

Immobilization of Cesium in Geopolymeric Matrix: a formulation study

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1. Abstract

Cementation is widely used as low- and intermediate level radioactive wastes encapsulating process. Among these wastes, cesium ions are yet poorly immobilized by Portland cement based materials. This work consists in an experimental investigation of the ability of geopolymers, which are mineral binders produced from alkali-activation of aluminosilicates, to effectively encapsulate this chemical specie. Geopolymers were synthesized following several compositions based on the activation of metakaolin with sodium hydroxide and potassium hydroxide solution containing cesium. Setting time, mineralogy, microstructure and mechanical properties of the samples were studied during one month. Leaching tests were conducted during the same period to determine the immobilization efficiency. Results strongly depend on the composition of activation solution in term of soluble silica content and alkali used. These parameters control simultaneously the condensation degree and the geopolymeric composition.

2. Introduction

Low and intermediate level radioactive liquid wastes are generated in most nuclear fuel cycle processes. In most cases, solidification and stabilization are required before final disposal. Among several inert binders used to immobilize liquid wastes, Portland cement-based materials are one of the widely used: these are low-cost, available, easy-to-use binders, compatible with aqueous waste streams and capable of activating several chemical and physical immobilization mechanisms for a wide range of inorganic waste species. Due to their high solubility and mobility in cement pore solution, alkali cations, among which cesium ion is a significant component of radioactive waste from nuclear industry, are poorly retained by Portland cement-based materials. In this context, geopolymers may be considered as alternative encapsulating materials. Geopolymers are indeed a class of largely X-ray amorphous three-dimensional aluminosilicate binder materials, usually synthesized by reaction of an aluminosilicate powder with a concentrated alkali metal silicate or hydroxide solution, cured at ambient or slightly elevated temperature [1].

The alkali cations usually used to synthesize geopolymer materials are usually potassium or sodium [2-4]. To the authors' knowledge, only few studies concerned mixed -alkali systems [5], and cesium immobilization was investigated only in trace amount [6]. Due to the possible wide range of cesium concentration in existing or forthcoming industrial wastes, this process as to be extended to higher cesium concentration in cesium alkali-mixed geopolymers; pure cesium-based geopolymers are then a theoretic limit. The aim of this work is to experimentally investigate the cesium encapsulation abilities of geopolymer materials: the incorporation rate has to be as high as possible while maintaining the requirements due to a nuclear industrial process at ambient temperature. Some of these properties may be highlighted: a material as fluid as possible before setting, compressive strength as high as achievable, a good resistance to leaching and a setting time included between 6 and 24 hours. Setting time, mineralogy, porosity and microstructure as well as mechanical strength or leaching behavior of cesium alkali-mixed or cesium-based geopolymers synthesized were studied during one month, and the influence of some formulation parameters investigated.

3. Experimental methods

3.1. Materials

In order to focus on a model system and avoid the precipitation of calcium silicate hydrate phases mixed with geopolymeric materials [7], the choice was made to synthesize metakaolin-based geopolymer paste. This product was purchased under the brand name of Pieri Premix MK from Grace Construction Products. The chemical composition of metakaolin determined by X-ray Fluorescence (XRF) can be found in table 1. Analyses made by X-ray Diffraction (XRD) prove that the metakaolin contained anatase, kaolinite and quartz as impurity. The Brunauer-Emmet-Teller (BET) surface area was 19.9 m²/g and the mean particle size (d50) determined by laser granulometer was 5.9 μm.

Table 1: Chemical composition of metakaolin used in this study

	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	MgO	L.o.I.*
Weight %	54.40	38.40	0.10	1.27	1.60	0.62	< 0.20	< 0.20	1.90

*Loss on ignition

Alkali hydroxide activating solutions were prepared by dissolution of NaOH, KOH (Prolabo, Rectapur, 98%) and CsOH (Alfa Aesar, 99.9%) pellets in Milli-Q water, with all containers kept sealed to minimize contamination by atmospheric carbonation.

Silica added to the mixed is amorphous silica provided by BDH with a mean particle size equal to 128.81 μm .

