Deliverable 7.1: State of the Art on novel matrices for

LILW immobilisation

Work Package L'OPERA

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Executive Summary

The EURAD-2 project, co-funded by the European Union, focuses on enhancing the management of radioactive waste through innovative research and development.

L'OPERA is a EURAD-2 Research and Development Work Package that aims to complete the evaluation of the long-term performances and demonstrate the long-term behaviour and durability of innovative matrices and waste forms for low and intermediate-level waste (LILW) immobilisation.

This document presents the State-of-Art (SotA) on the current knowledge and advancements in the field of low and intermediate-level waste (LILW) immobilisation, providing supporting background information relevant to the specific scientific and technical context investigated in L'OPERA.

In the SotA, a short introductory chapter summarizes the main scope and content of L'OPERA, against which the SotA is developed.

Section 2 discusses the durability tests and approaches for evaluating the long-term performance of waste forms used for LILW immobilisation.

Section 3 provides an overview on the current knowledge regarding the systems to be studied in L'OPERA and highlights the key findings and the existing gaps to be further investigated. The key matrices studied in WP7 L'OPERA are geopolymers, magnesium potassium phosphate cement (MKPC), Nochar and alkali-activated materials. Section 3 is structured into three sub-chapters to discuss the three key matrices, and each sub-chapter is supported by the list of relevant key literature cited.

§3.1 Geopolymers: are aluminosilicate materials that can be tailored to match the properties of immobilised waste. They offer flexibility in formulation but require further research on long-term stability under various conditions, including leaching, irradiation, thermal, and mechanical aging.

§3.2 Magnesium Potassium Phosphate Cement (MKPC): is a promising matrix for immobilising LILW, particularly for radioactive metals and spent ion-exchange resins. The matrix's performance is influenced by the magnesium-to-phosphate (M/P) ratio, water content, and curing conditions. Further research is needed to address uncertainties related to hydrogen release, long-term stability, and the impact of environmental conditions.

§3.3 Nochar: is a thermoplastic elastomer used for solidifying organic waste, such as oils. It has been successfully implemented in some countries for the solidification of low and intermediate-level waste. However, further research is required to evaluate its long-term sorption properties and performance under various aging conditions.

Section 4 summarises the identified gaps and the need for continued research and development to address those gaps and ensure the long-term safety and effectiveness of novel matrices for LILW immobilisation.

Keywords

Durability, long-term performances, waste form, conditioning, novel matrices

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Glossary

AAM	Alkali Activated Materials
BFS	Blast Furnace Slag
CAC	Calcium Aluminate Cement
CSA	Sulphoaluminate Cement
CSF	Central Storage Facility
DW	Deionized Water
DSW	Disposal Site Water
EURAD	The European Joint Programme on Radioactive Waste Management
FA	Fly Ash
GBFS	Granulated Blast Furnace Slag
GP	Geopolymer
IAEA	International Atomic Energy Agency
IER	Ion Exchange Resin
KDP	Monopotassium Dihydrogen Phosphate
LILW	Low and Intermediate Level Waste
LLWR	Low Level Waste Repository
L'OPERA	LOng term PERformAnce of waste matrices
LSC	Liquid Scintillation cocktails
MK	Metakaolin
MKPC	Magnesium Potassium Phosphate Cement
MLLW	Mixed Low Level Radioactive Waste
MPC	Magnesium Phosphate Cement
MSO	Molten Salt
NDP	Ammonium Dihydrogen Phosphate
NPP	Nuclear Power Plant
OPC	Ordinary Portland Cement
PE	Polyethylene
PREDIS	Predisposal Management of Radioactive Waste
SIER	Spent Ion Exchange Resin
SRA	Strategic Research Agenda
RAW	Radioactive Waste
RLOW	Radioactive Liquid Organic Waste
RSOW	Radioactive Solid Organic Waste
SCW	Synthetic Cement Water
TBP	Tributyl Phosphate
TOC	Total Organic Carbon
UHDMC	Ultra-High Ductility Magnesium phosphate Cement
WAC	Waste Acceptance Criteria
WIPP	Waste Isolation Pilot Plant
WP	Work Package

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Acknowledgements

1.   Scope and content of EURAD-2 L'OPERA

L'OPERA is a Research & Development Work Package, and the activities are linked with the EURAD Roadmap [1], Pre-disposal (Theme 2) and with domains:

- 2.2.3 Stabilise waste by conditioning prior to long-term storage (Conditioning)
- 2.3.2 Evaluate potential for improving and optimising implementation phases with new technologies, to improve costs and environmental impact while maintaining safety and accounting for potential accident scenarios (Optimisation)

Addressing one of the priority activities of common interest included in the EURAD Strategic Research Agenda (SRA) [2], (Scientific Theme 2), by providing demonstration of new matrices performance in representative disposal conditions, L'OPERA will contribute to the overall improvement and optimisation of pre-disposal operations.

