days curing at ambient temperature.

The development of compressive strength over time up to one year is presented in Figure 7-21. In agreement with other studies, the compressive strength of geopolymers does not increase after 28 days curing (Rovnaník, 2010). However, after adding reactive filler the compressive strength increases, depending on the type of filler, between 28 and 360 days. Surprisingly, the Ca(OH)$_2$ containing samples achieve the highest compressive strength although the volume percentage of filler was only 10.7.
Influence of inert and active filler on the mechanical properties

**Figure 7-21**: Compressive strength over time for all geopolymers/filler mixtures.

**Drying shrinkage**

In Chapter 6 it was shown that drying shrinkage can be an issue when metakaolin is used as a precursor. Figure 7-22a illustrates dilatometry results for the maximum percentage of each filler. In this figure the shrinkage was separated into three zones: loss of free water (A), loss of interstitial water (B) and loss of hydroxyl water (C). The loss of free water occurs without shrinkage up to a temperature of ~160 °C (zone A). Between 160 and ~325 °C interstitial (structural) water is lost and the specimens start to shrink. At temperatures above 325 °C hydroxyl water is removed and the samples shrink further. These shrinkage results are similar to shrinkage measurements conducted in Chapter 6. However, from this figure it is difficult to draw any conclusions regarding the total shrinkage, therefore a more detailed behaviour of the influence of active filler is presented in Figure 7-22b. These results were obtained by measuring the intercept point between a tangent on the interstitial shrinkage (a) and a tangent (b) on the hydroxyl shrinkage, exemplary shown in Figure 7-22a for CEM 1 (Beilmann et al., 2011). From Figure 7-22b it can be seen that all samples follow the same trend and the reduced shrinkage is independent on the filler type. Although, geopolymer samples show a reduced shrinkage when
reactive filler is added, compressive strength could not be measured after drying at 110 °C due to extensive cracks in the matrix.

**Figure 7-22:** Dilatometry results to determine the extent of shrinkage due to the loss of “free” water on samples cured 360 days at ambient temperature. a) geopolymer mixtures contain the maximum percentage, b) overview for all geopolymers/filler mixtures, the dotted lines mark the trend line.
Microstructural analysis

Figure 7-23 shows XRD data for four samples each containing the maximum possible amount of fillers. In all samples, the characteristic broad amorphous hump of the geopolymer between 20 – 40° 2θ can be seen and a weak signal at 25° 2θ from crystalline SiO₂ which is a common impurity in metakaolin. When reactive filler are added to geopolymers, the maximum of the broad hump shifts from ~27° to ~31°.

The MgO spectrum shows three intense peaks which are from unreacted MgO. Furthermore, two humps can be seen at 35 – 40° 2θ and 60 – 62° 2θ. These signals are from MSH gel which has been formed in the geopolymers (Brew and Glasser, 2005). It is of interest that no Mg(OH)₂ was detected which suggests that most of the MgO has transformed to MSH gel, probably via Mg(OH)₂, or remains unreacted. The un-reacted MgO results from an agglomeration of MgO during mixing. The weak signal at 30 degrees is tobermorite, a component of CSH gel, and is due to minor impurities of Ca in MgO (Zhang, 2012a).

For CEM 1 mixes crystalline phases of calcium silicates and tobermorite were identified.

When Ca(OH)₂ is mixed with metakaolin and activation solution, unreacted Ca(OH)₂ and tobermorite were detected. The un-reacted Ca(OH)₂ is probably due to agglomeration during mixing.
**Figure 7-23:** XRD spectra for four samples each containing the maximum possible amount of fillers after 360 days curing; key: a = SiO₂, b = un-reacted Ca(OH)₂, c = Tobermorite (crystalline CSH gel), d = calcium silicate (CSH gel), e = magnesium silicate (MSH gel), f = un-reacted MgO.

SEM images for fractured samples dried at 110 °C are shown in Figure 7-24. It can be seen that regardless of the type of filler, micro-cracks are present. This demonstrates that reactive fillers do not prevent drying shrinkage.
Influence of inert and active filler on the mechanical properties

Figure 7-24: SEM pictures for four samples each containing the maximum possible amount of one of the fillers, containing, a) Ca(OH)2, b) CEM 1, c) MgO, d) sand. Samples were cured 360 days at ambient temperature.

7.3.3 Discussion

From Figure 7-18 it can be seen that addition of MgO and CEM 1 delay the reaction time. A delay for CEM 1 has been reported earlier and is probably due to the high water content in the mixtures (Snelson et al., 2008). However, the delay of the reaction time using MgO was somewhat unexpected. It was expected that the total heat release would be similar since both elements are located in Group II. Previous studies focusing on the setting time of FA mixtures with MgO and Ca(OH)$_2$ showed similar setting times (Lee and van Deventer, 2002). The calorimetry results indicate that the setting times for geopolymers mixed with Ca(OH)$_2$ and MgO are different. This is probably due to the low reactivity of MgO used in this study. Earlier research compared different MgO samples and indicated that depending on the MgO type the reactivity can vary (Liska et al., 2006). A high reactive MgO would release 81.0 kJ/mol during hydration which is fairly similar to CaO which releases 65.4 kJ/mol (Shi et al., 2002, Kato et al., 1996). According to these data a strong exothermic reaction should be expected after MgO is mixed with water. However, in this study the hydration of MgO is delayed as can be seen by comparing the total energy release within 30 hours which is higher compared to a
Influence of inert and active filler on the mechanical properties of geopolymer/sand mixture. However, the addition of Ca(OH)$_2$ appears to increase the reaction. This is in agreement with earlier findings on the fast reaction of Ca(OH)$_2$ with silicate solution (Mostafa and Brown, 2005). This reaction also causes the higher total heat output. For samples containing CEM 1, it is difficult to draw any conclusions due to the closeness of results with the geopolymers/sand mixture. The total heat release was only measured for 30 hours and the total heat release already indicated a delay of the reaction. It is most likely that the hydration of CEM 1 has not been recorded.

Based on XRD results, it was possible to identify reaction products which show that other reactions are taking place in addition to geopolymerisation. In samples containing Ca(OH)$_2$, CSH gel were observed which is in agreement with work from other researchers (Granzio et al., 2002, Alonso and Palomo, 2001). Similar results were obtained for MgO mixes, where MSH gel was detected. Unsurprisingly for CEM 1 samples, CSH gel was present. The presence of these different gel types causes a shift of the maximum in the XRD spectra due to the different structure. While geopolymers have a three dimensional structure CSH and MSH gel are based on the two dimensional network (Garcia-Lodeiro et al., 2011). In addition, these phases were shown to influence the mechanical properties resulting in less porous materials with higher compressive strength. Although, the decrease of the porosity is independent on the type of filler, the compressive strength is highly depending on the formed CSH or MSH gel. It was shown that the highest strength is obtained when Ca(OH)$_2$ is added, followed by MgO and CEM 1.

When dried, all samples showed significant cracking as seen in SEM and it was not possible to measure the compressive strength of dried samples. This has previously been reported as a result of drying shrinkage due to the loss of interstitial or structural water from the geopolymers structure (as discussed in Chapter 6). Although the addition of filler reduces drying shrinkage, the observed extensive cracking can be related either to the low concentrations of filler used or to the small particle size of the fillers, as discussed in section 7-2. Therefore, a relatively course inert filler, which is also inexpensive is probably the best way to increase the resistance to drying damage.

### 7.3.4 Conclusion

In this study, the effect of the addition of several active fillers to metakaolin based geopolymer mixes on the final mechanical properties was investigated. It was found that active fillers can interact with the geopolymer matrix and reduce porosity and increase compressive strengths. The reduction of the porosity is independent on the active filler but the increase of strength is
controlled by the formed MSH or CSH gel with the order Ca>Mg>PC. It was shown that the addition of active fillers reduces the drying shrinkage regardless the filler type but drying shrinkage could not be totally avoided at the level of addition.

7.4 Overall conclusion
In this chapter, the influence of inert and active fillers in geopolymers was investigated to reduce the ambient temperature drying shrinkage. It was shown that when geopolymers are mixed with inert, the paste viscosity increases immediately. Furthermore, the mechanical strength is not influenced by the addition of inert fillers, provided that the added volume percentage is less than 25%. In addition, the strength and hardness behaviour can be calculated using the rule of mixture. By replacing inert fillers with active fillers, geopolymers interact chemically and result in a material with reduced porosity and increased compressive strength.

Drying experiments showed that due to the addition of fillers, the shrinkage can be significantly reduced but the formation of cracks could not be entirely avoided. It was found that the grain size of added fillers had a considerable effect on the drying shrinkage behaviour and the addition of larger particles improved the drying shrinkage resistance.
CHAPTER 8 ENCAPSULATION OF MAGNOX SWARF AND AI METAL
CHAPTER 8
ENCAPSULATION OF MAGNOX SWARF AND Al METAL

8.1 Introduction
The safe encapsulation of large amounts of intermediate level legacy nuclear waste is a challenge for many countries. The waste is often highly inhomogeneous and can contain reactive metals and a safe disposal cannot be solved with one solution. It would be advantageous if a toolbox of encapsulation matrices were available to allow matching of the encapsulation matrix with the waste properties (Milestone, 2006). A blend of PC and various supplementary cementing materials (SCMs) have been considered such as pulverised fly ash (PFA) and blast furnace slag (BFS) (Tsaousoglou, 2007). The advantage of these additives is that they have pozzolanic properties and therefore react with cement during hydration and improve the final mechanical properties. The benefit of using a PC blended system is high pH and the physical and chemical behaviour over time is widely known. At high pH dissolved metal ions precipitate as insoluble oxides or hydroxides. Although the pH value of a PC mixture can be an advantage for some waste streams, it can also cause durability issues (Setiadi et al., 2006). Problematic metal ions include zinc, tin, Magnox alloy and aluminium (Al) metal (Nishi et al., 1995). Magnox alloy and Al were the main components of the casing of the fuel rods of Magnox reactors which were used in the UK, as described in section 1.4.1. Most of these nuclear power plants have already been decommissioned, the waste is stored in special pits in Sellafield and needs to be encapsulated which is a major task of the Nuclear Decommissioning Authority (NDA, 2011). Research is investigating whether new cement systems such as geopolymers, Mg-based cements, calcium sulfoaluminate cement systems or epoxy resins can be used (Zhou et al., 2006, Mann, 2011, Zhang, 2012b).