3.2. Geopolymer Synthesis

The mix was performed in two steps. During the first step alkali silicate solutions were prepared by dissolving and mixing amorphous silica in alkali hydroxide solution during 30 minutes. The alkali hydroxide (MOH) solutions were prepared by dissolution of appropriate pellets in Milli-Q water. The composition of these activating solutions can be fully described on the one hand by the nature and, if needed, molar ratio of alkali used, and on the other hand by molar ratio $\text{H}_2\text{O}/\text{M}_2\text{O}$, noted here e , and $\text{SiO}_2/\text{M}_2\text{O}$ noted here s .

During the second step, geopolymer samples were prepared by mixing metakaolin and alkaline silicate solution. The $\text{Al}_2\text{O}_3/\text{M}_2\text{O}$ ratio was fixed equal to 1 in order to maximize mechanical properties [8]. The mix was performed at low speed for one minute and at high speed for two minutes in a standardized laboratory mixer (European Standard EN 196-1). The material was then transferred to 4*4*16 cm Teflon mould, vibrated during few seconds and sealed from the atmosphere. Samples were cured during 1 day at 20°C and at atmospheric pressure before being remove from the mould and stored in airtight bag at ambient temperature and pressure until testing.

3.3. Analytical methods

The fluidity of the mixed material is measured with a Marsh cone test (French standard NF P 18-507) and corresponds to the flow time of 250 mL geopolymer through an 8 mm opening.

The geopolymer setting time was conducted on Vicat apparatus, according to European standard EN 196-3.

Crystallized phases were identified using XRD (Siemens D8 – Copper anode $\lambda_{\text{K}\alpha 1} = 1.54056 \text{ \AA}$ generated at 40mA and 40 kV). Specimens were scanned from 10° to 60° 2 θ at 0.02° 2 θ steps integrated at the rate of 2 seconds per step.

Porosity accessible to water was determined following the AFPC-AFREM recommendation.

Ultimate compressive strength measurements were conducted according to European standard EN 196-1 on samples of geopolymer paste, using a 3R testing machine.

Leaching behavior was studied on material suspensions prepared by mixing crushed geopolymer paste samples (size < 100 μm), cured for 7 days in sealed bag at 20°C, with ultrapure water (liquid to solid ratio of 9 mL/g) and stirring for 24 hours, 7 days and 28 days. In some experiments, a complete solution renewing is conducted after these terms. Na^+ , K^+ and

Cs⁺ concentrations were carried out by ionic chromatography on a Dionex DX 500.

4. Results and Discussion

4.1. Major impacts of e ratio: fluidity of the material

Due to industrial context, the fluidity of the synthesized geopolymer has to be as low as possible after the mix step. Figure 1 represents the flow time of potassium based geopolymer in a Marsh cone test.

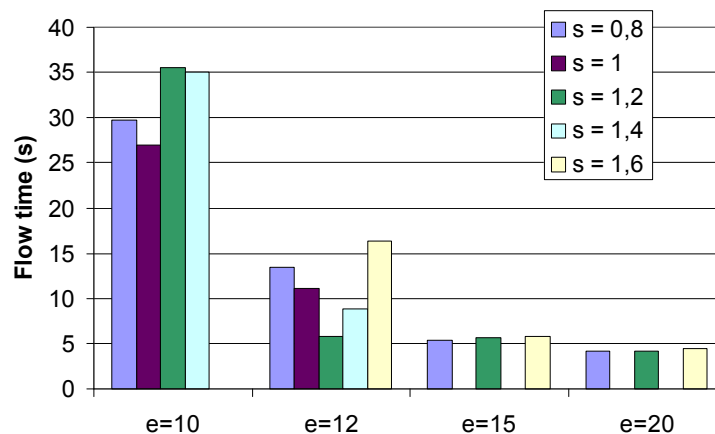


Figure 1: Fluidity evaluated on a potassium-based geopolymer following a Marsh cone test.

The fluidity of the mix increases with e, but a plateau seems to be reached for e greater than 15. No influence of s can be measured for this high e values. For the lesser e value, the global fluidity decreases and the addition of silica in activation solution becomes essential to obtain a fluid mix: without silica the flow was impossible for a K; e=10; s=0 geopolymer. However an optimal s value exists and is function of e and alkali cations used. The fluidity of the material depends mainly on the ratio e and on a lesser extend on the ratio s. Independently of the alkali used, a similar behavior is observed, and e=12 still corresponds to the break in fluidity. Although e could be of one of the parameters controlling mechanical strength, in this work the chose was made to consider fluidity as the first priority and to synthesize geopolymer with e=12.