Mainly built on the results obtained during the previous European "Predisposal Management of Radioactive Waste" (PREDIS) project [3], L'OPERA aims to complete the evaluation of the long-term performances and demonstrate the long-term behaviour and durability of innovative matrices and waste forms for LILW immobilisation. The innovative matrices to be studied are geopolymer, magnesium potassium phosphate cement (MKPC), Nochar and alkali-activated materials for the immobilisation of Radioactive Liquid Organic Waste (RLOW) such as oil, or Radioactive Solid Organic Waste (RSOW) such as Ion Exchange Resin (IER) or metallic materials.

This document presents the State of the Art on the novel matrices that will be studied in L'OPERA, providing supporting background information relevant to the specific scientific and technical studies that will be conducted in the different L'OPERA technical tasks.

Task 3 "boundary conditions" is focused on the identification of the representative conditions of disposal facilities for the long-term management of LILW. The main goal of the task is the identification and characterisation of the key parameters influencing the durability and the stability of the different waste matrices and waste forms to establish experimental protocols to be used in the other tasks.

Task 4 "inventory of the conditioned materials and complete characterisation" is focused on the collection of data from partners (both from WP7 L'OPERA and WP6 STREAM) on the different formulations of the waste matrices, physical and chemical composition of the conditioned materials and interactions between the waste and the matrices.

Task 5 "waste forms durability and stability testing" is focused on the determination of the key parameters influencing the durability and the stability of the conditioned waste and the characterisation of the long-term evolution of the conditioned materials under as representative as possible of disposal conditions. Different degradation processes will be considered: evolution of the material under irradiation, under presence of water (leaching), under temperature modification and mechanical ageing.

Task 6 "implementation" is focused on the development of modelling approaches of experimental results to predict the long-term performance of conditioned matrices.

The existing knowledge of the novel matrices that will be studied in L'OPERA, is still less mature compared to other conditioning matrices (i.e. cementitious materials), and the understanding of their long-term performance and durability under disposal conditions is required to consider them for the conditioning of specific wastes and obtain final waste forms which can meet the WAC (Waste Acceptance Criteria) of the disposal facilities.

Preliminary studies, namely conducted in the framework of PREDIS dealing with encapsulation of liquid organic, solid organic and metallic waste, have shown good properties for the waste encapsulation and short-term performances, but their long-term behaviour under disposal conditions is quite unknown. L'OPERA aims to evaluate the long-term behaviour of the matrices and waste forms by understanding the degradation processes and its consequences on the performance of the waste forms, as well as with the extrapolation of the data to a few hundred years for surface disposal and to longer periods for geological disposal.

2.   Durability performance and approaches

Durability is one of the main characteristics of the cemented waste form that needs to be demonstrated for a certain period of time to comply with the requirements for LILW disposal. The durability methods applied are similar to those used for traditional concrete materials in the building sector but tailored to potentially more stringent limits due to the harsher environment required for safe radioactive waste containment.

The main properties that need to be understood with respect to waste form durability are linked with the confinement of the radionuclides and other toxic-chemical species (release rates and mechanisms), and the waste form stability in the repository environment during its design life.

The physico-chemical properties of the waste form, including the nature of the contaminant, the conditioning matrix, and the environmental conditions, will determine the rate of radionuclide release. Depending on the type of waste form, radionuclide release mechanisms can vary significantly (i.e. cementitious waste forms exhibit diffusion-controlled release for many radionuclides while for activated metals the release is likely to be controlled primarily by the corrosion rate of the metal).

Cemented waste forms are among the most common immobilization matrices used due to their cost-effectiveness, versatility, and established technology. Ensuring the durability of cemented waste forms over the disposal period—often spanning hundreds to thousands of years—is essential to prevent the release of radionuclides into the environment.

Durability performance refers to the capacity of the cemented waste form to resist physical, chemical, and microbiological degradation over the disposal timeframe. The waste form needs to have multiple functionality properties to maintain its integrity under anticipated repository conditions.

The aspects that need to be addressed to assess the waste form durability include the following [4]:

Mechanical stability:

It is important that the waste form has a certain level of mechanical stability to maintain physical integrity after it has been produced and during storage and disposal operation.

Several key aspects influence the waste form mechanical stability:

- The waste form composition, including the type of cement and additives, influences the microstructure, porosity, and binding properties. A dense, well-cured microstructure minimizes pathways for water ingress and leaching (see chemical durability below), enhancing stability.
- The compressive strength of the cemented waste form must be sufficient to withstand handling, transport, and repository conditions without cracking or degrading. Testing the mechanical properties of a waste form typically involves compressive, tensile, and flexural strength measurements. Proper curing and formulation optimize these properties.
- Exposure to groundwater and other environmental factors can lead to chemical alterations of the cement matrix, potentially weakening the structure. Resistance to sulfate attack, carbonation, and other chemical processes is vital for long-term stability.
- The waste form must withstand physical stresses such as thermal expansion, shrinkage, and external loads from the surrounding geology or handling. Its design should accommodate these factors to prevent deformation or failure.

