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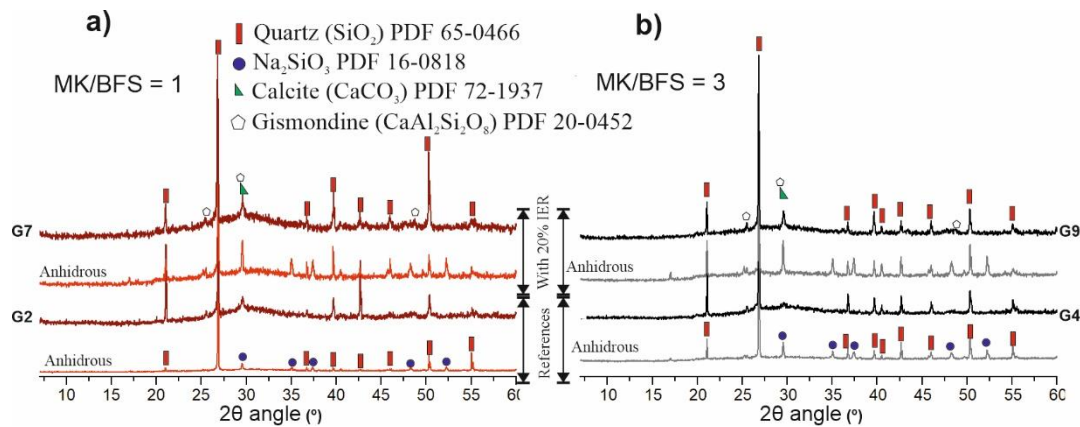


Figure 71. XRD patterns of geopolymer, without and with 20% IER, formulated with a) 9%Na₂O-MK/BFS=1, and b) 12%Na₂O-MK/BFS=3. The anhydrous corresponds to solid powders before the alkaline activation.

3. Conclusions and way forward

The findings of this study highlight the significance of considering the composition of precursors and the concentration of alkaline activator when developing geopolymer matrices for confining thermally treated ion exchange resins (IER). These variables play a crucial role in determining the properties of the resulting cementitious matrix.

Although the chemical and mineralogical composition of the cementitious matrix was found to be minimally affected by the presence of IER, its influence on the pore structure, structure and mechanical properties of the samples was significant. This observation underscores the importance of considering the impact of IER when designing geopolymer matrices.

Among the various formulations tested, the one-part geopolymer paste matrix, formulated with metakaolin and blast furnace slag in a mass precursor ratio of 1, and activated with 9% of Na₂O in the form of solid Na₂SiO₃ powder, exhibited remarkable performance. It surpassed the waste acceptance criteria for compressive strength by recording >40 MPa when 20% of IER was incorporated. This particular formulation was selected for the subsequent leaching test, as specified in T6.6.

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6.6 Immobilization of molten salt residue using alkali-activated and cement-based materials

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Keywords: alkali-activated materials, geopolymer, cementitious materials, molten salt oxidation

1. Introduction

Some radioactively contaminated solid organic waste streams are problematic to dispose of by direct immobilization in known matrices (e.g. cementitious binders), as they can potentially degrade after disposal, possibly resulting in the release of radionuclides. Within work package 6 of the PREDIS project, techniques for the treatment and disposal of these waste streams are investigated [1]. One of the possible ways of treatment is the molten salt oxidation (MSO) process, in which the bulk of the organic waste can be oxidized

at a high temperature in the presence of a sodium carbonate salt [2]. The residue after the MSO process is a salt containing radionuclides in carbonate forms. The goal of this study is to investigate whether it is possible to immobilize this salt residue in an alkali-activated or blended cementitious matrix resulting in a waste form with good mechanical properties and long-term durability. Previous experiments with direct immobilization of the salt into these matrices has been proven to be ineffective. Therefore, the salt will first be pre-treated to increase the compatibility with its matrix. After ensuring good mechanical properties, thermodynamic modelling of the system will be performed to understand the stability of the salt-related phases. Future work will include carbonation, leaching and resistance to alkali-silica reaction tests to ensure long-term durability of the waste forms.

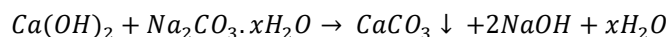
2. Description of work and main findings

Methods

Sample preparation & characterization

Initial characterization of the salt revealed it to be highly waterlogged at a water content of 60 wt.% after drying at 100 °C. In order to improve reproducibility of the tests, the salt was air-dried, after which the residual water content was approximately 16 wt.%. Detailed characterization of the air-dried salt revealed it to consist of different hydration states of sodium carbonate (Na₂CO₃), with thermonatrite (Na₂CO₃·H₂O) being the most dominant. Additionally, trona (Na₂CO₃·NaHCO₃·2H₂O) occurred in addition to small quantities of natron (Na₂CO₃·10H₂O) and gaylussite (Na₂Ca(CO₃)₂·5H₂O).