4.2. Effects of alkali species on geopolymerisation reactions

4.2.1. Effects of the alkali specie on reaction rate

The figure 2 represents diffractograms of metakaolin used and some sodium, potassium and cesium based geopolymers after 28 days storage in airtight bag at ambient temperature.

4.2.2. Effects of the alkali specie on reaction kinetics: setting time

One of the major prerequisites to industrial problem was to obtain a setting time included between 6 and 24 hours. On figure 3, the setting time is plotted in function of the nature of alkali element and on s ratio.

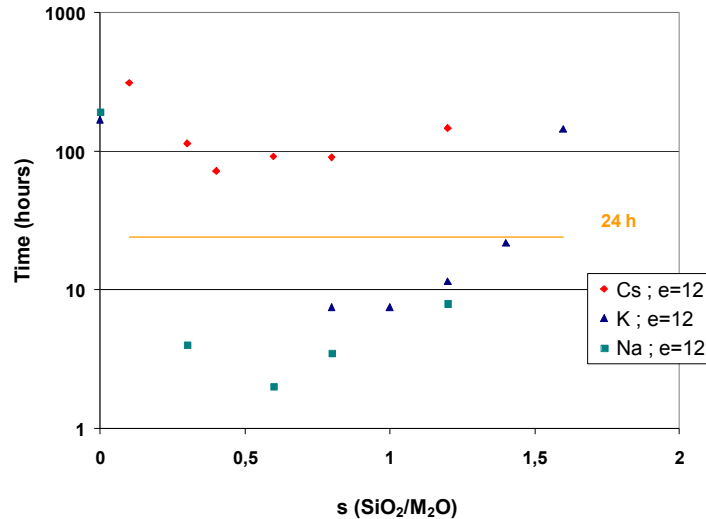


Figure 3: Setting time measured conducted on Vicat apparatus in function of s and alkali ion used for geopolymer synthesis.

These results show clearly that setting time of geopolymer material depends strongly of the alkali used for its synthesis. For each given activation solution composition, the greater the basicity of alkali hydroxide, the slowest the setting. On the other hand, for a given alkali specie setting time greatly depends on s ratio: for sodium-based geopolymers setting time spread from 200 hours for s=0 to 4 hours for s=0.6.

Basing on the present results, an increase in alkali basicity seems to induced simultaneously an increase in reaction rate, as previously observed [5, 9], and a slowing down of reaction kinetics. Some specific investigations are necessary to precise this behavior, for example by considering the structure breaking ability of larger alkali cations in comparison to the smallest [12].

However, on an industrial point of view, none of cesium-based geopolymers reach a setting time equal to 24 hours at 20°C. Without increasing the temperature at which the synthesis is conducted, this value can be obtained by considering mixed alkali geopolymer containing cesium. Some values of setting time are reported in table 2.

Table 2: Setting time of potassium/cesium-mixed geopolymer.

Alkali (M)	Cs/M	s	e	Setting time (hours)
K	0.15	1.2	12	16h30
K	0.3	1.2	12	23h
K	0.5	1.0	12	23h
K	0.5	1.2	12	21h
K	1.0	1.0	12	24h
K	1.0	1.2	12	24h
K	1.5	0.8	12	30h

In this range of activation solution composition, the setting time of the materials seems to be directly linked to the amount of cesium in the material. No influence of s ratio can be noticed. This point corroborates the hypothesis of the ability of cesium to slowing down the geopolymerisation reactions.

4.3. Impact of s ratio: mechanical properties

The influence of s ratio on setting time for a given nature alkali ions was exposed in figure 3. An optimal s value, minimizing the setting time, exists for each alkali ions or each alkali-mixed solution. On an industrial point a view, s ratio may be considered as an essential formulation parameter which allowed reaching the required properties. The influence of s ratio on geopolymer microstructure was reported elsewhere [3].

On a macroscopic scale, this change is expressed by an increase mechanical behavior (Figure 4). In this graph the compressive strength reached at 28 days range from 15 to 50 MPa, depending on s value. At a given s ratio, the smaller the cation, the higher the compressive strength. This underline that an advanced rate of reaction, furthers by large alkalis, does not necessarily mean high mechanical performances at a given time: the structure making ability of smallest alkali cations must also be taken into account.