This chapter investigates the use of Na based geopolymers as the encapsulation matrix for mixed reactive metal waste.

8.2 Materials and Methods
Preparation of the geopolymer and control samples
The Al:Si:Na:H₂O molar ratio of the precursor geopolymer was 1:2:x:8. In this chapter Na based geopolymers have been used due to the fact that potassium based geopolymers have a reduced acid resistance. Although different metakaolins do not influence the mechanical properties as discussed in Chapter 5, it was noticed that different Al:Si molar ratios in metakaolin lead to the addition of more or less sodium silicate solution which is shown in Table 8.1 for two different metakaolins with a molar Al:Si:Na:H₂O ratio of 1:2:1:8.
Table 8.1: Comparing of the activation solution for two metakaolins with a different molar Al:Si ratio.

<table>
<thead>
<tr>
<th>metakaolin</th>
<th>MetaStar</th>
<th>MetaMax</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ [wt%]</td>
<td>56.04</td>
<td>53.0</td>
</tr>
<tr>
<td>Al₂O₃ [wt%]</td>
<td>38.14</td>
<td>43.8</td>
</tr>
<tr>
<td>molar Al:Si ratio</td>
<td>0.80</td>
<td>0.97</td>
</tr>
</tbody>
</table>

activation solution for 10 g metakaolin

| Na₂SiO₃ solution (SiO₂ [wt%] = 26.2, Na₂O [wt%] = 8.0) | 12.92 | 18.19 |
| NaOH [g]                                                | 1.66  | 1.56  |
| H₂O [g]                                                 | 1.82  | 0.06  |

It can be seen that with increasing of the molar Al:Si ratio in metakaolin more Na₂SiO₃ solution has to be added and less NaOH to reach a final molar Al:Na ratio of 1. Furthermore, it has been noted that the addition of NaOH to Na₂SiO₃ has a strong influence on the pH of the activation solution, as shown in Figure 8-1 (PQ, 2004) To reduce the pH even further the sodium content x, was varied between 0.9 and 1.0 and the results compared with a control matrix which is currently in use, a PC/BFS mixture. The mass ratio of PC:BFS was 1:3 and the w/s was 0.3. The details of all prepared geopolymers samples, including molar ratios are shown in Table 8.2.

Figure 8-1: pH value for different Na₂SiO₃ solutions with varying molar Si:Na ratio and comparision of the expected pH value for activation solutions for metakaolins with a different Si:Al ratio (PQ, 2004).
Table 8.2: Prepared geopolymers samples and their molar ratios to study corrosion between encapsulation matrix and metal.

<table>
<thead>
<tr>
<th>sample</th>
<th>metakaolin</th>
<th>Al</th>
<th>Si</th>
<th>Na</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetaStar Al:Na 1:1</td>
<td>MetaStar 501</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>MetaMax Al:Na 1:1</td>
<td>MetaMax</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>MetaMax Al:Na 1:0.95</td>
<td>MetaMax</td>
<td>1</td>
<td>2</td>
<td>0.95</td>
<td>8</td>
</tr>
<tr>
<td>MetaMax Al:Na 1:0.9</td>
<td>MetaMax</td>
<td>1</td>
<td>2</td>
<td>0.90</td>
<td>8</td>
</tr>
</tbody>
</table>

Magnox swarf was obtained from NNL (UK) and is shown in Figure 8-2a. Due to long storage under water the Magnox was covered with a white layer of brucite (Mg(OH)₂) according to XRD. In section 7.3, it was already shown that Mg(OH)₂ reacts with the activation solution and forms MSH. Although the surface of Magnox swarf reacts and the formed MSH gel possible acts as protective layer, it cannot be guaranteed that the “clean” metal is never in contact with the reacting geopolymer paste. Therefore, to study the effect of a metakaolin/activation solution mixture on “clean” Magnox this layer was removed using 1M HNO₃.

Figure 8-2: a) Magnox alloy as received, b) XRD spectrum of white powder on Magnox surface, a = brucite (Mg(OH)₂).

Preparation of samples

Geopolymer samples were prepared as discussed earlier in section 4.2.

As control mixture a PC:BFS mixture with a mass ratio of 1:3 and a w/s ratio of 0.3 has been used. This mixture was mixed by hand for 3 minutes and cured in either plastic bags or steel moulds for 2 days at ambient temperature (22 ± 3 °C). After two days the samples were demoulded, covered in cling film and allowed to further cure at ambient temperature (22 ± 3 °C).
Corrosion measurements
To measure the corrosion rates of Magnox swarf and Al metals at different pH, buffer solutions were used. The metal was placed in the solution and Al corrosion measured by monitoring the H\textsubscript{2} release and Magnox corrosion by analysing the amount of dissolved Mg over time measured. Both methods are explained below. The buffer solutions were prepared according to Prideaux and Ward (Küster and Thiel, 1993). During the corrosion measurements the buffer solutions with the metal were not stirred. This was done due to two reasons:

1) When ILW is encapsulated, the waste and the encapsulation matrix are only mixed at the beginning for a short period to ensure a good distribution of waste and matrix.

2) When metal is placed into a corrosive medium and stirred, higher corrosion rates are measured, as shown in Figure 8-3. The shear stress influences direct the corrosion rate of the metal and with increasing shear stress the corrosion of metal increases (Balbaud-Celerier and Barbier, 2001). At low shear rates the corrosion rate is mostly controlled by mass transfer (Region A). This means that the dissolution rate of the metal is greater than the mass transfer into the solution and the corrosion product interface concentration is at saturation or equilibrium. With increasing shear rate, the mass transfer rate becomes high enough to remove corrosion products close to the solid surface and the corrosion of the metal increases (Region B). However, up to this point the metal can form a protective layer which reduces the actual corrosion rate. At very high stresses, the protective layer is partially stripped and further corrosion occurs (Region C). This means, stirring of the buffer solution can lead to wrong conclusions.

Figure 8-3: Corrosion of metal as a function of shear stress in corrosive medium, modified from (Balbaud-Celerier and Barbier, 2001).
**Al corrosion**

In this study the aluminium corrosion rate in alkaline environment was determined by monitoring the \( \text{H}_2 \) gas evolution in a gasometric assembly (Onuchukwu, 1990). Figure 8-4 illustrates the experimental setup. Al rods of 6 mm diameter and 12 mm length were either encapsulated within the geopolymers matrixes or placed in pH buffer solutions in sealed containers and the hydrogen gas collected via a tube into a measuring cylinder under a head of water. In general ~ 20 g of geopolymers matrix or buffer solution were mixed with 1.0 to 1.5 g of Al metal.

The gas volume was measure by displacement of the water. All measurements were carried out at room temperature and readings corrected against a reference standard for volume fluctuations.

![Figure 8-4: Schematic apparatus to measure the corrosion rate of Al-metal.](image)

Another possibility to measure the corrosion of Al would be by ICP-OES which has been applied to measure the corrosion rate of Magnox swarf. The disadvantage of using ICP/OES is that it cannot be used to measure the extent of corrosion between metal and geopolymer mixture.

**Magnox corrosion**

Magnox corrosion was measured using Magnox plates with the dimension of 10 mm x 0.1 mm x 40 mm. The plates were placed in pH buffer solutions and after various time periods, solution samples were taken and analysed using ICP-OES. This technique had to be used because the corrosion rates of Magnox were too low to be measured by \( \text{H}_2 \) evolution.
**pH experiments**

The pH of the buffer solutions were controlled using a pH meter. The method is explained in section 4.9.1.

**Mechanical test**

Compressive strength has been determined as discussed in section 4.4.1.

**Micro-structural analysis**

To measure the influence of metal in geopolymers SEM and XRD were used. The method is explained in detail in section 4.7. However, it was difficult to measure the crystalline phase of the ITZ between Al metal and geopolymer using powder samples. Therefore, geopolymer samples were placed on top of an Al sheet using a circular mould. After 28 days curing, the mould was removed from the metal and the geopolymer contact surface direct analysed by XRD.

**8.3 Results**

**Corrosion of Al versus pH**

Figure 8-5 shows the hydrogen evolution curves after an Al-rod was added to three different pH buffer solutions. It can be seen that with increasing pH the corrosion of Al increases. Furthermore, by taking the linear slope, it can be seen that the corrosion of Al in all buffer solutions is delayed.
Encapsulation of Magnox swarf and Al metal

By measuring the linear slope of the H₂ release and using the ideal gas equation (Equation 8-1) the amount of hydrogen can be related to the amount of corroded Al. With the ideal gas equation molar concentration (\(n\)) of released H₂ can be calculated by adding the known volume (\(V\)) in the equation. As pressure (\(p\)) the standard pressure of 101.3 kPa was used, \(R\) is the universal gas constant of 8.314 Jmol\(^{-1}\)K\(^{-1}\) and temperature \(T\) was set to 298 K.

\[
\frac{n}{RT} = \frac{V_p}{RT}
\]

\[
8-1
\]

To model the corrosion rate of Magnox at different pH, the linear slope of the ICP results was calculated. The ICP results are shown in Figure 8-6.

