

Encapsulation of Cs/Sr contaminated clinoptilolite in geopolymers produced from metakaolin

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Abstract

The encapsulation of caesium (Cs) and strontium (Sr) contaminated clinoptilolite in Na and K based metakaolin geopolymers is reported. When Cs or Sr loaded clinoptilolite is mixed with a metakaolin geopolymer paste, the high pH of the activating solution and the high concentration of ions in solution cause ion exchange reactions and dissolution of clinoptilolite with release of Cs and Sr into the geopolymer matrix. The leaching of Cs and Sr from metakaolin-based geopolymer has therefore been investigated. It was found that Na-based geopolymers reduce leaching of Cs compared to K-based geopolymers and the results are in agreement with the hard and soft acids and bases (HSAB) theory. Cs ions are weak Lewis acids and aluminates are a weak Lewis base. During the formation of the geopolymer matrix Cs ions are preferentially bound to aluminate phases and replace Na in the geopolymer structure. Sr uptake by Na-geopolymers is limited to 0.4 mole Sr per mole of Al and any additional Sr is immobilised by the high pH which causes precipitation of Sr as low solubility hydroxide and carbonate phases. There was no evidence of any other phases being formed when Sr or Cs are added to metakaolin geopolymers.

Keyword: Leaching, encapsulation, nuclear waste, clinoptilolite

Introduction

Geopolymers are inorganic materials containing a network of Si-O-Al bonds. The aluminate and silicate groups have tetrahedral structures. Al bonded to four oxygen atoms has a negative charge and this is balanced by an alkaline ion, typically Na⁺ or K⁺. The production of a geopolymer requires aluminate and silicate materials [1]. Alumino-silicates are typically solids while additional silicate is added as an alkaline silicate solution [2]. Metakaolin (MK), coal fly ashes and metallurgical slags are typical alumino-silicates [3, 4] and these are mixed with a highly alkaline solution or alkali silicate solution [5-9]. On mixing dissolution/precipitation reactions occur which results in the formation of a geopolymer structure [10].

Geopolymers have been proposed as a potential replacement for Portland cements because of their lower carbon footprint and suitable mechanical properties [11-14]. Significant research has been completed to understand the reaction kinetics, the influence of different alumino-silicate sources, and the influence of reaction parameters such as the curing temperature and time on mechanical properties [15-17]. Further properties such as fire and acid resistance, micro-bacterial resistance and high compressive strength make geopolymers attractive materials to encapsulate intermediate level nuclear waste (ILW) such as radioactive Cs and Sr [18-24] produced during fission of uranium [25]. Radioactive 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 [26, 27]. There it undergoes β decay which can damage the cell structures. Radioactive Sr has similar properties to Ca and therefore concentrates in bones and teeth [28, 29] with Sr decay causing bone tumours and leukaemia.

The radioactive isotopes of Cs and Sr are always present in the cooling water of nuclear reactors and in storage ponds as ions and this means the water cannot be disposed into the sea until Cs and Sr have been removed. The natural zeolite clinoptilolite has high exchange capacity for both ions and is widely used as an absorbent. The clinoptilolite is then classified as intermediate level waste (ILW) and therefore needs to be encapsulated [30]. The most widely used encapsulation matrices for ILW are cement-based systems. It has been reported that the high pH of cement paste will partially dissolve clinoptilolite with ion exchange of Cs and Sr [31-33] and when these elements are released into the cement matrix further leaching may occur.

Geopolymers have been proposed as an alternative encapsulation matrix for Cs and Sr loaded clinoptilolite [22] and the aim of this research was to understand the behaviour of Cs and Sr doped clinoptilolite when encapsulated in metakaolin based geopolymers.

Materials and Methods

Materials

A commercially available metakaolin (MK) was used in all experiments (MetaStar 501, Imerys, UK). The chemical composition (XRF) and the mean particle size of the MK are shown in Table 1. Activating solutions were prepared using sodium silicate solution (26wt% SiO₂/8wt% Na₂O, VWR International, Pennsylvania, USA), potassium silicate solution (23.4wt% SiO₂/11.5wt% K₂O, PQ Corporation, UK), NaOH pellets and KOH pellets (Fisher Ltd, New Hampshire, USA) and deionised water. Caesium hydroxide (CsOH) and strontium hydroxide (Sr(OH)₂) were obtained from Sigma-Aldrich (Missouri, USA). Clinoptilolite (KNa₂Ca₂(Si₂₉Al₇)O₇₂ x 24H₂O) with a particle size of between 1 and 4 mm was obtained from Sellafield (UK) to produce a simulated nuclear waste. This was loaded with Cs and Sr ions using caesium nitrate (CsNO₃) and strontium nitrate (Sr(NO₃)₂) solutions (Fisher Ltd, New Hampshire, USA).