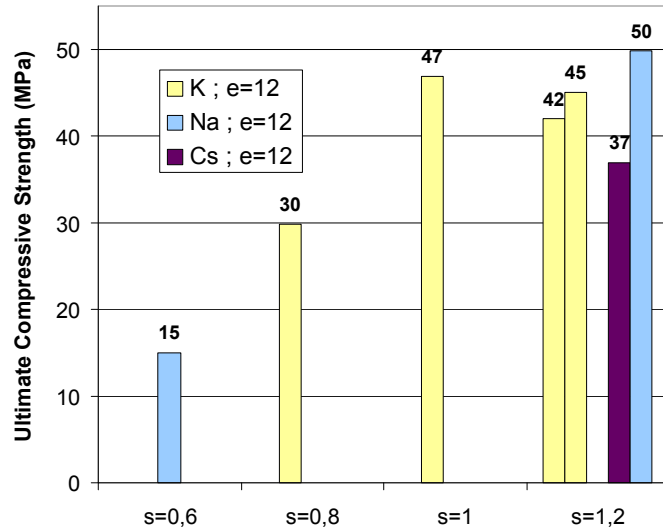


Figure 4: Compressive strength of some sodium and potassium-based geopolymers after 28 days curing.

Concerning the mixed alkali geopolymers, the cesium/sodium based materials present higher compressive strength than cesium/potassium at a given composition. For example a $s=1$, $e=12$ geopolymer reached 34.3 MPa for $Cs/K=1$ and 44.1 MPa for $Cs/Na=1$.

4.4. Alkali/geopolymer interactions: leaching study

Figure 5 summarizes the results of leaching experiments on cesium/potassium alkali-mixed geopolymer after 28 days. A complete renewing of the leaching solution after 24 hours and 7 days does not increase the total amount of alkali leached. Therefore the amount of alkali leached after 24 hours experiment is believed to correspond to the alkali which was not integrated into the geopolymer structure. Indeed, after 7 day curing at ambient temperature, the whole metakaolin has not reacted and the whole aluminum is not integrated into the geopolymeric matrix. An improvement in metakaolin dissolution should also improve the leaching properties of the material.