**Figure 8-5:** Corrosion of Al-rod in different buffer solution. The dotted lines point out the linear slope which has been used to calculate the amount of H₂ released.
In Figure 8-7 the early age corrosion rates at different pH are illustrated for Magnox and Al. Magnox alloy corrodes at a pH below 10 and Al shows rapid corrosion at pH greater than 11.5. Between pH 10 and 11.5 the corrosion was too low to be measured. Additionally, the corrosion rates of Magnox are very low compared to Al.
Encapsulation of Magnox swarf and Al metal

![Corrosion kinetics of Magnox alloy and Al metal at different pH values](image)

**Figure 8-7:** Corrosion kinetics of Magnox alloy and Al metal at different pH values.

From the corrosion experiments and Figure 8-1, it can be expected that Magnox does not corrode when mixed with the activation solution due to the high pH value. Nevertheless, to investigate the surface corrosion of Magnox SEM-EDX has been used. The results are presented in Figure 8-8. Figure 8-8a shows the MetaStar based geopolymers, respectively. The crack between the metal and matrix is due to shrinkage of the geopolymers. Figure 8-8b gives the intensity of the Mg signal in all encapsulation matrices. To measure the depth of corrosion a line scan analysis has been used. At the interlayer of Magnox alloy and the encapsulation matrix the intensity of the signal reduces and levels off and Mg cannot be detected.
Figure 8-8: a) Backscattered SEM-EDX analysis of a MetaStar 501 based geopolymer and Magnox alloy. The molar Al:Si:Na:H$_2$O ratio was 1:2:1:8. The line indicates where the line scan was taken. b) EDX analysis of MetaMax based geopolymers, molar Al:Si:Na:H$_2$O ratio was 1:2:1:8 and control mixture PC/BFS.

From Figure 8-8b, it can be seen that Magnox swarf is stable at high pH values. However, according to Figure 8-1 corrosion for Al would be expected when placed in activation solution. The corrosion of Al after encapsulation in geopolymers matrixes and PC/BFS is represented in Figure 8-9. This corrosion was calculated by measuring the H$_2$ gas evolution and converting the volume into corrosion product using Equation 8-1. The expected corrosion was calculated from the measured corrosion kinetics. The corrosion of Al varies between each mixture from
0.3 mg mm\(^{-2}\) in less than one day, for geopolymers using MetaStar 501, to zero for geopolymers based on MetaMax metakaolin with a reduced Na:Al ratio. The intermediate geopolymers mixtures show a linear corrosion up to approximately 10 days, whereas the PC/BFS control mixture shows Al corrosion over the whole time period. According to Figure 8-1, the pH value of all activation solutions is higher than 12.5, all corrosion rates are lower than expected.

![Figure 8-9: Corrosion of Al metal after encapsulation in different matrices. The molar Al:Si:Na:H\(_2\)O ratio in all geopolymers was 1:2:x:8.](image)

SEM-EDX results after Al was placed in the encapsulation matrixes reveal penetration of Al species into the geopolymer and PC/BFS matrix, as shown in Figure 8-10 (a to c). The images show only MetaMax based geopolymers. Samples based on MetaStar could not be measured, the evolution of H\(_2\) was too high and samples broke before they could be placed in the instrument. However, between the encapsulation matrix and the Al-rod pores are formed due to the H\(_2\) release. This H\(_2\) porosity is dependent on the Na concentration in the precursor mixture; with reduced Na content leading to reduced porosity due to a lower pH of the activation solution, as shown in Figure 8-1.

By measuring the intensity of Al between the interlayer of encapsulation matrix and metal using EDX (Figure 8-10d) it can be seen that Al is penetrating into the encapsulation matrix. The crystalline phase in the interlayer was analysed by XRD and the data is shown in Figure 8-10. Three characteristic peaks can be seen along with a large amorphous hump. These peaks can be identified as bayerite (\(\alpha\)-Al(OH)\(_3\)), gibbsite (\(\gamma\)-Al(OH)\(_3\)) and quartz (SiO\(_2\)). The quartz is already
Encapsulation of Magnox swarf and Al metal

present in the metakaolin and the formation of Al(OH)$_3$ phases is consistent with previous studies (Tsaousoglou, 2007).

Figure 8-10: Backscattered SEM-EDX MetaMax samples and control mixture, the Al:Na ratio was altered in the geopolymers samples. a) molar Al:Na ratio of 1:0.9, b) molar Al:Na ratio of 1:1, c) control sample OPC/BFS 1:3 and d) shows the EDX results on the interlayer.
Figure 8-11: Crystalline analysis of the interlayer of MetaMax based geopolymers and Al metal. The molar Al:Si:Na:H$_2$O ratio was 1:2:0.9:8, Key= a = bayerite (α-Al(OH)$_3$), b = gibbsite (γ-Al(OH)$_3$), c = quartz.

Although the strength development of the encapsulation matrix is only from secondary consideration, it is a helpful tool to investigate how the waste has to be handled after setting. In addition, it was reported that geopolymers produced at a pH value lower than 13 have a compressive strength of less than 10 MPa, as shown in Figure 2-11 (Phair and van Deventer, 2001). In Figure 8-12 the development of mechanical strength for all samples over time can be seen. All geopolymer mixtures reach maximum compressive strength within 7 days, except the sample with the lowest Na concentration, which takes 28 days. Furthermore, on reducing the Na concentration the setting time increases steadily and samples containing a molar Na:Al ratio of 0.9 require 4 days curing to reach a minimum of strength. The strength of the control mixture increases over 90 days.
Figure 8-12: Compressive strength over time after curing at ambient temperature.

8.4 Discussion

In Figure 8-1, it can be seen that a reduction of the initial pH in geopolymers can be achieved by using a metakaolin with a higher Al:Si ratio and a reduction of the Na concentration in the activation solution. A lower Si concentration in metakaolin means more silicate solution is necessary to reach an Al:Si molar ratio of 1:2, but to keep a molar Na:Al ratio of 1, the Na in the activation solution has to always be the same. Although, the pH value of the activation solution can be controlled by altering the molar Al:Si ratio in metakaolin, it is still difficult to reach a pH value between 10 and 11. In this range the lowest corrosion rates were measured and it is most likely that stress cracking due to H₂ release can be avoided.

In addition, the corrosion rate measurements for Al can be separated into two steps. In the beginning the graph shows almost no corrosion although H₂ evolution can be seen visually. This is due to the measuring system. The system has to build up initially pressure (step 1). After this initial pressure is reached, a linear H₂ evolution and therefore linear corrosion of Al can be seen (step 2). Consequently, to analyse the corrosion rate at different buffer concentrations only the linear slope can be taken.
However, according to Figure 8-1, it can be seen that the pH-value of all mixtures is so high that a corrosion of pure Magnox does not occur. This is in agreement with the Pourbaix diagram shown in Figure 1-3 (Pourbaix, 1966). Cracks which can be seen in the SEM pictures at the interlayer are due to water loss and resulting shrinkage of the sample. When Al metal is mixed with metakaolin/activation solution corrosion occurs due to the high initial pH value. This corrosion has somehow been expected although the extent of the corrosion was relatively low when MetaStar is replaced with MetaMax. Furthermore, a significant reduction in H₂ formation can be measured with reducing of the molar Na:Al ratio in MetaMax based geopolymers. This decrease is probably due to two reasons. A decrease of pH close to the Al surface occurs because hydroxides are consumed during dissolution of metakaolin and Al metal and the formation of a protective layer on the Al surface. In addition, when the molar Na:Al ratio is reduced to 0.9 no significant corrosion was observed. Although for a molar Na:Al ratio of 0.9 no corrosion was detected by H₂ release, there are indications from SEM-EDX and XRD that the surface of Al slightly corrodes. The reason why no corrosion gas is detected is probably due to the low pressure which is produced in the burette system during corrosion.

SEM-EDX shows surface corrosion of Al in all samples with a depth varying between 50 to 100 μm. The crystalline peaks in the XRD trace of the surface reveal that on the interlayer between geopolymers and Al a mixture of gibbsite (γ-Al(OH)₃) and bayerite (α-Al(OH)₃) is formed. This is in agreement with other researcher who analysed the solid phases of Al(OH)₃ as a function of pH and time (Vermeulen et al., 1975, Li et al., 2005, Gerson et al., 1996). At high pH the surface of Al is dissolved and forms Al(OH)₄⁻ close to the metal surface. This means hydroxide ions close to the metal surface are consumed and the pH decreases (Pyun and Moon, 2000). The free aluminate reacts immediately with free silicate and forms alumino-silicate monomers (Sagoe-Crentsil and Weng, 2007). Hydroxides are required to dissolve metakaolin which also influences the pH. The reduced pH close to the surface initiates passivation of the metal and further metal corrosion becomes more difficult. The XRD revealed that the passivation layer consist mainly of bayerite, whose formation is favoured at low temperatures (Addai-Mensah, 1997). However, over time bayerite transforms in situ into gibbsite (Addai-Mensah, 1997, Counter et al., 1997). Based on the fact that no boehmite or pseudoboehmite (AlO(OH)) have been detected, the electrochemical reaction on the Al surface during dissolution can be described as follows (Pyun and Moon, 2000):

$$Al + 3H_2O + OH^- \rightarrow \frac{3}{2}H_2 + Al(OH)_4^-$$
With reducing pH, the formation of the passive layer on the Al surface can be expressed as follows:

\[
Al + 3OH^- \rightarrow amorphous Al(OH)_3 + 3e^-
\]

\[
amorphous Al(OH)_3 \xrightarrow{\text{time}} \alpha Al(OH)_3
\]

\[
\alpha Al(OH)_3 \xrightarrow{\text{time}} \gamma Al(OH)_3
\]

A possible reason why a crystalline phase of AlO(OH) cannot be seen indicates that the formation of bayerite is very rapid. This is in agreement with previous work showing that the formation of boehmite is dependent on pH and time (Hazden and Rubin, 1976). However, limiting Al corrosion is only viable at lower pH and with increasing pH more free hydroxides are available and the formation of a passivation layer takes too long to avoid cracks due to corrosion. The modelled Pourbaix diagram for amorphous Al(OH)$_3$ shows corrosion at pH 12.5 as shown in Figure 8-13 (Outotec, 2008).