Sample preparation

The molar Al:Si:x:H₂O ratio was 1:2:y:9, where x = sodium or potassium and y = 0.7, 1.0 or 1.3. A H₂O/Al ratio of 9 was chosen to obtain a low viscosity paste to ensure suitable mixing. The activating solution was prepared using appropriate quantities of sodium silicate solution, KOH/NaOH and water and these were mixed and stirred for 24 hours. After reaching equilibrium the activation solution was mixed with metakaolin and CsOH and Sr(OH)₂. The paste formed was stirred for 3 minutes and then placed in sealed polyethylene bags for curing at ambient temperature (22±3°C) for 14 days. Previous encapsulation experiments had added Cs and Sr as nitrates [22]. However, during preliminary tests mixing up to 12.5 wt% of CsNO₃ and Sr(NO₃)₂ in the geopolymer paste decreased the paste pH and this led to incomplete dissolution of metakaolin and incomplete geopolymer formation. Furthermore, it was assumed that if Cs and Sr are leaching from clinoptilolite they would form hydroxides because of the high pH of the activating solution.

Preparation of simulated waste

Simulated ILW in the form of contaminated clinoptilolite was prepared by mixing 25g of clinoptilolite with 250 ml of solution containing 0.5 M CsNO₃ and 0.5 M Sr(NO₃)₂. This was heated to 60°C and stirred at this temperature for 4 days. After cooling to room temperature, the clinoptilolite was washed with deionised water to remove unabsorbed Cs⁺ and Sr²⁺ ions and dried at 110°C. The contaminated clinoptilolite was then dissolved in 1M HCl and analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) from Perkin Elmer (Massachusetts, USA). It was found that clinoptilolite had absorbed 18wt% of Cs⁺ and 3wt% of Sr²⁺.

Structural interactions of clinoptilolite with geopolymers

To determine the effect of potential dissolution of clinoptilolite after encapsulation, dry clinoptilolite was mixed with geopolymer paste, placed in a plastic mould, covered with cling film to avoid moisture evaporation and cured for 14 days at room temperature. After demoulding, approximately 2 mm of the surface was removed and analysed using SEM-EDX (JEOL JSM6480LV, Massachusetts, USA). To simulate the stability of Cs⁺ and Sr²⁺ contaminated clinoptilolite after mixing with the activation solution, different buffer solutions with a pH of 10 to 13.5 have been prepared. In this study, it was demonstrated that this pH range corresponds to the potential pH-value of the geopolymer paste after metakaolin is mixed with the activation solution. 100mg of contaminated clinoptilolite have been milled to a mean particle size of 44µm, dried at 110°C for 24h and mixed with 10ml buffer solution. The suspension was stirred for 7 days at RT, filtered and analysed by ICP-OES (Optima 7300 DV, Perkin Elmer, Massachusetts, USA).

Leaching of Cs and Sr

Leaching of Cs and Sr from geopolymer samples was determined using European Standard BS EN 12457-2:2002 [34]. After 14 days curing, samples were dried at 110°C for 24 hours, milled to a mean particle size of 44 µm and 1.50 g of the milled material mixed with 15 ml deionised water and stirred for 1 day at room temperature. The solutions were then filtered and analysed by ICP-OES (Optima 7300 DV, Perkin Elmer, Massachusetts, USA).

Interactions of Cs and Sr with the geopolymer matrix

Changes in the crystalline structure due to incorporation of Cs and Sr were assessed using Cu K α radiation diffraction (PANalytical X-Pert Pro MPD diffractometer, Philips, Netherlands).

In addition, Sr containing samples have been analysed using thermo-gravimetric analysis (TGA, Netzsch-STA 449 f1 Jupiter, Germany). TGA/DSC measurements were only conducted for Sr containing samples because previous work showed that Cs does not influence the properties at high temperatures [35].

pH change during setting and leachate pH

To measure the change of the pH during setting and curing of geopolymers as well as of the leachate, geopolymer samples were prepared as explained earlier and the pH measured by extraction. Samples were milled without drying to a fine powder (mean particle size 44 μm) and mixed with deionised water at a w/s ratio of 3:2 ml/g [36]. This was the lowest possible w/s ratio as it has been suggested that low w/s ratios provide more accurate results [36]. The mixtures were stirred for 15 minutes to obtain equilibrium. Before each measurement, the pH meter (FisherbrandHydrus 500 pH-meter, New Hampshire, USA) was calibrated using a three point calibration.

Results and Discussion

Interaction of clinoptilolite with the geopolymer matrix

The interface between a clinoptilolite particle and the Na based geopolymer encapsulation matrix is shown in Figures 1, with similar results obtained using K based geopolymer. Figure 1 shows that a clear interfacial transition zone (ITZ) forms between the clinoptilolite particle and the geopolymer matrix. In this zone, the molar Si:Al ratio gradually increases from 2 at the edge of the ITZ to 5 near the clinoptilolite particle as can be seen in Figure 1b. The thickness of the ITZ zone is approximately 0.15 mm. The Si:Al ratio of 2 agrees with the composition of the geopolymer matrix, whereas as a Si:Al ratio of 5 is consistent with the Si:Al ratio in clinoptilolite. The gradual change of the Si:Al ratio in the ITZ indicates that as the geopolymer matrix forms the surface of the clinoptilolite dissolves due to the high pH. This means that the mechanical properties in the ITZ will be different from those of clinoptilolite and the geopolymer matrix [8, 37]. Furthermore, a crack between the geopolymer matrix and the clinoptilolite particle can be seen. This crack appeared during the SEM analysis and is due to water evaporation following shrinkage of the geopolymer matrix after the vacuum was applied.