Over extended periods, processes like slow dissolution, microcracking, and potential swelling can impact stability. Proper formulation and quality control during fabrication help mitigate these effects.

Chemical durability:

One of the most important phenomenon to be considered in the long term is the eventual release of radionuclides from the waste form and repository into the environment due to contact between water and the waste form.

Leaching resistance, that is one of the key functions of the waste form, can be measured with laboratory tests by providing a realistic approximation of the chemical conditions of the repository. The different

factors that may affect the radionuclide release from a waste form (leaching rate), such as leachate composition, temperature, carbonation phenomenon, formation of radiocolloids, and backfill moisture content, can be simulated in laboratory scale. Indeed, the water immersion could induce cracking or lead to modification of several waste form characteristics, such as porosity, phase composition, morphology, etc, leading to degradation of mechanical properties and leaching resistance.

Moreover, for organic materials, radiolytic and chemical degradation of organic wastes/matrices in contact with water can lead to the release of water-soluble organic species. The related safety issues are to assure that the presence of the radiolytic and chemical degradation products will not increase the radionuclide migration rate by increasing their solubility and/or reducing their sorption.

For special cases, such as the encapsulation of organic liquids and oils, an important issue is the confinement of matrix in order to limit liquid and hazard species release to the long-term.

Radiation stability:

Stability of the immobilized waste form due to the effects of radiation damage from the decay of the radionuclides is an important property to be considered for the long-term durability. Exposure to radiation can induce physical, chemical, and microstructural changes in the conditioning matrix, influencing the long-term stability of the waste form.

The conditioning of radioactive waste in cementitious matrices is considered the most robust solution, due to its high technical performance relative to cost. However, there are restrictions on the amount of radioactivity that can be incorporated into the matrix, primarily for storage and disposal safety. When the waste contains high levels of alpha emitters, radiolysis of water occurs during long-term storage of solidified radioactive waste, leading to the release of radiolytic gases, predominantly H_2 and O_2 [12][13]. Since cementitious matrices retain water in their microstructure, it is essential to consider the effect of radiation on cement material properties, particularly the formation of hydrogen due to water decomposition. The impact of γ-radiation on chemical transformations and matrix stability is a key parameter in standard tests used to assess waste package performance [4].

Effect of irradiation on the waste form can lead to:

- volume changes
- gas generation
- increases in leach rate
- cracking of the immobilized waste form, thus worsening mechanical properties and creating a greater surface area (higher leaching rates)
- Release of degradation products.

When organic materials are immobilized, the effects of radiolytic gas generation need to be properly evaluated as excessive gas generation from any waste form can lead to undesirable pressurization of the containers.

Moreover, in case of RSOW (i.e. spent ion exchange resins) there is the possibility that high absorbed doses of radiation might lead to resin swelling due to changes in the resin structure, thus resulting in conditioning matrix cracking and weakening of mechanical properties.

Microbiological durability

Microbiological degradation, especially in presence of organic materials, can lead to production of gas or other chemical interactions with the conditioning matrix and should be properly evaluated. Microorganisms such as bacteria, fungi, and archaea may infiltrate waste forms or surrounding materials and their presence can lead to biochemical processes that compromise the waste form integrity.

Factors such as moisture availability, temperature, pH, and presence of oxygen influence microbial activity.

Laboratory studies simulate microbial interactions with cemented waste forms under controlled conditions are needed to evaluate potential degradation pathways.

Thermal stability

A good thermal property is one of the most important requirements for waste package materials, since fires may occur in transportation, or after emplacement into an engineered repository (either for temporary or final storage) [14][15] as well as environmental temperature changes (freeze-thaw, wet-dry). The waste packages must have good thermal properties and maintain a stable structure as primary engineered barrier, minimising the release of radioactive material in such fire conditions, which may burn hotter and longer due to limited access, especially if deep underground in a geological disposal facility.

Thermal cycling also affects the integrity of waste package materials, if water seeps through a breach in a hardened cement or concrete until a certain saturation state is reached. If the ambient temperature keeps alternating between freezing and over-freezing temperatures, the state of the capillary pore water in the cement or concrete changes to a certain temperature below freezing, and the capillary pore wall is affected by frost pressure (freezing of the water) and osmotic pressure (migration of supercooled water). This leads to tensile stresses in the microstructure surrounding the crack, which ultimately deteriorates the performance of the material, with decay of mechanical strength, with the possible release of radionuclides, which will cause great damage to people's life safety and social economy, must be investigated as prescribed by WAC.

Thermal stability is particularly important in case of organic material in the waste form due to the possibility of thermal decomposition of the organic material at relatively low temperatures. When exposed to elevated temperatures, organic materials decompose, releasing gases such as CO_2, H_2O, and in some cases, toxic or radioactive gaseous compounds. The accumulation of gases can generate internal pressure, affecting the mechanical integrity of the matrix and facilitating the release of radionuclides.