![Pourbaix diagram of amorphous Al(OH)$_3$, modelled using HSC Chemistry® 6.1.](image)

**Figure 8-13:** Pourbaix diagram of amorphous Al(OH)$_3$, modelled using HSC Chemistry® 6.1.

The compressive strength evolution over time is shown in Figure 8-12. By taking into account Figure 8-1, it can be seen that the pH of the activation solution directly influences mechanical strength development over time although a similar strength is measured after approximately 100 days of curing. The higher the pH of the activation solution the faster metakaolin dissolves and therefore the faster maximum strength is reached. Previous research had shown that a certain pH
of the activation solution is required to dissolve enough aluminate to initiate geopolymerisation reactions (Phair and van Deventer, 2001). However, from the strength results it can be seen that by reducing the molar Na:Al ratio, and therefore reducing the initial pH of the activation solution, geopolymer samples reach their maximum strength within 7 days, except MetaMax Al:Na 1:0.9. Furthermore, the maximum strength is only slightly reduced for geopolymer samples with the lowest Na concentration. This shows that that the dissolution and reaction of metakaolin occurs over a relatively wide pH range and indicates that as soon as the pH is high enough to dissolve metakaolin all precursor dissolve and react.

8.5 Conclusion
The optimum pH range to encapsulate Magnox and Al has been shown to lie between 10 to 11. However, it is difficult to obtain this pH range with cementitious systems based on PC due to the intrinsically high pH of the hydration products. Likewise, for geopolymer systems, the use of high pH was suggested in order to achieve good solubility of the solid precursor. This study has shown that a lower pH geopolymer system can be achieved by controlling the metakaolin source and reducing the Al:Na ratio. A high pH does not affect Magnox alloy but corrodes trace Al metals in the waste. It was shown that the pH in geopolymer systems can be lowered to within a range suitable to encapsulate Al metal. However, it was not possible to reduce the pH to the point that corrosion of Al was completely avoided. At the interlayer between the geopolymers matrix and Al, bayerite and gibbsite ($\text{Al(OH)}_3$) could be found which are corrosion products. The formed amorphous $\text{Al(OH)}_3$ acts as a passivation layer that reduces further metal corrosion. Over time the amorphous $\text{Al(OH)}_3$ crystallises to bayerite and later to gibbsite. However, a lower activation solution pH reduces the setting time and reduces slightly the maximal strength.
CHAPTER 9  ENCAPSULATION OF Cs/Sr CONTAMINATED CLINOPTILOLITE
CHAPTER 9  ENCAPSULATION OF Cs/Sr CONTAMINATED CLINOPTILOLITE

9.1  Introduction

Cs and Sr are products formed during the fission of U-235, the fuel for nuclear power plants. Fission is the process whereby an atom splits asymmetrically into two large fragments, combined with the release of neutrons and energy (Seaborg and Loveland, 1990). These fragments have a mass number between ~75 and ~165 and some of these nuclides are Cs and Sr as shown in Figure 9-1 (Schmitt et al., 1962). After the fuel has reached the end of life, it is stored in special ponds filled with water where the Cs/Sr ions dissolve in the water. Before disposing of the water to sea it is treated with an ion exchanger usually clinoptilolite, a member of the zeolite group of minerals which absorbs the hazardous Cs/Sr ions (Smičiklas et al., 2007a).

![Figure 9-1: Relative mass yields for fragments from U-235 thermal neutron induced fission, modified from (Schmitt et al., 1962).](image)

Normally, ILW is encapsulated using a cementitious matrix. However, previous research has shown that the high pH of cement system dissolves clinoptilolite and may exchange cations with Cs and Sr (Gordon et al., 2008, Cotton, 2008, Jenni and Hyatt, 2010). Although the mechanism of interactions between cement and clinoptilolite are not entirely understood, it is clear that Cs and Sr leach into the cement matrix. After leaching of these elements into the cement matrix neither ion is immobilised and further leaching is possible. Geopolymer chemistry indicates that they might be a suitable material for an encapsulation matrix for Cs and Sr contaminated...
Encapsulation of Cs/Sr contaminated clinoptilolite

clinoptilolite. Recent work has shown promising results, but this work was mainly focused on aqueous Cs and Sr ions (Perera et al., 2006, Fernandez-Jimenez et al., 2005). However, to use geopolymers as an alternative encapsulation matrix several aspects have to be considered such as:

- Interactions of geopolymers matrix with clinoptilolite
- Interactions of Cs and Sr with geopolymers

In addition, Cs and Sr are located in different groups in the Periodic Table of Elements, the alkali group (I) and the alkaline earth group (II) and therefore both elements have different chemical behaviour in the matrix as shown in section 7.3. To investigate the effect of Cs\(^+\) and Sr\(^{2+}\) in more detail, each ion was studied separately.

9.2 Influence of high alkaline geopolymers on clinoptilolite

9.2.1 Measuring of the stability of clinoptilolite in geopolymers

Materials and Methods

It is difficult to measure the stability of clinoptilolite in geopolymers. However, to investigate the surface interactions of clinoptilolite in a geopolymer matrix two different methods have been applied.

Solubility of clinoptilolite

In Chapter 8 it was already established that the pH value of the activation solution can be between 12.5 and 14, depending on the molar Si:Al in metakaolin. To determine the solubility of clinoptilolite in different pH environments 100 mg of a fine, dry powder were placed in 10 ml buffer solution with a pH in the range 10 to 13.5. The suspension was stirred for 7 days at ambient temperature, filtered and analysed using ICP, as explained in section 4.9.3. The pH values of the buffer solutions were controlled as discussed in Chapter 4.9.1.

Interactions of clinoptilolite with geopolymers

In the second experiment clinoptilolite was added into a geopolymer mixture. The molar Al:Si:Na:H\(_2\)O ratio was 1:2:1:9 and as metakaolin MetaStar has been chosen. In this study, a higher Al:H\(_2\)O ratio was used because the mechanical properties are only secondary consideration and more important is a homogeneous mixture. The preparation of the geopolymers is explained in section 4.2. After 28 days curing was the sample polished and analysed using SEM-EDX. The method is described in more detail in section 4.7.2.


**Results**

Based on the pH ranges for activation solutions shown in Figure 8-1 different buffer solution were prepared covering the pH range expected in geopolymers. The dissolved Si$^{4+}$ and Al$^{3+}$ from the clinoptilolite were measured and the results are depicted in Figure 9-3. Dissolution starts at a pH value of 11 and as the pH increases more Si and Al dissolves, increasing steadily up to 5 mg/ml for Si and 0.5 mg/ml Al at a pH of 13.5. Although, Al and Si dissolve at high pH, the results show that the Si:Al ratio which goes into solution is not consistent and that Si dissolves preferentially compared to Al. The higher solubility is most likely due to the high molar Si:Al ratio in clinoptilolite which is around 5, shown in Figure 9-3b. More silicate is present and therefore has a higher tendency to dissolve. The dissolved Si$^{4+}$ influences the molar Si:Al ratio of the geopolymers close to the clinoptilolite surface. It can be seen that the molar Si:Al ratio steadily decreases to ~2 over a distance of around 0.15 mm. This dissolution indicates that immobilised Cs$^+$ and Sr$^{2+}$ ions can be released. Furthermore, the dissolution process close to the surface indicates that the surface of clinoptilolite is bonded chemically with the geopolymer matrix. The visible cracks are due to the loss of hydration sphere water and the resulting shrinkage, as discussed in detail in Chapter 6.

![Dissolution of clinoptilolite in buffer solutions](image-url)

*Figure 9-2: Dissolution of clinoptilolite in buffer solutions.*
9.2.2 Cs and Sr diffusing from clinoptilolite

**Materials and Methods**

In section 9.2.1 it was shown that the surface of clinoptilolite dissolves which influences the molar Al:Si ratio in the geopolymers. During the dissolution, immobilised Cs\(^+\) and Sr\(^{2+}\) ions can leach into the encapsulation matrix. To investigate this effect, MetaStar 501 based geopolymers with a molar Al:Si:Na:H\(_2\)O ratio of 1:2:1:9 were prepared, as explained in section 4.2.
Encapsulation of Cs/Sr contaminated clinoptilolite

To prepare Cs/Sr contaminated clinoptilolite, 25 g of clinoptilolite was mixed with 250 ml solution containing 0.5 M CsNO₃ and Sr(NO₃)₂, heated up to 60 °C and stirred at this temperature for 4 days. After cooling, the clinoptilolite was washed with deionised water to remove unabsorbed Cs⁺ and Sr²⁺ ions and then dried at 110 °C.

This dry, simulated waste was then placed on top of a central area of the geopolymer paste and cured for 14 days at room temperature at 95±5 % relative humidity, as shown in Figure 9-4. This assembly was used to study the lateral leaching of Cs⁺ and Sr²⁺ ions into the geopolymers using SEM-EDX. Samples were not cut and polished because preliminary experiments showed that during this preparation step Cs and Sr were smeared over the whole sample and leaching from clinoptilolite could not be studied.