In previous work, it was demonstrated that metakaolin based geopolymers have the tendency to shrink and crack when structural water is removed [38].

The formation of an ITZ with a length of 0.15 mm indicates that during geopolymerisation the surface of clinoptilolite dissolves and the released aluminates and silicates take part in the reaction. This dissolution of clinoptilolite is most likely initiated from the high pH of the activation solution, although a decrease over time is measured, as shown in Figure 2a. This decrease over time is due to the consumption of hydroxides during the dissolution process and polymerisation step. Based on the measured pH in the geopolymer matrix, buffer solutions were prepared covering the expected pH range and the dissolved Si^{4+} and Al^{3+} and released Cs^+ from Cs/Sr contaminated clinoptilolite were measured using ICP-OES. The dissolution results are shown in Figure 2b. Although this dissolution method does not consider any precipitated products such as $\text{Al}(\text{OH})_3$, it can be seen that dissolution of clinoptilolite starts at a pH of 11 and as the pH increases more Si and Al dissolves. Of interest is that Cs ions are already released into the leachate at a pH of 10 when no dissolution of clinoptilolite can be measured. This is due to ion exchange reactions which take place when clinoptilolite is in contact with high concentration solutions [33]. However, as soon as the pH is high enough to dissolve the surface of clinoptilolite, even more Cs is released into the leachate. It is most likely that Sr is also released during the dissolution but this has not been measured due to the low solubility of $\text{Sr}(\text{OH})_2$ at high pH values.

Leaching of Cs from geopolymers

It is clear that Cs and Sr have potential to migrate into the encapsulating matrix during geopolymer formation although precise quantification of this effect is difficult. It is expected that near clinoptilolite particles the Cs^+ and Sr^{2+} concentration will be higher and that this will reduce gradually with distance and therefore it is necessary to investigate the leaching of Cs and Sr ions from a geopolymer matrix. However, both ions have different characteristics and will have different chemical interactions with the geopolymer matrix.

The interaction of Cs with geopolymer paste was studied by varying the molar Al:x (x=Na or K) ratio while keeping the molar Al:Si ratio constant at 2 [39]. The molar Al:x ratio was varied between 0.7 and 1.3 and the corresponding leaching results are shown in Figures 3 and 4. Leaching of charge balancing cations occurs before Cs is added and the release of Na

demonstrates that metakaolin does not fully react during the formation of the geopolymer matrix [40]. Leaching of Na and K reduces when the molar Al:x ratio is reduced to 1:0.7 and remains low even when Cs is added. Cs⁺ ions accelerate dissolution of metakaolin and act as additional charge balancing cation. When the molar Al:x ratio is higher at 1.0, leaching of Na and K increases. No Cs initially leaches from the matrix, independent of the amount of Na or K or whether Na or K is used. However, when high Cs concentrations are present this effect only remains for Na based geopolymers. When K is used as the charge balancing cation, Cs begins to leach at molar Al:Cs ratios of 1:0.2. This indicates that K-based geopolymers have a lower selectivity for Cs compared to Na-based geopolymers which is in agreement with previous studies [41]. This observed selectivity of Cs when Na and K are present is probably due to the hard and soft acids and bases (HSAB) principle [42, 43]. By comparing the charge densities of the different ions it can be seen that Na⁺ has the highest charge density due to a small ion radius followed by K⁺ and then Cs⁺ as shown in Table 2. This means that Na⁺ is a stronger Lewis acid compared to K⁺ and Cs⁺. Furthermore, by considering Al(OH)₄⁻ as a weak Lewis base, a reaction between aluminate and Cs⁺ is favoured, followed by K⁺ and Na⁺. However, the charge density of Cs⁺ and K⁺ is fairly similar which means that with increasing Cs content, aluminate selectivity reduces due to the high availability of each ion. This explanation is in agreement with previous work where for a mixed K/Na system it was observed that K⁺ was preferentially absorbed at AlO₄⁻ sites rather than Na⁺ [44].

The amount of leached Na and K also indicates the applicability of the HSAB principle. When Cs is replacing Na or K as the charge balancing cation, the amount incorporated should displace an equal amount of the charge balancing cations. When 0.1mol Cs is incorporated, 0.1mol of either Na or K should be released as seen in Figures 3 and 4 for a molar Al:Na/K ratios of 1:1. The interaction of Cs with the geopolymer matrix appears limited to an exchange with the charge balancing counter ions. There is limited change to the geopolymer structure as shown in Figure 5, as the XRD data is that of a normal geopolymer, with an amorphous phase being the main feature.