Methodologies for waste form durability assessment

Methodologies for waste form durability assessment depend on the characteristics of the waste and the matrix. Most methods are well established from the concrete building materials sector, and others are developed further to be applicable to the nuclear sector. There are many international guidelines about qualification and testing of immobilized materials and cemented waste forms, such as those provided by IAEA in references [4], [5].

The EN 196 series is a set of European standards detailing methods for testing cement. It's a multi-part document, with each part focusing on a specific aspect of cement testing, like strength, chemical analysis, setting time, etc. Other international standards exist to provide methods for specific durability tests [5].

Testing approaches includes: (i) laboratory tests, to determine the mechanisms and processes that impact on performance and precisely controlling relevant parameters; (ii) field tests, to closely mimic the real environmental conditions and provide more representative performance data, and (iii) natural and archaeological analogue studies, to provide information on long-term stability and durability.

Both laboratory and field tests can be carried out over short periods of time, whereas the disposal period could be 300 years or longer.

Accelerated testing methods are essential for evaluating the long-term degradation behaviours of cemented waste forms in a shorter time frame. These tests simulate the conditions that waste forms might experience over extended periods, allowing researchers to assess their durability, stability, and containment performance efficiently.

Some of the common accelerated testing approaches used to evaluate degradation mechanisms in cemented waste forms include:

- Exposure to elevated temperatures: to accelerate chemical reactions such as leaching, carbonation, and cement hydration/degradation and to provide insight into long-term stability and potential changes in microstructure and leachability over time.

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- Increased humidity and moisture conditions: to accelerate processes like sulfate attack, carbonation, or leaching. It can help to evaluate how moisture ingress influences degradation and radionuclide mobility.
- Chemical attack simulations: to assess resistance to aggressive agents such as sulfates, chlorides, or acidic solutions and to determine susceptibility to chemical degradation and potential pathways for deterioration.
- Leaching tests under accelerated conditions: to quantify radionuclide and chemical element release rates and predict long-term leachability and containment performance.
- Microstructural and mineralogical analyses post-testing: by using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and porosimetry after accelerated tests, to identify changes in microstructure, porosity, and mineral phases, and correlate microstructural evolution with observed degradation and leaching behaviour.

The selection of accelerated conditions must be justified to avoid non-representative degradation mechanisms.

To predict the long term-performances of the waste forms, modelling approaches can be developed. Some experiences in extrapolation of short-term observations to the long-term are reported in [4], [5], [6].

Experimental data should be used in conjunction with long-term performance models to predict real-world behaviour.Compliance with WAC

The waste acceptance system outlines requirements for managing waste at different stages [7]:

- Predisposal waste acceptance criteria are based on the technological needs of radioactive waste processing, focusing on radionuclide activities and hazardous species that require specific treatments.
- Acceptance criteria for final waste forms at storage or disposal facilities include a parameter, its value, and a measurement method.
- The waste form qualification process ensures that a selected waste form is suitable for disposal, addressing its long-term performance and providing inputs to predisposal criteria.

The Waste Acceptance Criteria (WAC) specify the physical, chemical, and radiological properties that waste must meet to be accepted at the disposal facility, ensuring safe management and disposal.

The WACs are linked to safety assessments and broader waste management principles, with clear justifications for each criterion. Common WAC elements include limiting surface contamination, dose rates, and specific activity limits of radionuclides. Disposal WAC also address physicochemical characteristics, limiting hazardous materials and ensuring waste form stability. Solid or solidified waste forms are preferred for disposal, with solidification media ensuring long-term stability.

New waste forms must undergo a qualification process [8] to ensure compliance with existing WAC and safety standards.

3. Overview on the current knowledge regarding the systems to be studied in L'OPERA

Immobilising radioactive waste in a Portland cement matrix is the most widely used method globally, particularly in countries with nuclear energy programs [8], [10] However, for safety reasons, the encapsulation of nuclear waste in conventional OPC systems is becoming less desirable for some radioactive wastes, as organics and metals. This is mainly due to compatibility issues between the waste and the matrix. OPC-based systems harden through hydration reactions, leading to high water content, which, in the presence of radioactive elements, can undergo radiolysis, releasing hydrogen gas and posing a risk of leaks and explosions in the containment material. Additionally, cement solidification of SIERs in OPC-based systems shows swelling and cracking troubles that are produced during setting time, or under conditions of storage (humidity or water immersion, changes of temperature, etc.) [11]. These issues increase with higher loadings of resin and are subordinated to the kind of cement, type and form of resin and immobilisation. All these factors highlight the need to develop alternative cementitious systems, with lower water content, for a safer and proper encapsulation.