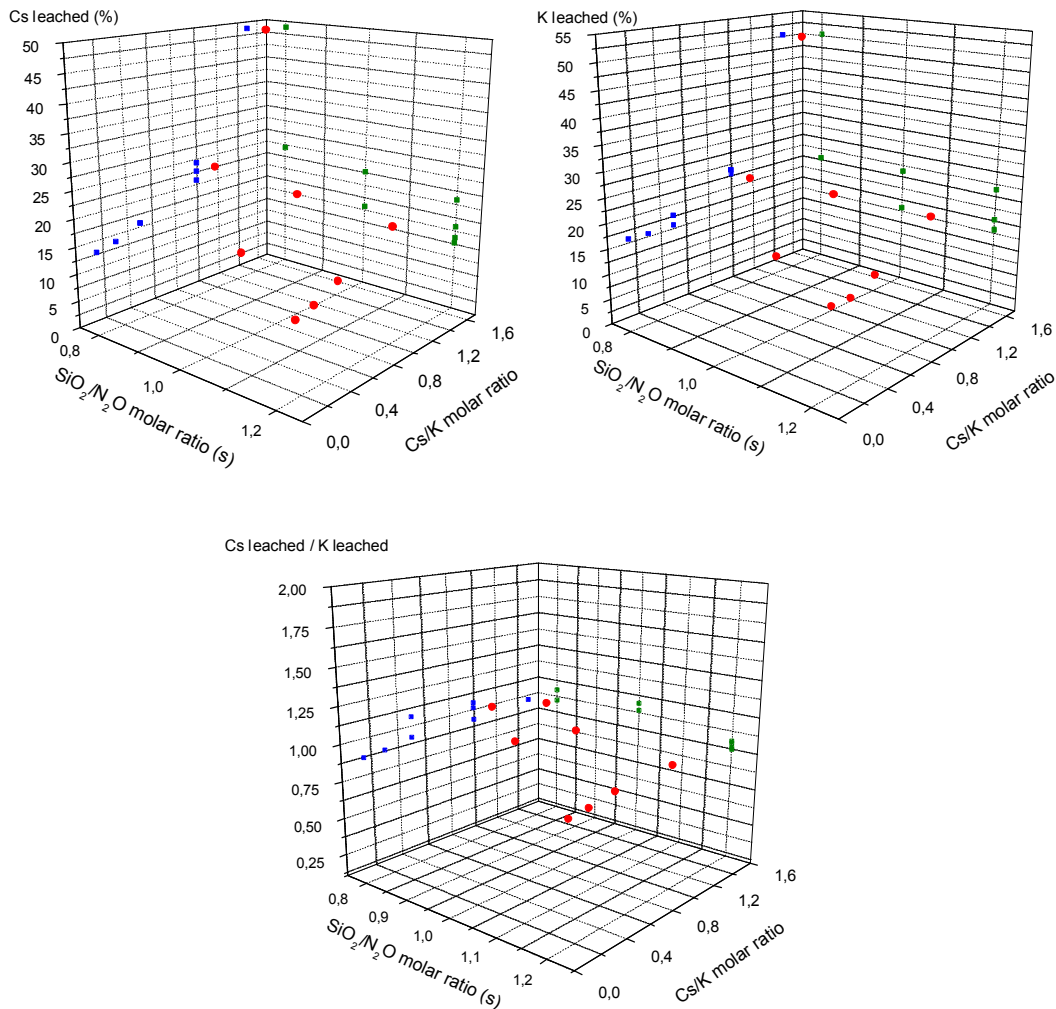


Figure 5: Leaching results on cesium/potassium mixed geopolymers after 28 days.

However, these results highlighted three major comments. First, the higher the cesium concentration, the higher the amount of alkali leached. As underlined in 4.2.2, an increase in alkali basicity induced a slowing down of reaction kinetics: after 7 days of storage the amount of unreacted metakaolin is higher in geopolymers with high cesium content than with low cesium content. The amount of leachable alkali species, *i.e.* not integrated into geopolymer structure, is therefore greater in cesium concentrated systems.

In the composition range of this study, s ratio has also an impact on the amount of alkali leached: an increasing s decreases the leaching of alkali species. This effect is particularly detected between $s=0.8$, for which 50% of cesium is leached, and $s=1$, for which the amount leached corresponds to 25% of initial cesium contain. This point may also be related to the impact of s on mechanical properties (§ 4.3), where compressive

strengths strongly increase for s value contained between 0.8 and 1, and slightly increase for higher s values.

The ratio Cs leached/K leached do not depend neither on s nor on the amount of cesium in activating solution. Furthermore, whatever the geopolymer composition, this ratio remains close to one. This point suggests that cesium and potassium as a comparable leaching behavior in geopolymer system: no one seems to be preferentially incorporated into the geopolymer binder.

5. Conclusion

In this work, the cesium encapsulation abilities of geopolymeric binders were experimentally investigated. Cesium-based and cesium/alkali mixed geopolymers were synthesized at ambient temperature and tested in terms of setting time, mineralogy as well as mechanical strength or leaching behavior.

This study has highlighted some new points. The geopolymerisation reactions involving cesium, and leading to material set, are much slower than those involving smaller alkalis (sodium and potassium), but the amount of unreacted raw materials is lesser. At a given geopolymer composition, the use of cesium in activation solution decreases the mechanical strength. This comforts the point previously noted, that geopolymer properties depend on the alkali used and probably more precisely on the alkali cation hydration sphere which controls the local structure of geopolymers and affects therefore the properties of the whole material. Some complementary and specific analyses are still needed to precise the cesium behavior in geopolymers.

On an industrial point of view, some enhancement may be proposed, as synthesized the binder at a slightly elevated temperature or the use of mortar-based geopolymer to increase the overall performances. In pure geopolymer pastes, the only way to synthesize material reaching the criteria of setting time below 24 hours is to consider cesium/alkali mixed binders, considering the s ratio as a key formulation parameter.

Geopolymers may be considered as alternative wastes encapsulating materials, but an increase in immobilization efficiency can only be reached by a more extensive understanding of geopolymerisation reactions. This knowledge is the only way to allow future geopolymer formulations to be designed on a microstructural and chemical level for specific applications.

6. References

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