Encapsulation of Sr in Na based geopolymers

The encapsulation of Cs in geopolymers shows promising results and these are enhanced when Na is used as the charge balancing cation, in agreement with the HSAB principle. Therefore, the Sr encapsulation experiments focussed only on Na based geopolymers.

Leaching results are shown in Figure 6. Without adding Sr, approximately 0.1 mol Na⁺ ions are leaching from the pure geopolymer, in agreement with Figures 3 and 4. With increasing Sr content in the geopolymer the amount of Na leached from the matrix increases but the Sr leaching remains below detection limit, probably due to the pH of the leachate. Sr(OH)₂ has a relatively low solubility at pH 7 and solubility decreases with increasing pH. At lower Sr concentrations leaching of Na follows a linear trend which is similar to the leaching of Na when Sr replaces Na as the charge balancing cation. This indicates that at least some of the Sr is the charge balancing cation. With increasing Sr concentration the linear Na⁺ leaching stops and stabilises at approximately 0.4 mol Na per mole Al. This indicates that up to 0.40 mole of Sr per mole of Al can be incorporated as a charge balancing ion.

At higher concentrations Sr could possibly be incorporated in the geopolymer gel structure. For Na based geopolymers containing Ca it has been suggested that a C-S-H or (N,C)-A-S-H gel is formed [45-48]. These studies showed that the aluminate competes with Ca for the free silicates and the formation of CSH gel was observed [45, 49]. Because the chemistry of Sr and Ca are similar Sr may be consumed in a similar manner to Ca in the formation of an analogous gel phase. However, it is difficult to prove the presence of such a gel from the leaching results. Therefore the thermal decomposition behaviour of Sr²⁺ containing geopolymers was determined using thermogravimetric analysis (TGA). In previous studies, TGA has already been used to characterise CSH gel [50, 51]. Here, it was used to evaluate indirectly the Sr uptake by the measurement of the de-hydroxylation of Sr(OH)₂. From the results shown in Figure 7, it can be seen that up to ~300°C the mass loss that occurs can be attributed to the loss of structural water from the geopolymer. Although all samples were dried before measuring, the mass loss is relatively high indicating that the geopolymer samples are hygroscopic and contain free hydroxide groups. Between 400°C and 500°C another mass loss is observed due to de-hydroxylation of Sr(OH)₂ to SrO [52]. From this mass loss it is possible to stoichiometrically determine the amount of un-reacted Sr(OH)₂ shown in Figure 7b. From this figure, it can be seen that for a molar ratio Sr:Al of 0.6 approximately 70% of the added Sr(OH)₂ has reacted and been incorporated into the geopolymer structure. Since 70% of 0.6 is 0.42 mole Sr per mole Al, which is the maximum amount of Sr built in as charge balancing cation, it appears that there is no real evidence for an analogue gel similar to CSH gel in the geopolymers.

The XRD results in Figure 8 strengthen this interpretation of the experimental data. Up to 0.1 mole Sr per mole Al, there are hardly any crystalline phases containing Sr, consistent with Sr

replacing other charge balancing ions, whereas at 0.6 mole Sr per mole Al, significant amounts of strontium hydroxide and strontium carbonate are found. Although there are some peaks that might be attributed to strontium silicate, the majority of the Sr is present as hydroxide or carbonate and the low leaching is due to the low solubility of these phases.

Conclusions

Metakaolin based geopolymers can be used to encapsulate and immobilise contaminated clinoptilolite. However the high pH of the activating solution dissolves the clinoptilolite surface and an interfacial transition zone is formed with higher Al to Si ratio. The dissolution leads to the release of Cs and Sr and the interaction of these ions with the geopolymer. Cs and Sr will exchange with Na and K ions within the geopolymer and therefore become immobilised. Up to 0.2 mole Cs per mole of Al can displace K and a larger amount can displace Na in accordance with the HSAB principle. The uptake by Na-geopolymers of Sr is limited to 0.4 mole Sr per mole of Al. Any excess Sr is also immobilised due to the high pH, which leads to precipitation of the Sr in low solubility hydroxide and carbonate phases. There is no evidence for any other phases forming when Sr or Cs are added to geopolymers.

Acknowledgement

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Table 1: Chemical composition of metakaolin percent and mean particle size.

	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	other oxides	LOI	mean particle size [μm]
MK	59.49	34.01	0.00	1.95	3.09	1.11	3.90

Table 2: Physical properties of Na⁺, K⁺ and Cs⁺ cations [51]. The ion radius is given for a coordination number of 6.