3.1 Geopolymers and alkali-activated materials

3.1.1. Nature of the matrix and immobilised waste

Geopolymers (GP) are materials based on natural aluminosilicate minerals or industrial aluminosilicate waste and activators. The aluminosilicates commonly used in GP are metakaolin (MK), fly ash (FA), and blast furnace slag (BFS). Sodium or potassium hydroxide and silicate are usually used as activators, which is why they are alkali-activated materials (AAM). After mixing the activators and aluminosilicates, dissolution-polycondensation reactions occur (Figure 1). The products of those reactions are three-dimensional aluminosilicate networks that can incorporate radioactive waste into their structure. Geopolymer properties can be enhanced by adding other materials (for example sand) [16], [17], [18], [19], [20], [21].
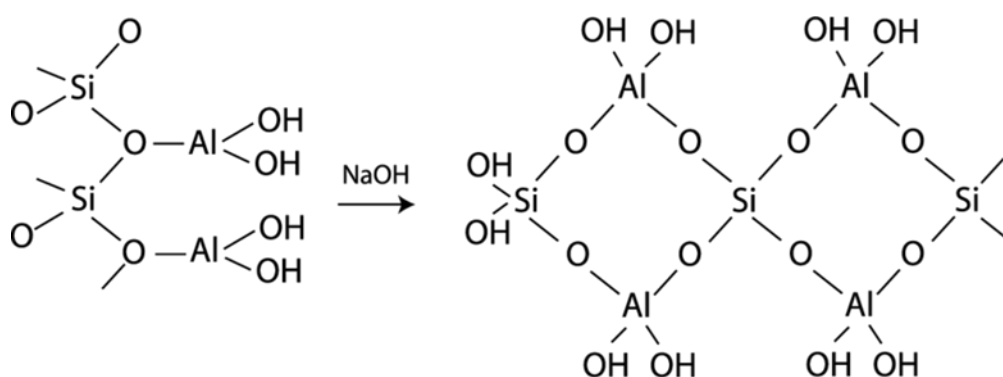
Figure 1: *Polycondensation reaction of kaoline*

Depending on the aluminosilicates used for the preparation, geopolymers can be grouped: [19], [20], [21]

- Single-aluminosilicate-based
    - Metakaolin-based (MK)
    - Blast furnace slag-based (BFS)

- o   etc.
- MIX-based

The advantage of MIX-based GP is that the matrix can be fitted to the waste more easily. Also, if one ingredient is expensive but has good properties for waste immobilisation, a necessary amount of it can be used, and the matrix can be diluted by cheaper aluminosilicate (e.g. MK and BFS).

The three-dimensional aluminosilicates can encapsulate problematic radioactive waste inside the geopolymer structure. There are two main types of RW immobilised in GP: radioactive liquid organic waste (RLOW) and radioactive solid organic waste (RSOW). In many countries, free liquid waste is not allowed to be disposed of. The problem with RLOW is the chemical properties: volatile, combustible, immiscible with water, etc. The RLOW can be, for example: [19], [20]

- Mechanical oil
- Organic solvents
- Paraffin oil
- Scintillation cocktails (LSC)
- Spent ion-exchange resin (SIER, sometimes assumed as RSOW)
- Sludge

The problem with RSOW is compatibility with the matrix. For example, waste can be hydrophilic and expand after contact with water, and this could lead to cracks in waste form. Or it can easily dissolute in water and be aggressive to the matrix and damage it. The RSOW can be for example: [21]

- Spent ion exchange resins
- Operational waste (gloves, paper, etc.)
- Ashes obtained by the treatment of organic waste
- Waste produced by the maintenance or decommissioning of an NPP

There are several routes to incorporate RLOW into GP, as illustrated in Figure 2: [18]

- Direct process
- Pre-emulsification process
- Solid-impregnation process

The direct process is simple. First, solid materials (aluminosilicates) are mixed into the activating solution. Then, RLOW is added under strong mechanical mixing. This process is also called a one-pot or one-step process.

The next process is called pre-emulsification. The RLOW is mixed into the activating solution. Once a stable emulsion is obtained, the solids are added, and hardening begins. Surfactants or polymers can be added to the liquid solution in the first step. They will stabilise the emulsion.

The RLOW is first adsorbed on solid materials; this is called a solid-impregnation process. These materials can be aluminosilicates used for the GP preparation or specialised adsorbing powders. The impregnated powder is mixed into the activation solution or processed by a direct process.
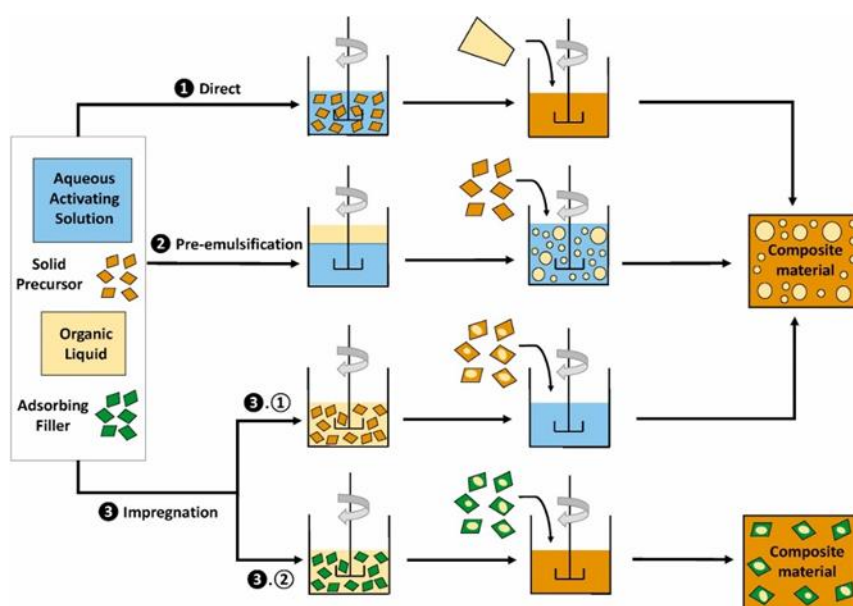
Figure 2: *Schematic of three main RLOW immobilisation processing routes in the GP matrix [18]*