As initial experiments revealed that direct immobilization of the salt was ineffective due to the strongly hygroscopic nature of sodium carbonate, a pretreatment was necessary. As sodium carbonate is highly soluble, a double displacement reaction to form the insoluble calcite (CaCO₃) was proposed to be an effective way to improve the compatibility with the cementitious and alkali-activated matrices. A number of possible reagents exist, such as CaCl₂, Ca(NO₃)₂ and Ca(OH)₂. The former two were found to be ineffective as they either introduce new complications to the waste form (chloride attack in case of CaCl₂), or negatively impact the properties of the waste form (in the case of Ca(NO₃)₂). Ca(OH)₂ was therefore chosen as a reagent, with an additional benefit that the reaction (shown below) produces NaOH, which acts as an activator for the precursor of the alkali-activated matrices.



The pre-treatment was tested in two ways. Firstly, Ca(OH)₂ and the salt residue were both mixed together in water for three days (P1). Secondly, the salt residue was slowly added to a Ca(OH)₂ suspension over the course of three weeks (P2), to allow a more gradual reaction between both components, to prevent an overly Na-rich environment due to the low solubility of Ca(OH)₂.

After -, the resulting sludges were incorporated into either an alkali-activated or blended cementitious matrix. Waste loadings, expressed as the weight percentage of air-dried salt residue relative to the total mass of the waste form, varied from 10 to 20 wt.% in case of the alkali-activated matrices and 10 to 14 wt.% for the cementitious matrix. The fresh waste forms were cured in humid conditions (nearly 100% RH, room temperature) for 28 days to ensure that the waste form can withstand a high humidity environment.

Table 12. Details of the recipes used for the immobilization of the molten salt residue. Abbreviations are as follows: BFS = blast furnace slag; MK = metakaolin; LF = limestone filler; L = limestone; LS = limestone sand; SF = silica fume; SCM = supplementary cementitious material.

Recipe	Activator/SCMs	Precursor/Binder	Waste Loading (wt%)
AAS	Na ₂ O·2SiO ₂	BFS	10–20
CEM	BFS, LF, L, LS, SF	OPC (CEM I)	10–14

The waste forms were characterized by X-ray diffraction. Thermodynamic modelling was performed using HP Geochemistry.

Results

Synthesis of waste form

Both the alkali-activated slag and blended cementitious waste forms showed good mechanical properties after 28 days curing, with the compressive strength of AAS at 42 and 37 MPa (for 10 and 20 wt.% waste loading) and 15 MPa for the CEM waste forms (for both 10 and 14 wt.% waste loading). The samples also did not show any signs of bleeding or efflorescence, proving their good resistance to high humidity environments. Mineralogical characterization of the waste forms (Figure 72) revealed that, in both cases, all the sodium carbonate species had reacted away. Instead of everything transforming into calcite, an important crystallization of gaylussite was also observed. The crystallization of gaylussite was found to be more prominent relative to the amount of calcite formed in case of pre-treatment P1, in which $\text{Ca}(\text{OH})_2$ and the salt residue were directly mixed.

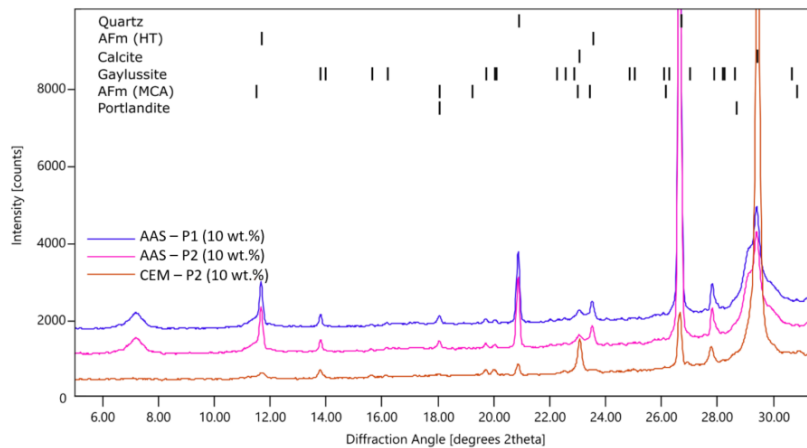


Figure 72. XRD analysis of the waste forms containing 10 wt.% of salt residue. P1 and P2 indicate the type of pre-treatment.

To understand the mechanism behind the formation of gaylussite, thermodynamic modelling was performed. In a simulation of pre-treatment P1, it was found that, in the case only a small amount of $\text{Ca}(\text{OH})_2$ (or portlandite) is in solution, gaylussite will be the preferred phase to precipitate due to the sodium rich nature of the solution. As more Ca comes into solution, calcite will be more stable. By contrast, a simulation of pretreatment P2 revealed that gaylussite should never be stable, as the gradual addition of salt to a Ca-rich suspension ensures the stability of calcite.