	Na ⁺	K ⁺	Cs ⁺
Ion radius [\AA]	1.02	1.38	1.67
Charge density [Z/r]	1	0.75	0.60

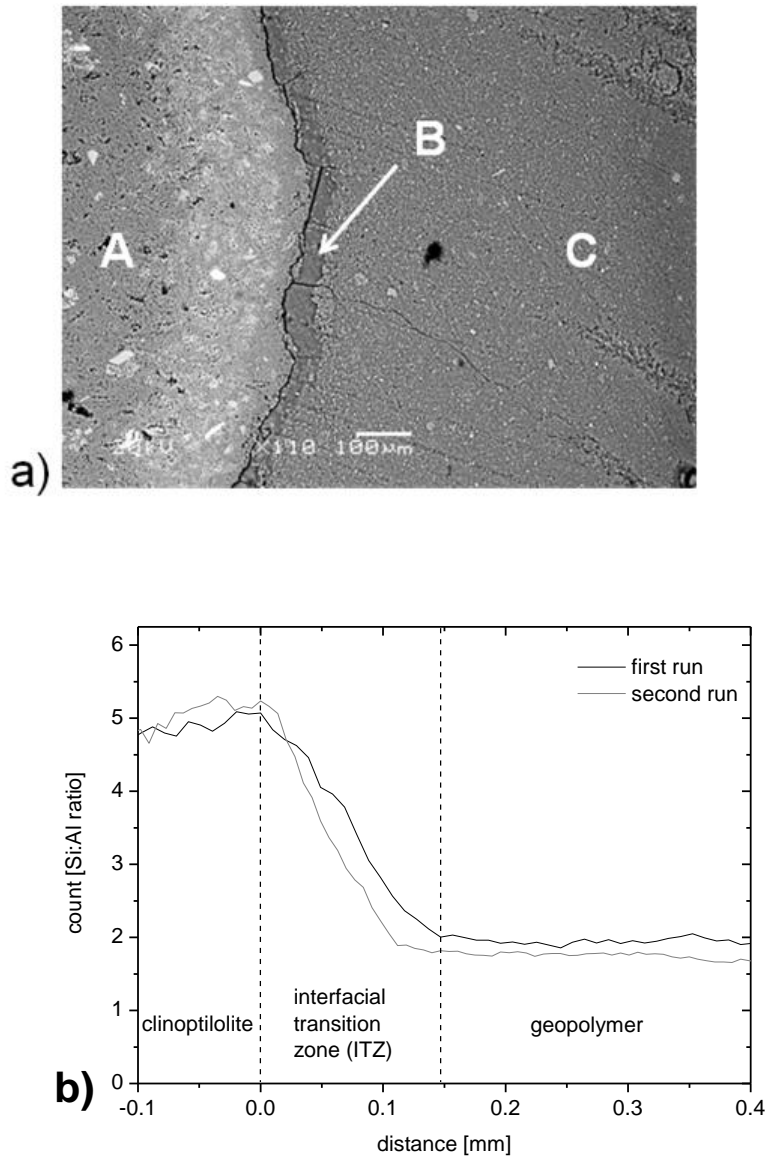


Figure 1: SEM image of polished Na based geopolymer after 28 days curing. The molar Al:Si:Na:H₂O ratio of the geopolymer paste was 1:2:1:9, A = clinoptilolite, B = interfacial transition zone (ITZ), C = geopolymer matrix, b) EDX results of two independent measurements.