![Figure 9-4: Schematic experimental procedure to measure the interactions of waste and geopolymers.](image)

**Results**

The results of the diffusing experiments are shown in Figure 9-5. It can be seen that Cs⁺ and Sr²⁺ ions are diffusing into the geopolymer matrix and Na⁺ ions are moving into the clinoptilolite. From the EDX images it is clear that Cs and Sr are not only located near the interfacial reaction zone (IRZ) but over the whole sample. However, the intensity of both ions decreases with increasing distance. In contrast to Na ions which show a high concentration near the IRZ, but the concentration decreases rapidly in the clinoptilolite.
Encapsulation of Cs/Sr contaminated clinoptilolite

9.2.3 Discussion of the stability and diffusion experiments

From Figure 8-1, it can be concluded that the high pH value of the activation solution can partly dissolve clinoptilolite. This dissolution influences the molar Al:Si ratio of geopolymers close to the zeolite surface, as shown in Figure 9-3b. This means that different mechanical properties are expected in the IRZ and a higher Si:Al ratio results in higher compressive strength, as discussed in section 2.2.3 (Rowles and O’Conner, 2003, Weng and Sagoe-Crentsil, 2007, Sagoe-Crentsil and Weng, 2007, Duxson et al., 2007b).

However, with the dissolution of clinoptilolite not only the strength can be influenced more important a release of absorbed Cs$^+$ and Sr$^{2+}$ into the matrix occurs. From Figure 9-5 it is clear that Cs and Sr do not appear locally around the clinoptilolite but are widespread over the sample confirming their high mobility. The traces of Na that can be seen in the clinoptilolite indicate that

**Figure 9-5:** SEM and SEM-EDX results for MetaStar 501 based Na geopolymers after mixing it with Cs/Sr contaminated clinoptilolite showing the diffusion of Cs and Sr into the matrix. The sample was cured for 14 days. a) SEM image showing the transition zone between geopolymers and clinoptilolite, b) diffusion of Na from geopolymers into clinoptilolite, c) diffusion of Sr into the geopolymer matrix, d) diffusion of Cs into geopolymers.
Encapsulation of Cs/Sr contaminated clinoptilolite

an ion exchange process between Na and Cs/Sr takes place in addition to release by dissolution. This has also been reported for cement systems (Jenni and Hyatt, 2010). This is due to the high concentration of ions in the activation solution. The SEM images in Figure 9-3 and 9-5 clearly show cracks close to the clinoptilolite surface. This is probably caused by a significant increase in water evaporation of clinoptilolite because of its high surface area.

Another aspect, which has to be considered when clinoptilolite is introduced into geopolymers is the long term stability. The crystalline zeolite can act as a seed for crystal growth and increase the phase transition from an amorphous to a crystalline material (De Silva and Sagoe-Crenstil, 2008, Lloyd, 2008). Previous research has shown that over time amorphous geopolymers form Zeolite P1, as shown in Figure 9-6a and b for a geopolymer with a molar Si:Al ratio of 1.6 (sample preparation can be found in the appendix) (Lloyd, 2008, De Silva and Sagoe-Crenstil, 2008). Furthermore, after the addition of clinoptilolite this phase transition into Zeolite P1 can be influenced and the formation of other crystalline phases can be preferred. This can have another significant influence on further leaching of Cs and Sr.

**Figure 9-6:** Geopolymer with a molar Al:Si:Na:H₂O ratio of 1:1.6:1:9, cured in sealed bags for 9 month, a) room temperature, b) 75 °C.

### 9.2.4 Conclusion of the stability and diffusion experiments

The pH of the activation solution is too high and the surface of clinoptilolite dissolves partially which means that Cs and Sr can be released into the encapsulation matrix. In addition, the high concentration of cations in the activation solution initiates an exchange reaction in the clinoptilolite and immobilised Cs and Sr are released into the matrix.
9.3 Interactions of Cs with geopolymers

9.3.1 Materials and Methods

Materials
To study the interactions of Cs\(^+\) ions and geopolymer pastes, CsOH was mixed with Na and K based geopolymers. CsOH was added up to a maximum of 16 wt\% based on dry geopolymer mass. Previous researcher used CsNO\(_3\) to study the interactions of Cs and geopolymers (Perera et al., 2006). However, the NO\(_3^-\) anion can influence the pH of the activation solution and therefore CsOH was chosen. The sample preparation can be found in section 4.2, as metakaolin MetaStar 501 was used. To obtain a fundamental understanding of the chemical interactions of Cs in geopolymers the molar Al:Si:Na/K ratios were varied, as shown in Table 9.1. Previous research has been focused on a molar Al:Si:Na ratio of 1:2:1 but in order to understand the importance of each parameter the Al:Si and Al:Na/K ratio was altered. The molar Al:H\(_2\)O ratio was 1:9 for all samples to provide a homogeneous mixture.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.6</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2.4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>2</td>
<td>0.7</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>2</td>
<td>1.3</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>2</td>
<td>0.7</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>2</td>
<td>1.3</td>
<td>1</td>
</tr>
</tbody>
</table>

Methods
Leaching experiments
Leaching tests are important to evaluate the waste retention properties of a matrix and for determining the degree of immobilisation. This can be achieved by bringing the solid immobilisation matrix into contact with a liquid phase, leachant, typically deionised water. The contamination in the leachant can be measured and this information can be used to characterise the immobilisation process.

Currently, there are no standard leaching tests for ILW but the most used methods are the ANS and ASTM tests (ANS, 2003, ASTM, 2002). The ANS standard measures the leaching of a rectangular sample and the ASTM the leaching of ions from a powder. Although both tests are used, each test has its disadvantage. With the ANS test only the small surface of a solid material
can be determined whereas with the ASTM test samples have to be heated for 7 days in sealed container. This procedure makes it difficult to prepare many samples at the same time. In this study the leaching was measured according to BS EN 12457-2:2002 which is widely used for materials containing waste products (BSI, 2002). For the BS EN test 1 kg of dried sample is mixed with 10 l of water and stirred for 24 hours at room temperature.

Samples were dried at 110 °C for 24 hours, milled, and a quantity of 1.5 g mixed with 15 ml deionised water and stirred for 1 day at room temperature. The solutions were filtered and analysed using ICP-OES, as explained in section 4.9.2.

**Fourier-transformation-infrared-spectroscopy (FTIR)**

Chemical bonds with a dipole moment can rotate or vibrate by absorbing specific frequencies of IR radiation. The wave lengths required to activate these movements are specific for each different chemical bond and can be measured (Barnes et al., 1936). The results can be used to identify the different chemical bonds present and can help to determine the structure of a compound.

Interactions between the IR radiation and the compound can only occur when the structure contains an electrical charge. This is always the case when the molecule has a changeable or an inducible dipole moment. All molecules are able to vibrate but only for small molecules such as CO$_2$ and H$_2$O can rotation be detected. Vibrations include the stretching and bending of bond as well as other deformations (Barnes, 1936). In this study a Thermo Scientific Nicolet iS10 spectrometer (Massachusetts, USA) was used. Approximately 0.01 g of sample was mixed with 1 g KBr, pressed to a pellet and analysed.

**Micro-structural analysis**

XRD data for powder samples were obtained according to section 4.7.1.

### 9.3.2 Results

The leaching behaviour of Cs and Na/K from geopolymers is depicted in Figures 9-7 to 9-9. In Figure 9-7 and 9-8 either the Si or the Na content was varied. Of particular interest is that in all cases more Na diffuses from of the geopolymers when more Cs ions are added. A change of the molar Al:Na ratio, does not influence the leaching of Na but a reduction in the Na$^+$ concentration reduces the leaching of Na. In addition, in both graphs the Cs leaching is below the detection
limit over the whole range up to a concentration of 0.3 mol Cs/mol Al. Figure 9-9 refers to the leaching of Cs and K in K-based geopolymers. It can be seen that at a molar Al:K ratio of 1:1 Cs is leaching for a Cs/Al ratio of ~0.2 and higher.

**Figure 9-7:** Leaching of Na and Cs of Na-based geopolymers, altering the molar Al:Si ratio, in all cases the Cs concentration was below the detection limit.
Encapsulation of Cs/Sr contaminated clinoptilolite

Figure 9-8: Leaching of Na and Cs of Na-based geopolymers, varying the molar Al:Na ratio, in all cases the Cs concentration was below the detection limit.

Figure 9-9: Leaching of K and Cs out of K-based geopolymers, altering the molar Al:K ratio, the molar Al:Si ratio was 1:2.
The FTIR and XRD spectra for Na based geopolymers with a loading of 0.3 mol Cs/mol Al in the structure reveal no difference from the unloaded geopolymers, as shown in Figures 9-10 and 9-11. Similar results were obtained for K based geopolymers. The FTIR spectrum for metakaolin shows one strong signal at 1050 cm\(^{-1}\) and two weak signals at 550 cm\(^{-1}\) and 790 cm\(^{-1}\) (labeled as 1 to 3). After geopolymerisation with and without Cs four signals can be observed. Three week signals at 550, 690 and 866 cm\(^{-1}\) (labelled as 4 to 6) and one strong signal at ~980 cm\(^{-1}\) (7).

![FTIR spectra](image)

**Figure 9-10:** FTIR spectra of MetaStar 501 Na-based pure geopolymer and mixed with 16 wt% Cs.

The XRD spectrum for geopolymers with and without Cs shows the characteristic amorphous hump at ~25° 20 and traces of crystalline SiO\(_2\).
9.3.3 Discussion

Cs leaching results of Na-based geopolymers show that Cs is locked into the geopolymer structure and with increasing Cs concentration more Na leaches from the geopolymer. The Na leaching is similar for different Al:Si ratios. These leaching results indicate that Cs is replacing Na in the structure as the charge balancing cation and therefore Na leaches out from the geopolymer matrix. Reducing the Al:Na concentration, reduces the leaching of Na out of geopolymers. This reduction is due to the number of ions in the activation solution. The activation solution has insufficient cations to balance the negative aluminate charge and therefore geopolymerisation is incomplete. The final product still contains un-reacted metakaolin. When Na\(^+\) is replaced with K\(^+\), it can be seen that at high Cs content K-based geopolymers have lower selectivity compared to Na-based geopolymers, this is in agreement with previous studies (Berger et al., 2009).