The observation of gaylussite in the P2 waste forms can be attributed to the fact that, after pre-treatment, the sludges are mixed with other phases, i.e. the binder, activator, SCMs, ... which can affect the stability of the gaylussite. In the case of the AAS waste form, the addition of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ as an activator ensures that the system contains sufficient sodium for gaylussite to be thermodynamically stable. In the case of the CEM waste form, no additional source of sodium is added, so the continued presence of gaylussite can best be understood as that of a metastable phase, which will on the long term react with the available $\text{Ca}(\text{OH})_2$ to form additional calcite crystals.

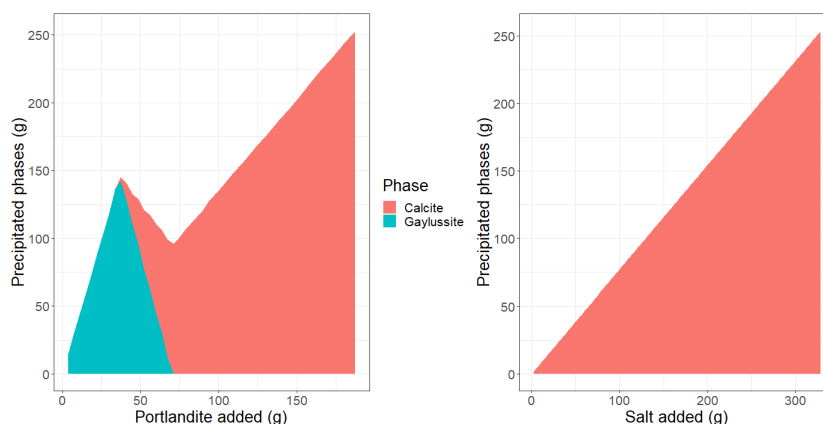


Figure 73. Thermodynamic simulation of the precipitation of calcite and gaylussite during the pre-treatment. The diagram on the left simulates pre-treatment P1, while the one on the right simulates pre-treatment P2.

3. Conclusions & way forward

This study has shown that it is possible to design both cementitious and alkali-activated matrices which are able to retain a highly hygroscopic sodium carbonate salt after pre-treatment. The waste forms showed good mechanical properties which are unaffected by changes in temperature or humidity. The pre-treatment was effective in eliminating all hygroscopic sodium carbonate from the system, although an intermediary Na-Ca carbonate phase, gaylussite, was still present. Through thermodynamic modelling, its presence can best be explained by the low solubility of $\text{Ca}(\text{OH})_2$ artificially creating a high-sodium rich environment in which gaylussite is more stable than calcite, combined with the additional contribution of Na from the sodium disilicate used as an activator in the AAS waste form.

Now a set of stable waste forms has been attained, durability tests will be performed, including carbonation resistance experiments, leaching experiments and alkali-silica reaction experiments (in the case of the CEM waste form).

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6.7 Characterisation of the ash and their encapsulation after thermal treatment of IER

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Keywords: IER, ash, encapsulation, geopolymer

1. Introduction

Spent ion exchange resins (IERs) represent a waste stream generated during NPP operation. Direct solidification is commonly used to treat spent IERs due to simple operation and equipment and has been widely accepted cementation using Ordinary Portland Cement (OPC). Removal of organic matter by thermal gasification results in significant volume reduction demonstrated successfully in many projects [1]. The remaining radioactive ashes must be transferred to treated waste forms. Cementation, traditionally used for encapsulation, is a conventional method to bind the gasified resin ash. TECDOC of IAEA reported that geopolymers were used to solidify radioactive wastes at Dukovany NPP [2]. The last time, many works indicated that alkali-activated geopolymer binders might be suitable matrices for encapsulating and stabilising IERs. Geopolymer is amorphous to a semi-crystalline three-dimensional Si–O–Al framework. It is synthesised by a polycondensation reaction of solid aluminosilicate materials such as metakaolin (MK) or blast furnace slag (BFS), and alkaline solutions known as the geopolymerisation process [3]. Potassium hydroxide and sodium silicate solution have been used as activators. The potential to combine gasification as thermal treatment and various inorganic binders as encapsulation matrices were tested in the VTT [4]. This work aims to evaluate the application of the geopolymerisation to ash after gasification of the IER and the problems associated with the specificities of the ash.

2. Description of work

A significant gasification problem is the completeness of thermal treatment, which allows removing organic substances from IER without releasing large amounts of radionuclides. The ion exchange resin combustion method is optimised by determining the temperature of the gasification process for the gradual conversion of mobile and volatile Cs species into inorganic and thermally stable compounds. The transition time and the rate of temperature rise of the thermal process are optimised by conducting a preliminary thermogravimetric analysis. The combustion was carried out at different temperatures. The resulting ash was characterised using FTIR spectroscopy, SEM and DTA to monitor the decomposition of organic matter. Previously, it was