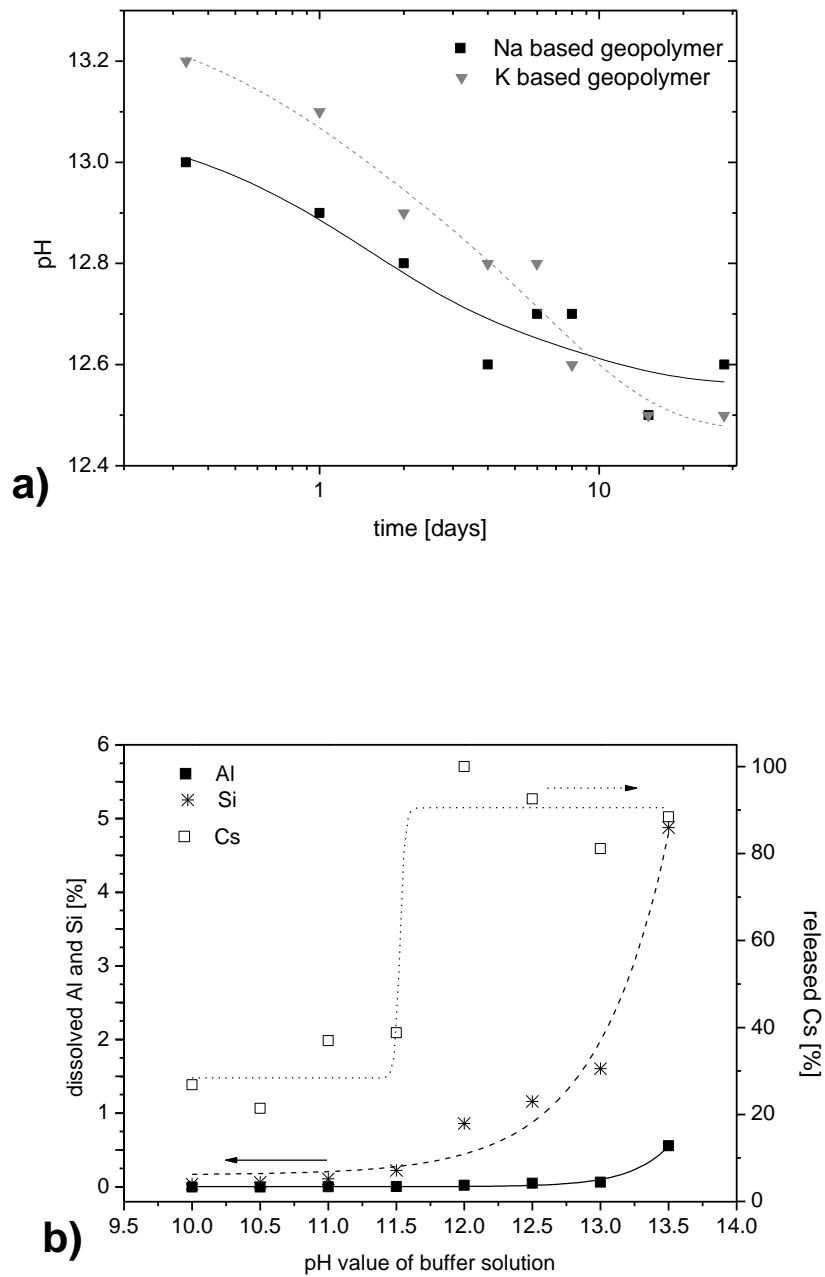


Figure 2: a) Change of the pH value of geopolymers during setting using different cations; b) Dissolution of clinoptilolite and release of Cs⁺ at different pH-values. The measured concentration of Al and Si does not consider any precipitation products.

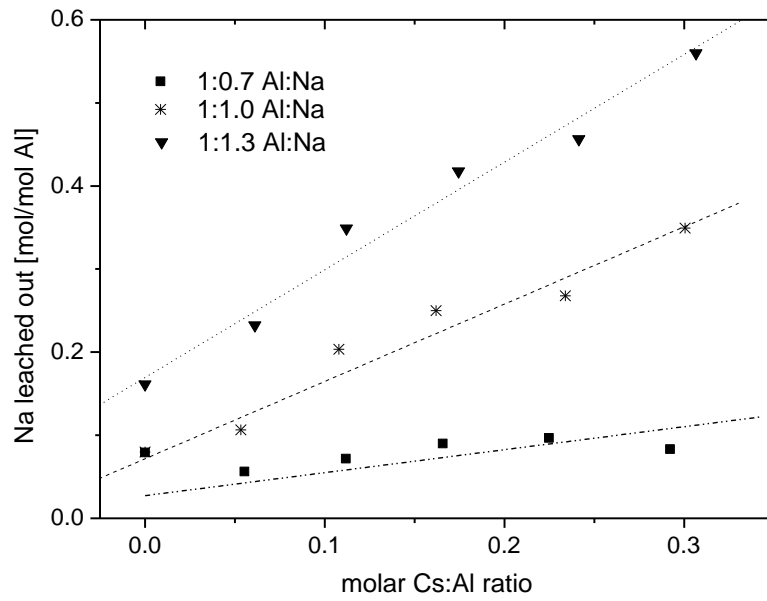


Figure 3: Leaching of Na and Cs of Na-based geopolymers, varying the molar Al:Na ratio, in all cases the Cs concentration was below the detection limit of 5ppm.

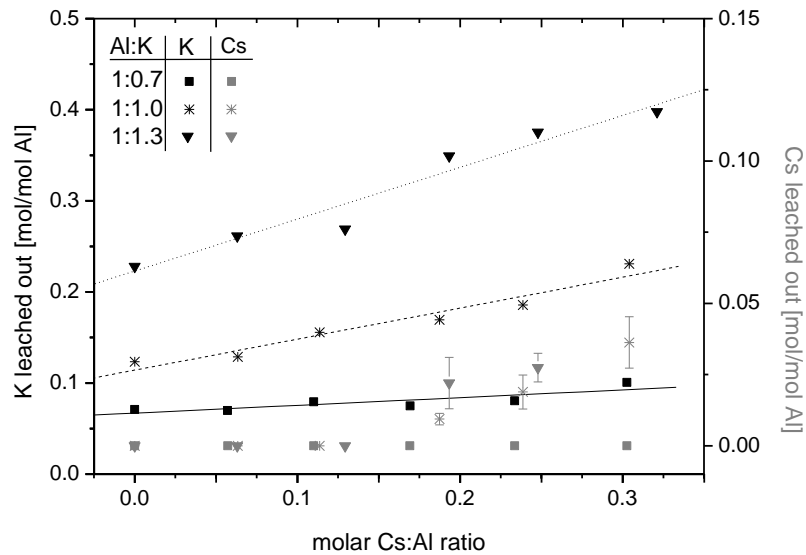


Figure 4: Leaching of K and Cs out of K-based geopolymers, altering the molar Al:K ratio, the molar Al:Si ratio was 1:2.