There are two possible mechanisms to resolve the difference in selectivity. The first is due to the principles of the hard and soft acids and bases (HSAB principle) (Pearson, 1963, Pearson, 1990). Cs\(^+\) ions are better retained in Na-based geopolymers as Na\(^+\) is a stronger Lewis acid compared
to the K\(^+\) and Cs\(^+\) acids which are quite similar to each other. The physical properties of Na\(^+\), K\(^+\) and Cs\(^+\) are presented in Table 9.2. Considering that Al(OH)\(_4\)\(^-\) is a weak Lewis base, it favours forming a stable compound with a weaker Lewis acid, according to the HSAB principle. With increasing Cs content and the similarity of the charge density for K\(^+\) and Cs\(^+\) aluminate loses the selectivity because of high availability of each ion. This theory is in agreement with results obtained by Duxson et al. who measured that for mixed K/Na system K\(^+\) is preferentially absorbed at AlO\(_4\)\(^-\) sites rather than Na\(^+\) (Duxson et al., 2006).

**Table 9.2**: Physical properties of different cations (Weast, 1987).

<table>
<thead>
<tr>
<th>Ion radius [Å]</th>
<th>Na(^+)</th>
<th>K(^+)</th>
<th>Cs(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge density [Z/r]</td>
<td>0.98</td>
<td>1.33</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.75</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Another potential mechanism is that geopolymers contain nano crystals which form cages and lock in the Cs ions. Previous studies have discussed the possibility of nanometer sized crystals in fly ash and metakaolin based geopolymers (Provis et al., 2005b, Fernández-Jiménez and Palomo, 2005, Hemni, 1987, Bell et al., 2008a). For example, in fly ash based geopolymers crystals of hydroxyl-sodalite (Na\(_8\)(Al(SiO\(_4\))\(_6\)OH) were found and in metakaolin K-based geopolymers leucite (KAlSiO\(_6\)*xH\(_2\)O) was present. An analogue material to lecicht which contains Na instead of K is analcime (NaAlSiO\(_6\)*xH\(_2\)O). In addition, it has been reported that some crystalline phases such as hydroxy-sodalite can influence Cs leaching (Fernandez-Jimenez et al., 2005, Zhao et al., 2004). However, crystalline phases are more likely to be present in fly ash based geopolymers because they are often cured at elevated temperature (~80 °C). These are hydrothermal conditions under which zeolites are formed and so the formation of crystalline phases can be expected. Nevertheless, researchers have shown that it is possible to form crystalline zeolite phases at ambient temperature (Nenoff et al., 1991, Bell et al., 2008a). This means there is a possibility that during geopolymerisation crystalline phases are formed which reduce the leaching of Cs\(^+\) and increases the leaching of Na\(^+\). When K is used instead of Na the structure is more open due to the larger ion size and therefore geopolymers have a lower selectivity.

The influence of Cs\(^+\) on chemical bonding in geopolymers is reported in Figure 9-10. The different vibration signals have been analysed and can be found in Table 9-3 (Yunsheng et al., 2008). In previous studies a significant shift from 1050 cm\(^{-1}\) to 980 cm\(^{-1}\) of the Si-O vibration bond during polymerisation was observed (Rovnaník, 2010, Rees et al., 2007). Additionally, during the dissolution process, the signal at 790 cm\(^{-1}\) disappears due to the formation of Al(IV)
Encapsulation of Cs/Sr contaminated clinoptilolite during geopolymerisation (Singh et al., 2005, Duxson et al., 2005a). However, no influence of Cs on the chemical structure was seen. Furthermore, similar results were obtained by analysing the crystalline phase. Geopolymers with or without Cs ions show only an amorphous hump at ~25° 20. This indicates that Cs⁺ is only replacing Na⁺ or K⁺ close to the aluminate groups as charge balancing ions, and is not bound chemically into the actual structure. However, from these leaching experiments it is difficult to judge which proposed mechanism is the reason for the good bonding of Cs ions in the geopolymer matrix.

Table 9.3: FTIR vibration signals (Yunsheng et al., 2008).

<table>
<thead>
<tr>
<th>Types of species</th>
<th>wavenumber [cm⁻¹]</th>
<th>Characteristic bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O</td>
<td>1086</td>
<td>symmetrical vibration</td>
</tr>
<tr>
<td>Si(Al)-O</td>
<td>1003-1035</td>
<td>asymmetrical vibration</td>
</tr>
<tr>
<td>Al-OH</td>
<td>914</td>
<td>6 coordinated Al-OH swing vibration</td>
</tr>
<tr>
<td>SiOH</td>
<td>840</td>
<td>bending vibration</td>
</tr>
<tr>
<td>Al-O</td>
<td>798</td>
<td>6 coordinated Al-O stretching vibration</td>
</tr>
<tr>
<td>Si-O</td>
<td>694</td>
<td>symmetrical stretching vibration</td>
</tr>
<tr>
<td>Si-O-Al</td>
<td>540</td>
<td>bending vibration</td>
</tr>
</tbody>
</table>

9.3.4 Conclusion

This section reports on an investigation of Cs in Na- and K-based geopolymers. The leaching results showed that Na-based geopolymers have high selectivity compared to K-based geopolymers. However, at relatively low concentrations of Cs, Na and K are replaced in the structure. With increasing amount of Cs in K-based geopolymers low concentrations of Cs leach. Two different mechanisms have been proposed to explain this effect. One theory is based on the HSAB principle, assuming that Cs is a weak Lewis acid which bonds to weak Lewis bases such as aluminate. The other possible explanation is based on the formation of a cage structure. By using Na ions the cage is smaller due to the smaller ion size and Cs is more effectively blocked in the structure.
9.4 Interactions of Sr with geopolymers

9.4.1 Materials and Methods

**Materials**
To study the interactions of Sr\(^{2+}\) ions on the geopolymer matrix, Sr(OH)\(_2\) and Sr(NO\(_3\))\(_2\) have been mixed with Na based geopolymers. Sr(OH)\(_2\) and Sr(NO\(_3\))\(_2\) has been added up to a maximum of 21 wt% based on dry geopolymers mass, as shown in Table 9.4. The metakaolin MetaStar 501 has been used and the molar Al:Si:Na:H\(_2\)O ratio was 1:2:1:9. The higher molar Al:H\(_2\)O ratio was chosen to provide a homogeneous mixture.

**Table 9.4:** Concentration of Sr in the prepared geopolymer samples.

<table>
<thead>
<tr>
<th>Sr in wet GP [wt%]</th>
<th>Sr in dry GP [wt%]</th>
<th>molar Sr/Al ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.8</td>
<td>0.04</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>5.3</td>
<td>0.13</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>0.17</td>
</tr>
<tr>
<td>5</td>
<td>8.6</td>
<td>0.22</td>
</tr>
<tr>
<td>7.5</td>
<td>12.8</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>16.7</td>
<td>0.46</td>
</tr>
<tr>
<td>12.5</td>
<td>20.5</td>
<td>0.59</td>
</tr>
</tbody>
</table>

**Methods**

*Sample preparation*
Geopolymers were prepared as explained in section 4.2.

*Leaching experiments*
Leaching of Sr\(^{2+}\) ions were measured according to the method discussed in section 9.3.1.

*Micro-structural analysis*
FTIR was measured as explained in section 9.3.1 and XRD spectra have been collected as discussed in section 4.7.1.

*Quantification of formed products*
DSC/TGA can be used to quantify the formed products. The measurements were completed according to section 4.8.1.
9.4.2 Results

Influence of Sr on the structure

In Figure 9-12 the FTIR results of pure geopolymers and after mixing with Sr(NO$_3$)$_2$ and Sr(OH)$_2$ are shown. The results for the geopolymers before and after activation are given in Figure 9-12a. To measure the extent of the geopolymerisation reaction only the main Si-O peak is used due to the significant shift from 1050 to 950 cm$^{-1}$ during the reaction. With the addition of Sr(NO$_3$)$_2$ to the geopolymer mixture, there is an interesting transition in the Si-O bonding, with a shift back to 1050 cm$^{-1}$, as found in un-reacted metakaolin, as shown in Figure 9-12b. This backward shift can only be observed when Sr is added as Sr(NO$_3$)$_2$ and becomes more dominant with increasing Sr concentration. Furthermore, in the Sr(NO$_3$)$_2$ spectra, at ~1400 cm$^{-1}$ a broad signal appears which can be attributed to the N-O vibration. After the addition of Sr(OH)$_2$ two signals centring around 1480 cm$^{-1}$ and 1650 cm$^{-1}$ can be measured. The peak at 1480 cm$^{-1}$ is possible due to remaining hydroxide from un-reacted Sr(OH)$_2$ and the signal at 1650 cm$^{-1}$ is believed to be due to CO$_3^{2-}$ vibration in the sample (Alavi and Morsali, 2010).

![Figure 9-12: FTIR results after Sr is incorporated into metakaolin based geopolymers with a molar Al:Si:Na:H$_2$O ratio of 1:2:1:9.](image)
From Figure 9-12 it is difficult to determine the extent of reaction between Sr and silicates or aluminates. TGA is a helpful tool to resolve the amount of Sr(OH)$_2$ which has reacted during geopolymerisation. In Chapter 6 it was shown that geopolymers lose their free and structural water below 300 °C, de-hydroxylation of Sr(OH)$_2$ occurs at temperatures between 400 and 500 °C. This means, by determining the mass loss during de-hydroxylation it is possible to measure indirect the amount of reacted Sr. The TGA results are plotted in Figure 9-13. It can be seen that at low temperatures below 300 °C a large mass loss due to the evaporation of free water occurs. After this mass loss the curve stabilises until a further significant mass loss can be seen at approximately 450 °C which can be attributed to water removal during de-hydroxylation of Sr(OH)$_2$. Although the samples were dried before measuring in the TGA to increase the intensity of the de-hydroxylation signal, some water had been re-absorbed from the humidity at ambient temperature. This can be an indication that there are un-reacted hydroxide groups available because these groups are hygroscopic. As explained earlier, by measuring the amount of water lost during de-hydroxylation it is possible to stoichiometrically link to the un-reacted Sr(OH)$_2$, as shown in Figure 9-13b.
Encapsulation of Cs/Sr contaminated clinoptilolite

Figure 9-13: TGA results from geopolymers containing Sr(OH)$_2$, a) mass loss over temperature, b) calculated un-reacted Sr(OH)$_2$ based on TGA results using mass loss from de-hydroxylation.