RSOW can be conditioned by direct process, or it can be treated before conditioning by several ways (thermal treatment – pyrolysis, incineration, molten salt oxidation; chemical treatment – wet oxidation; etc.)

3.1.2. Waste form durability and stability

Extensive literature exists to provide data on the geopolymer waste form durability and stability [23][24][25].

Current studies [24] highlight that the effectiveness of GPs is influenced by several key factors, including the type of precursor, the type of activator, the Si/Al ratio, the water content, and the curing conditions. However, there is still a lack of comprehensive studies that investigate the impact of these variables on the immobilization of nuclear waste within GPs.

Durability of AAM and OPC-based materials has been compared under sulphate attack, acid corrosion, carbonation, and chloride penetration [25] showing that different AAMs have distinct durability properties due to different compositions being formed when different raw materials are used.

An extensive review of the main published results on the applications of geopolymer for organic liquid incorporation [18] highlighted that the main experiences are linked with oil incorporation and that there is a need to consider the industrial feasibility and potential practical issues when choosing the method for organic liquid incorporation. Additionally, it was concluded that future research may explore stabilizing different types of organic liquids in geopolymers to develop materials with emerging properties, such as high corrosion resistance.

During the PREDIS project an extensive experimental work was conducted to explore the incorporation of different types of organic liquids (WP5) and solid organics (WP6) in geopolymers and alkali activated materials.

In the following sections the summary of the conducted tests and obtained results on the different waste forms is reported. In addition, some other references are included. Radioactive waste surrogates were used in most cases; if real waste was used, it is stated.

3.1.2.1 Scintillation cocktail

Very few experiences exist on the incorporation of Scintillation cocktails in geopolymer, and alkali activated materials.

The effect of storage for one year on the LSC waste form based on MK was studied by Watanabe et al [41]. The samples were cured for one year under laboratory conditions. After one year, no free liquids were observed inside the matrix, so incorporation of the organic liquid into the structure of GP was assumed. Organics in leachate were observed, total LSC release was 1 % of the original amount incorporated in the matrix.

During the PREDIS project different geopolymer matrix were tested [19], [20] and some durability tests were conducted.Mix-Based GP

Different MIX-based GP formulations for immobilisation of LSC were tested. No hardening was observed in samples with waste loading greater than 15 %. Only one formulation had 11 MPa compressive strength and bleeding was observed. If the surfactant was added, no leaching was observed, and the compressive strength was small.

BFS-Based GP

A volcanic tuff-BFS based GP was tested and surfactant was added to obtain good workability and mechanical properties,. The maximum waste loading was 10 wt.%. However, to achieve compressive strength greater than 5 MPa (minimum value defined in PREDIS WP6), the maximum waste loading was 8 wt.%.

In addition, BFS-based GP with the addition of sand was also used. BFS from two suppliers was tested. Differences were observed between the two BFS-based GP in terms of waste loading and mechanical strength.

The immobilisation of the real waste sample, LSC in BFS-based (sand addition) and MK-based GP, was studied. The waste contained ^{14}C (25 kBq/ml) and ^{63}Ni (8 kBq/ml). The waste loading was 10 % and the compressive strength was around 20 MPa (after 28 days of curing), there was no significant difference between inactive matrix and matrix with real waste. In both matrixes, high sorption was observed for ^{63}Ni, but it was negligible for ^{14}C. The leaching tests were performed following the ANSI/ANS-16.1. method[1] [29]; the last sampling day was after 90 days. The leachability index was higher than 8 for all combinations of matrixes and radionuclides. It was slightly higher for ^{14}C.

MK-Based GP

Different waste loading in MK-based GP were studied. Mechanical strength tests were performed with a waste loading of 10, 20 and 30%, they were performed after 1, 7, 28 and 90 days of curing (20 °C, 90% rel. humidity) (Figure 3). Strength developed mainly in the first 7 days; after that, only a slight increase was observed, all samples had compressive strength greater than 10 MPa. For leaching tests in milliQ water cylindrical samples were used. The leachant had to be swapped after determined time (last for 375 days). Samples cracked in water. The pH value decreased after 42 days (9 leachate replacement) from approx. 13 to approx. 10 and stabilised after around 120 days of leaching (Figure 4). High TOC values were observed in LSC leachate (Figure 5), according to which leaching of LSC was suspected.