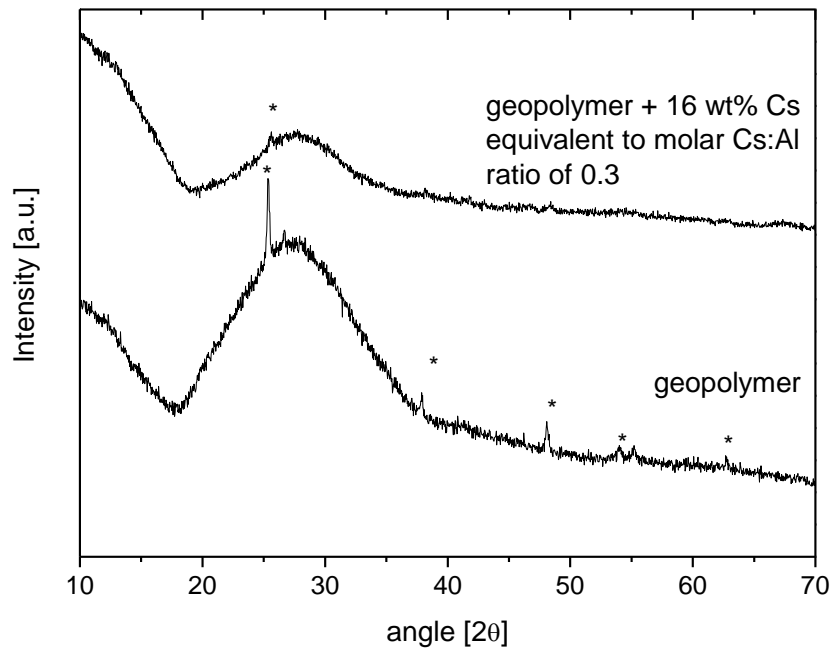


Figure 5: X-ray diffraction data for Na-based geopolymer loaded with Cs. The molar Al:Na ratio was 1:1. Key *= quartz (SiO_2).

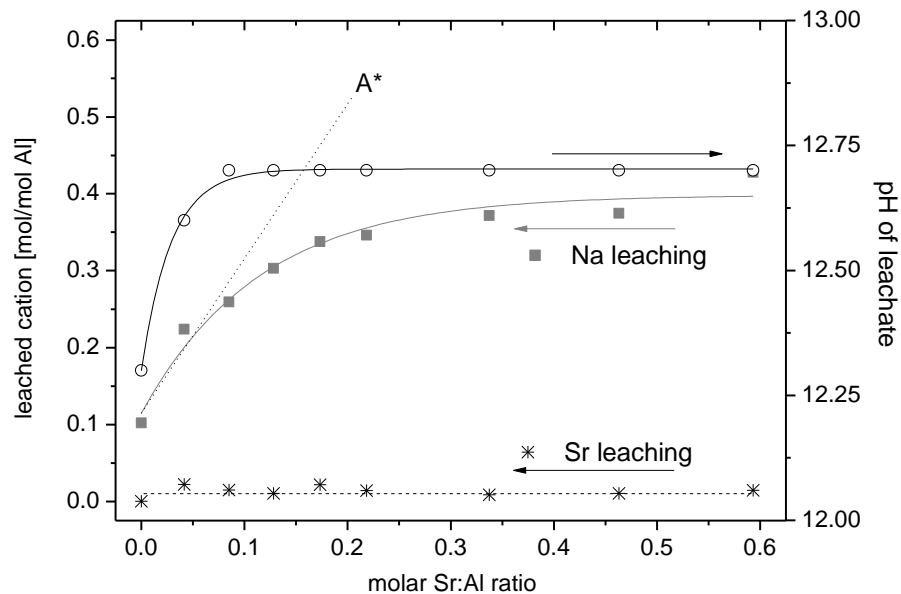


Figure 6: Leaching of $\text{Sr}(\text{OH})_2$ and Na from geopolymers. A*= expected Na leaching if Sr replaces Na as the charge balancing cation. The molar Al:Na ratio was 1:1.