A similar quantification for geopolymers mixed with Sr(NO$_3$)$_2$ is not possible. At higher temperature a decomposition of nitrates occurs but it from the mass loss results it is difficult to differentiate between NaNO$_3$ and Sr(NO$_3$)$_2$. However, by comparison of the heat flow signal it is possible to qualitatively assess the presence of these different salts, as depicted in Figure 9-14. In
Figure 9-14 three main endothermic peaks can be seen whereas the signal between 600 and 800 °C overlays another peak at around 550 °C. The first endothermic peak at temperatures below 250 °C is due to the loss of free water and has been previously described (Duxson et al., 2007a). At ~310 °C the second endothermic peak appears which can be related to the melting of NaNO₃ (melting point according to literature 308 °C). The prominence of this melting signal increases with increasing Sr content. In addition, with increasing Sr content in the sample a melting signal of Sr(NO₃)₂ can be measured. However, this peak is overlaid by the broad peak from the decomposition of nitrates.

![Figure 9-14: DTA of geopolymers containing Sr(NO₃)₂.](image)

From FTIR, TGA and DSC experiments, the presence of crystalline Sr(NO₃)₂, Sr(OH)₂, SrCO₃, and NaNO₃ would be expected. Their presence can be confirmed by the analysis of the crystalline phases. as shown in Figure 9-15a and b. Irrespective of the addition of Sr compounds, the characteristic amorphous hump of geopolymers can be observed. When Sr(OH)₂ is added, it is present in a crystalline form as Sr(OH)₂ in all samples with traces of SrCO₃. The formation of CO₃²⁻ is due to the high pH and has been reported earlier (Blackford et al., 2007). The XRD spectra of geopolymers after addition of Sr(NO₃)₂ shows the presence of NaNO₃ for even the
Encapsulation of Cs/Sr contaminated clinoptilolite

smallest addition, but for higher Sr/Al ratios un-reacted Sr(NO$_3$)$_2$ can be seen. This is in agreement with the results obtained by DSC.

Figure 9-15: Crystalline phase of geopolymers phases, a) Sr(OH)$_2$ in geopolymers, b) Sr(NO$_3$)$_2$ in geopolymers, key: a: un-reacted Sr(OH)$_2$, b: SrCO$_3$, c: strontium aluminate silicate, d: SiO$_2$ from metakaolin, e: NaNO$_3$, f: un-reacted Sr(NO$_3$)$_2$. 

179
Encapsulation of Cs/Sr contaminated clinoptilolite

Leaching of Strontium

The leaching results of Sr and Na for Sr(OH)$_2$ in geopolymers are shown in Figure 9-16a. Without adding a Sr compound 10% of the Na$^+$ ions leach from the pure geopolymers which has been shown by other researcher using the ASTM test (Aly et al., 2008, ASTM, 2002). With increasing Sr(OH)$_2$ in the sample the amount of Na leached increases, stabilising at approximately ~40% for molar Sr/Al ratios of 0.2 and above. At lower Sr concentrations the leaching of Na follows a linear trend which is similar to the expected leaching of Na when Sr is replacing Na as charge balancing cation. Additionally, the leaching of Sr is below the detection limit of the ICP instrument, which is probably due to the high pH of the leachate. Sr(OH)$_2$ has a relative low solubility at pH 7, which decreases further with increasing pH. When Sr is added as Sr(NO$_3$)$_2$ a significantly higher amount of Na and Sr is observed in the leachate, as shown in Figure 9-16b. By adding Sr as nitrate the Na leaching does not follow the linear trend observed in Figure 9-16a and is even higher but levels off at approximately 80 mol%. However, the leaching of Sr at lower concentrations is similar to the results obtained in Figure 9-16a, only at a molar Sr/Al concentration above 0.22 an exponential increase is measured. This increase corresponds with the pH decrease of the leachate and is in agreement with results obtained by other researcher (Perera et al., 2006).
Figure 9.16: Leaching of Sr$^{2+}$ and Na$^+$ from Na based geopolymers, $A^*$ = expected Na leaching if Sr replaces Na as charge balancing cation, a) geopolymers mixed with Sr(OH)$_2$, b) geopolymers mixed with Sr(NO$_3$)$_2$. 
9.4.3 Discussion

FTIR results for geopolymers containing Sr(NO$_3$)$_2$ show that the Si-O vibration from geopolymers shifts back to its original metakaolin position with increasing Sr content in the sample. This shift can only be seen for Sr(NO$_3$)$_2$ and indicates that metakaolin remains un-reacted in the system. It can be deduced that Sr(NO$_3$)$_2$ lowers the pH of the activation solution by consumption of hydroxides and the formation of low soluble Sr(OH)$_2$. Next to the formation of Sr(OH)$_2$, Sr can react with the silicate in the solution to SrSiO$_3$ and remove it from the geopolymerisation reaction. Furthermore, in samples mixed with Sr(OH)$_2$ traces of carbonate can be seen due to peaks at ~1500 cm$^{-1}$ and 1600 cm$^{-1}$. This is in agreement with results obtained from XRD analysis. The carbonation of the materials is due to the absorption of CO$_2$ from the atmosphere by the highly alkaline activation solution (Danckwerts and Kennedy, 1958).

From the FTIR data it is difficult to determine the extent of the reaction and how Sr is held in the structure. For Na based geopolymers containing Ca it has been suggested that a CSH or (N,C)ASH gel is formed (Yip et al., 2005, Puertas et al., 2011, Garcia-Lodeiro et al., 2011). In geopolymers synthesised using metakaolin and Ca(OH)$_2$ the formation of CSH as calcium silicates and tobermorite has been measured, as shown in Chapter 7.3 (Murat, 1983). As the chemistry of Sr and Ca are similar it is expected that Sr is consumed in a similar manner during the polymerisation reaction. To evaluate the extent of the reaction, TGA for Sr(OH)$_2$ and DSC for Sr(NO$_3$)$_2$ has been used. TGA measurements indicate that at least 70% of Sr(OH)$_2$ reacts during geopolymerisation. This de-hydroxylation method cannot be applied to the Sr(NO$_3$)$_2$ due to the thermal decomposition of Sr and Na nitrates occurring at similar temperatures. However, a difference in the melting points of the compounds allow for a qualitative analysis by DSC. The results show that the Sr(NO$_3$)$_2$ is dissolving in the activating solution, and most likely reacting with dissolved silicates and hydroxides to precipitate as SrSiO$_3$ and Sr(OH)$_2$. Although, it has to be mentioned that geopolymers mixed with Sr(NO$_3$)$_2$ no Sr(OH)$_2$ can be measured by DSC. This indicates that all precipitated Sr(OH)$_2$ has been reacted with silicates to SrSiO$_3$.

From this conclusion it would be expected that crystalline phases of SrSiO$_3$ can be found measured using XRD. Though, only when Sr(OH)$_2$ is mixed with geopolymers this phase can be seen. The reason for this is that when Sr is added as Sr(NO$_3$)$_2$, Sr forms first highly reactive Sr(OH)$_2$, statu nascendi, which can immediately react with dissolved silicate to form amorphous Sr-Si-gel, most likely similar to CSH gel. Furthermore, in both mixes either un-reacted Sr(NO$_3$)$_2$ or Sr(OH)$_2$ can be measured. This presence of un-reacted strontium salts can be explained by the formation of a protective coating layer consisting of Sr-Si-gel which reduces further reaction of
Sr$^{2+}$ with silicate. A reaction with silicates at early ages it most likely due to the fact that aluminates have not dissolved and silicates are already present in the activation solution. After Sr(OH)$_2$ or Sr(NO$_3$)$_2$ is mixed with activation solution/metakaolin mixture the surface of the strontium salts starts to dissolve and react with free silicate. A schematic reaction for Sr(NO$_3$)$_2$ is shown in Figure 9-17, respectively. Once the whole surface is covered with a Sr-Si-gel layer, the dissolution of Sr is slowed down because Sr has to pass the protective layer. A similar mechanism has been proposed for cement systems (Stein and Stevels, 1964, Kanto et al., 1962, Gartner and Jennings, 1987).

**Figure 9-17:** Dissolution of Sr(NO$_3$)$_2$ in the activation solution and formation of a SrSiO$_3$ layer.
In Figure 9-16 the leaching results for both geopolymers mixtures either containing Sr(OH)$_2$ or Sr(NO$_3$)$_2$ are shown. It can be seen that the behaviour at low Sr concentrations is different to what is observed for higher concentrations. At low Sr$^{2+}$ concentrations there is a linear increase in Na$^+$ leaching, whilst effectively no Sr$^{2+}$ leaching. This indicates that at low Sr$^{2+}$ concentrations Sr has been fully reacted and is either acting as a charge balancing cation or build into the geopolymer matrix, as shown in Figure 9-18. These structures can be concluded due to the fact that when geopolymers mixed with MgO or Ca(OH)$_2$, the formation of MSH and CSH has been observed, as shown in Chapter 7.3. In addition, Mg, Ca and Sr are in the alkali earth group therefore a similar reaction would be expected. With increasing Sr$^{2+}$ concentration more Sr is un-reacted and therefore a higher leaching is expected. However, this can only be seen for geopolymers mixed with Sr(NO$_3$)$_2$ due to two reasons. At high Sr(NO$_3$)$_2$ concentrations most of the metakaolin remains un-reacted which means the formation of an encapsulation matrix is not completed. Second, the pH value of the leachate is lower compared to geopolymers mixed with Sr(OH)$_2$ and the solubility of nitrates at a lower pH is higher compared to hydroxides at a higher pH value.