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[1] Samples: cylindrical, $V_L/S = 0.1$ m; Leachate: demineralised water; Leachate replenishing: 1, 2, 3, 4, 5, 19, 47 and 90 days
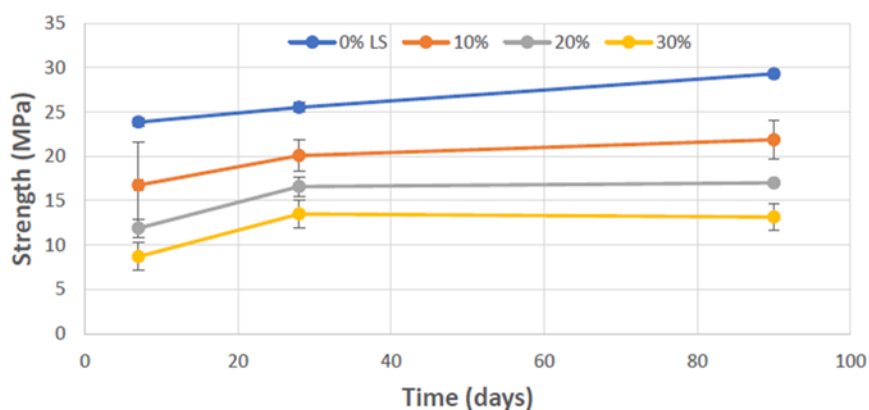
Figure 3: *Mechanical results in GP with liquid scintillation cocktail [20]*
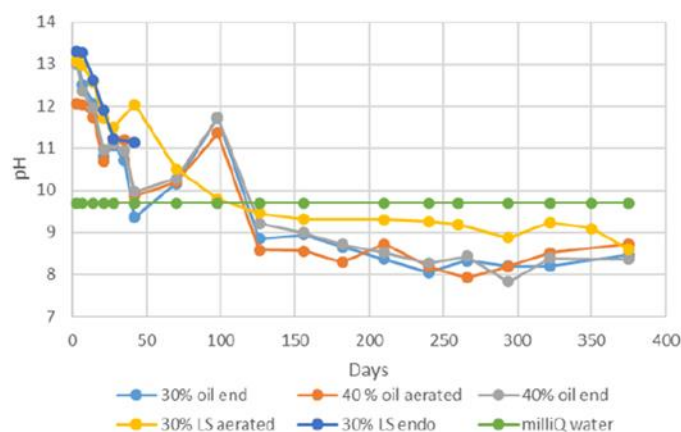
Figure 4: *pH values of leachant solution; GP with oil or LSC [20]*
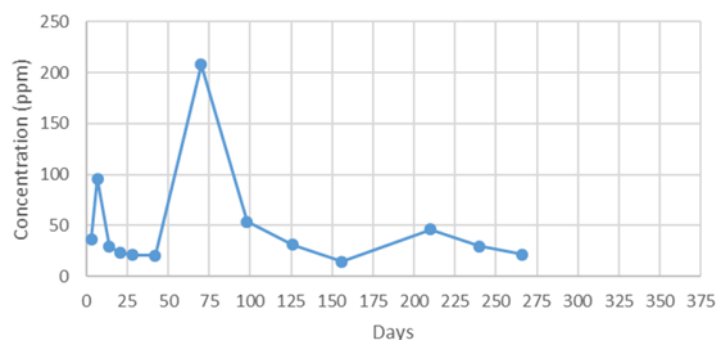
Figure 5: *TOC values in MK-based GP with LSC (30 %) [20]*

The real waste – LSC (containing [63]Ni, 19,8 Bq/mL) in MK-based GP was studied. The waste also contained stable Ni (94 mg/L) and was dopped with stable Cs (5 mg/L) and stable Ni (94 mg/L). The waste loading was 30 vol.% without surfactants. The samples were cured for 28 days in a humid environment or immersed in water. The compressive strength decreased by about 50 % for the waste-loaded matrix and the immersion only slightly affected the compressive strength. The leaching test was carried out following ANSI/ANS16.1-2019 protocol [29]. Only nonactive elements were measurable in leachate, and the radioactive element was below the limit of detection. The leachability index was 8.2 for Ni and 9.3 for Cs from immobilised LSC. They observed a cumulative release of 12.5 % of the initial organic content from real LSC waste after 28 days (from surrogate LSC waste it was only 4.5 %).

The effect of static water immersion (for 28 days) and irradiation (200 kGy) and their combination on the compressive strength of different LSC waste forms was studied both for MK-based and BFS-based GP.