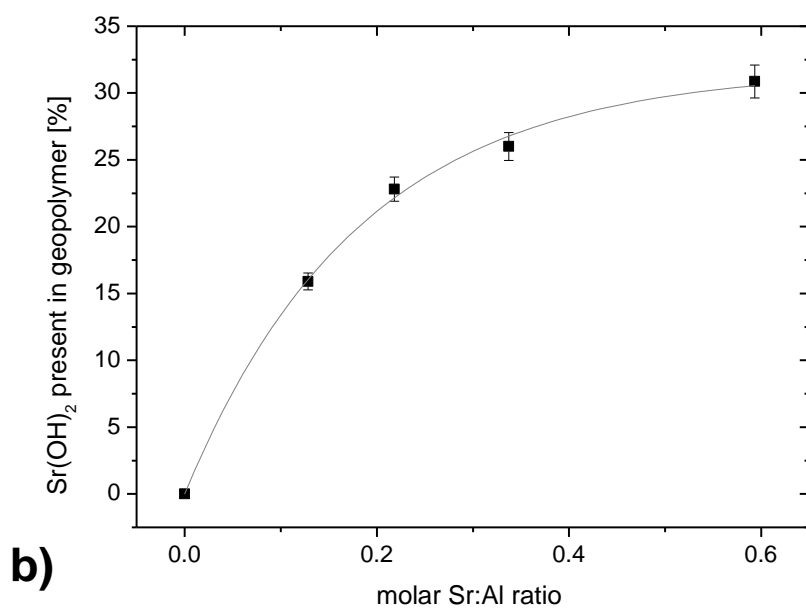
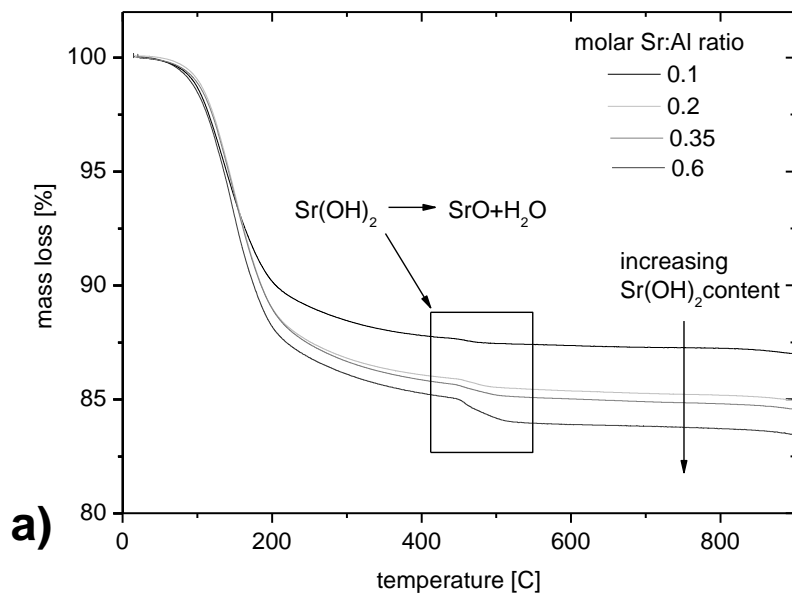


Figure 7: TGA results from geopolymers containing $\text{Sr}(\text{OH})_2$, a) Mass loss over temperature. The numbers for each line represent the molar Sr:Al ratio. b) Calculated $\text{Sr}(\text{OH})_2$ based on TGA results using mass loss from de-hydroxylation.

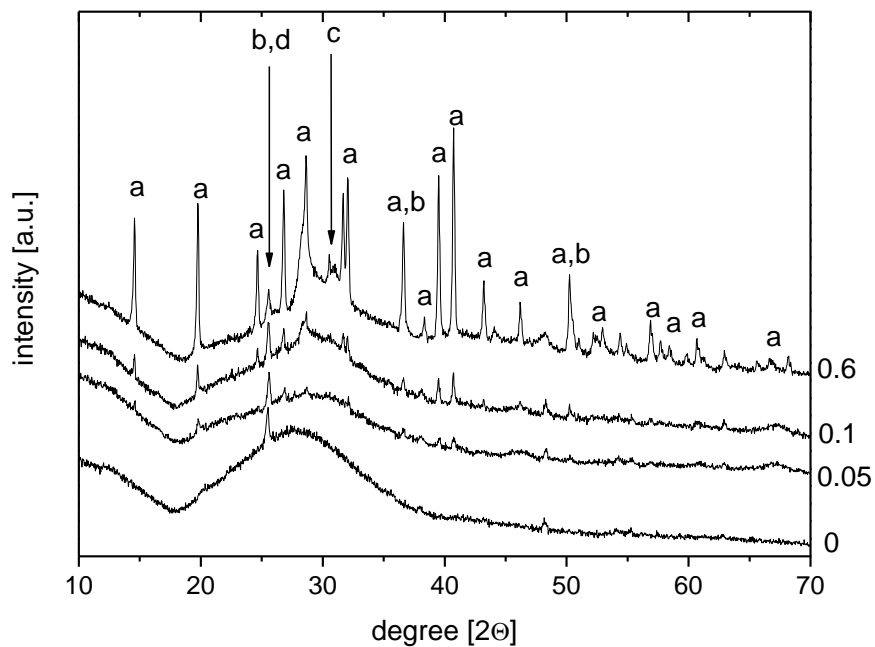


Figure 8: Crystalline phase of geopolymer phases in geopolymers mixed with Sr. The numbers represent the molar Sr:Al ratio. Key: a: $\text{Sr}(\text{OH})_2$, b: SrCO_3 , c: strontium silicate aluminate, d: quartz (SiO_2) from MK.