![Figure 9-18: Potential influence of Sr into the geopolymers structure.](image)

**Figure 9-18**: Potential influence of Sr into the geopolymers structure, left side: charge balancing cation, right side: integrated into the geopolymer gel based on results for tobermorite.

### 9.4.4 Conclusion

This research has shown that independent on the type of Sr, low concentrations can be successfully immobilised. However, when Sr is present as Sr(NO$_3$)$_2$ the activation solution is neutralised, metakaolin cannot dissolve and a geopolymer structure is not formed. This significantly influences the leaching of Sr. When Sr is present as Sr(OH)$_2$, Sr can be immobilised up to a molar ratio of 0.6 Sr/Al.
CHAPTER 10  CONCLUSION AND FUTURE WORK
CHAPTER 10 CONCLUSION AND FUTURE WORK

10.1 Conclusion

The feasibility of using metakaolin based geopolymers to encapsulate ILW has been studied. This work has focused on two problematic waste types, Magnox swarf waste contaminated with trace Al metal and clinoptilolite loaded with Cs/Sr.

Key conclusions from the research are:

1. Metakaolin derived geopolymers have poor stability during drying and high porosity due to the high water required during mixing to achieve good paste flow properties.

2. Geopolymers contain a critical amount of structural water. Removal of structural water causes shrinkage and cracking, and this can occur when samples are stored at a relative humidity below 80%.

3. Shrinkage cracking can be reduced by the addition of inert filler. It was found that the size of the filler particles is critical and that up to 30 volume percent filler addition can be added without adversely affecting workability. When the filler size is below 110 μm a higher amount of filler has to be added to reduce the shrinkage and cracking during drying. The higher water demand to maintain good workability leads to increased final open porosity.

4. The porosity can be reduced by using active fillers such as MgO or Portland cement. These types of filler can interact with the excess mixing water.

5. The Magnox swarf/Al metal encapsulation experiments showed that Magnox swarf can be encapsulated, but when Al metal is present the pH of the system needs to be reduced.

6. Geopolymer pH reduction can be achieved using a metakaolin with a low molar Si:Al ratio and by controlling the Al:Na ratio. As a result, a silicate solution with a high content of silicate has to be added to obtain a molar Al:Si ratio of 1:2 and sodium silicate solution can buffer the activation solution. However, using an activation solution with a lower pH does not avoid corrosion of the Al surface but reduces the extent so that stress cracking is avoided.

7. The encapsulation experiments using Cs and Sr contaminated clinoptilolite showed that the surface of clinoptilolite dissolves in high pH environments and immobilised Cs and Sr are released.

8. Ion exchange reactions of Cs and Sr on the clinoptilolite occur with Na and/or K cations from the activating solution.
Conclusion and future work

9. It was shown that Cs can be successfully immobilised in metakaolin derived geopolymer. Cs acts as a charge balancing cation and replaces the initial cation within the geopolymer. Leaching tests showed Na and K are preferentially leached compared to Cs.

10. The improved retention of Cs in Na-based geopolymers is believed to result from either the HSAB principle or the formation of nano-crystals which contain Cs ions.

11. Sr$^{2+}$ ions are believed to be contained in the geopolymer structure.

12. The mechanical properties of metakaolin derived geopolymers were found to be independent of the type of metakaolin.

10.2 Further work

In this study it was shown that metakaolin based geopolymers can be used to encapsulate and immobilise Magnox swarf/Al metal and Cs/Sr contaminated clinoptilolite. However, further work is necessary to expand upon the findings reported in this thesis. These have been identified and are discussed below.

10.2.1 Further characterisation of different formed geopolymer gels

In Chapter 5 it was found that seeding influences the setting time. This difference can have an influence on the gel structure formed in geopolymers. Further work is required to understand the structure of geopolymer gels and the importance of seeding on the structure. In addition, it is important to investigate size effects of seeds, to see how the seed sizes influence the final geopolymer structure and what quantity of seeds have to be added to obtain materials with improved mechanical properties.

10.2.2 Modelling drying shrinkage

It was shown that geopolymers shrink during drying. This shrinkage can result in cracks and loss of mechanical properties. It has been suggested that the amount of critical water in the geopolymer structure is related to the charge balancing ion and can be considered as hydration sphere water. In this study, only experimental data was used to draw this final conclusion. These results have been based on macro-scale samples. However, a more sophisticated method to understand drying shrinkage and the influence of relative humidity of geopolymers would be by using molecular modelling. In the last decade, molecular modelling methods have been
Conclusion and future work

Increasingly used to simulate a wide range of materials and to evaluate microscopic structure, physical, and thermo-dynamic properties. This is especially useful for clays and related hydroxide minerals which are poorly crystalline materials where experimental structural characterisation is limited. A theoretical treatment can provide significant insight into understanding the structures and properties of these complex phases on a molecular level.

10.2.3 Cs and Sr in geopolymers

Chapter 9 concluded that geopolymers can successfully immobilise Cs and Sr. In this thesis different techniques were used to gain a fundamental understanding of interactions of Cs and Sr in the structure. It was concluded that Cs replaces Na as a charge balancing cation and Sr is built into the geopolymer structure. These results were based mainly on leaching results. However, a more accurate technique that could be used to further investigate and confirm these findings is NMR.

Also, in this work each ion was investigated separately. To use geopolymers for encapsulation and immobilisation of Cs/Sr contaminated clinoptilolite a more detailed study is required to investigate the behaviour of the mixed ion waste.

10.2.4 Optimising geopolymers/clinoptilolite mixtures

It was concluded that geopolymers can be used to encapsulate clinoptilolite. However, it was recognised that by mixing dry clinoptilolite with geopolymers paste the viscosity increased due to water absorption during wetting. Wet geopolymer pastes did not set completely due to excess water. Research is required to improve the w/s content so that clinoptilolite does not increase the mixing viscosity and samples attain the minimum required mechanical properties.

10.2.5 Large scale experiments

The use of geopolymers to encapsulate Magnox swarf and Al metal has been successfully demonstrated. However, all of these experiments were carried out on a laboratory scale which is not representative of industrial application. To verify the feasibility of the investigated geopolymers for “real life” intended purpose, large scale experiments have to be conducted.
10.2.6 Optimising inert/active filler geopolymers

Although, the results for geopolymers mixed with inert and active fillers are promising, further work is required to optimise mixed proportions. This is necessary due to the difference in size of the inert and active fillers as this is a key factor in reducing drying cracking.

10.2.7 Fire resistance

Previous studies showed that geopolymers are fire resistant and can be heated to approximately 1100 °C before melting. During the heating process the material densify at around 850 °C and changes to crystalline nepheline (Kuenzel et al., 2012). However, those experiments were conducted using small samples. A problem which has not been addressed is the fire resistance of large samples in sealed containers. Geopolymers have a high water content which remains in the structure after geopolymerisation. Furthermore, when used for nuclear waste encapsulation the material is stored in closed metal drums. During a fire, geopolymers are heated rapidly. A concern is that the water evaporates but because of the closed system stays in the drum and explosion can occur. Recent literature has stated that due to the development of numerical techniques and an enhanced knowledge of the thermal and mechanical properties of materials at elevated temperatures, it is possible to determine the fire resistance by modelling. With this technique it should be possible to model the fire resistance of geopolymers on a larger scale as reported to use these materials for nuclear waste encapsulation.
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Products which are Stable for Intermediate Storage or Repository-Independent in Final Storage. *International Conference on Waste Management WM-06.* Tucson, Arizona, WM Symposia.


APPENDIX

A-1 Dissolution of metakaolin in 1 wt% HF and 8 M NaOH solution over time

Figure A-1: Dissolution of metakaolin in 1 wt% HF and 8 M NaOH solution over time.
## Appendix

### A-2 Size effects during drying

![Graph showing changes in flexural strength upon drying of prismatic samples comparing different sizes. Small sample = 8 x 8 x 40 mm³, big sample = 25 x 25 x 80 mm³. The molar Al:Si:Na:H₂O ratio was 1:2:1:9.5 and data points were averages of 5 measurements.]

**Figure A-2:** Changes in flexural strength upon drying of prismatic samples comparing different sizes. Small sample = 8 x 8 x 40 mm³, big sample = 25 x 25 x 80 mm³. The molar Al:Si:Na:H₂O ratio was 1:2:1:9.5 and data points were averages of 5 measurements.

### A-3 Accelerated ageing

To investigate the phase transition of geopolymers after a long time, accelerate ageing was used. To accelerate the ageing, samples were cured at accelerated temperatures. This is a standard technique for cement based materials and has already been employed for geopolymers (Lloyd, 2008, De Silva and Sagoe-Crenstil, 2008, Litherland et al., 1981). The ageing test proposed by Lloyd has been used in this study (Lloyd, 2008). After mixing, the samples were placed in sealed PE bags and cured at ambient temperature (22 ± 3 °C) for 28 days. Further curing was carried out either at ambient temperature or at moderately elevated temperature (75 °C) to accelerate the ageing process. Samples were analysed after 3, 6 and 9 months after further curing.
To produce the geopolymers Agrical M1200 was used as metakaolin and the final molar Al:Si:Na:H₂O ratio was 1:1.6:1:9 and 1:2:1:9. Samples were prepared as explained in section 4.2.

**Figure A-3:** The effect of curing time, curing temperature and Si:Al ratio on the evolution of crystalline phases in Agrical MK based geopolymers. Where a = initial crystalline phase (SiO₂); b = Faujasite; c = sodium aluminium silicate; d = Zeolite P1.