The MK-based irradiated samples were not properly stored during irradiation, that caused their dehydration, and they cracked after immersion in water as the result of the rehydration. Immersion in water seems to have a greater impact than irradiation. In the next step, they doped the waste with nonactive Ce, Co, Cs, Eu, Nd, Ni, Sr, Th, and U. All contaminants had a leachability index higher than 8. No significant differences were observed in the leachability indexes determined for the sample without waste. A higher release of LSC from the matrix after irradiation was also observed (Figure 6)
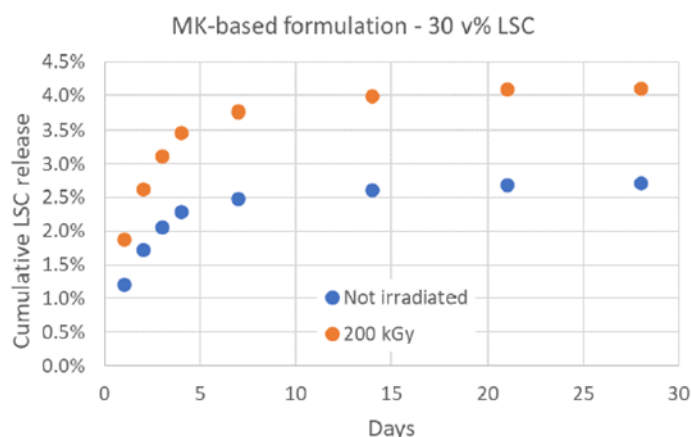
Figure 6: *Cumulative LSC release from MK-based GP for irradiated and not-irradiated samples [20]*

Experimental data showed that LSC can be successfully immobilised in different GP matrices and waste loading affect the mechanical properties. In some cases, the addition of emulsifier was needed to prevent bleeding. Leaching tests performed before and after irradiation, indicated that waste retention could be attributed to the radiolysis of the waste, and not to the degradation of the matrix. Lower molecular weight degradation products of LSC could in fact be of higher mobility, resulting in an increase of waste leaching.

3.1.2.2 Lubricant oils

Extensive studies for the immobilisation of lubricant oils were performed in the recent years [18].

It has been demonstrated that for oils with viscosities between 0.1–2 Pa s, up to 20 vol% could be easily incorporated into the geopolymer matrix, forming an emulsion of homogeneous, spherical droplets ranging from a few micrometers to 50 micrometers in size. The main population of droplets had a diameter of about 5 micrometers, indicating good dispersion.

The compressive strength decreases as oil content increases, but this effect is less pronounced than in ordinary Portland cement (OPC) matrices. Additionally, the cumulative quantity of oil compounds released in the leachate at 30 days was less than 0.19% of the initially encapsulated organic material, demonstrating effective oil encapsulation.

Unlike Portland cement, geopolymers do not show changes in geopolymerization kinetics or setting time when oils are added, due to their polycondensation reactions. The addition of surfactants can improve the droplet size distribution, incorporation quality, and rheology of the paste. Surfactants create a "shell" around each oil droplet, increasing viscosity and providing homogeneous size distributions of oil droplets.

In a recent study, *Hasnaoui et al.* [24] examined the management of radioactive liquid organic waste by analyzing the relationship between the viscosity ratios of geopolymer (GP) grouts and organic liquids. The research involved incorporating three types of mineral oils at a constant volume of 30% to observe how viscosity differences impact the rheological, mechanical, and microstructural properties of

GP/organic liquid composites. The findings revealed that organic liquids with viscosities above 0.05 Pa.s can be effectively encapsulated in MK-based GP grouts without the need for surfactants, emphasizing the importance of viscosity ratio in determining emulsion characteristics. Increasing the viscosity of GP grout improved the encapsulation of organic liquid droplets, and the study established strong correlations between rheological parameters and the viscosities of both phases. This enabled the development of empirical models with over 90% accuracy for predicting final rheological properties. Overall, the study confirmed that MK-based GPs are suitable for solidifying large volumes of organic liquid waste.

During the PREDIS project different GP matrices were tested and included both surrogated and real waste testing approaches

Mix-Based GP

Up to 30 % of waste loading was achieved without any surfactant with compressive strength greater than 10 MPa (after 28 days of curing). For a greater waste loading (> 30%) the addition of surfactant was needed to improve the rheological properties of the sample (Figure 7).

Figure 7: *Samples with 40 % waste loading without (left) or without (right) addition of surfactant [19]*

The influence of material supply and oil composition was evaluated and it was concluded that the source of the materials can significantly affect the properties of the final waste form [19], [20], [32].

Leaching of the MIX-based GP was investigated with a dedicated protocol, based on renewing the leachant (90 days in total) and employing as a leachant a solution with pH = 12.7.

Calcium, silicon, and aluminium were measured in leachate. A small amount of oil was observed to leached. Leaching of silicon and aluminium slowed after the first month. [20]

The immobilisation of real waste was tested but without any success confirming that the formulation is strongly affected by source of materials and oil type.

BFS-Based GP

BFS-based GP with the addition of sand was tested. The addition of surfactant was needed to incorporate oil. The presence of oil in the matrix decreased mechanical strength [19], [20], [26], [27], [28].

The carbonatation of BFS-based GP with two different oils was studied. The carbonation depth and compressive strength were measured (Figure 8). It was assumed that oil clogs the pores and that carbonation is slower. No significant changes in compressive strength were observed.
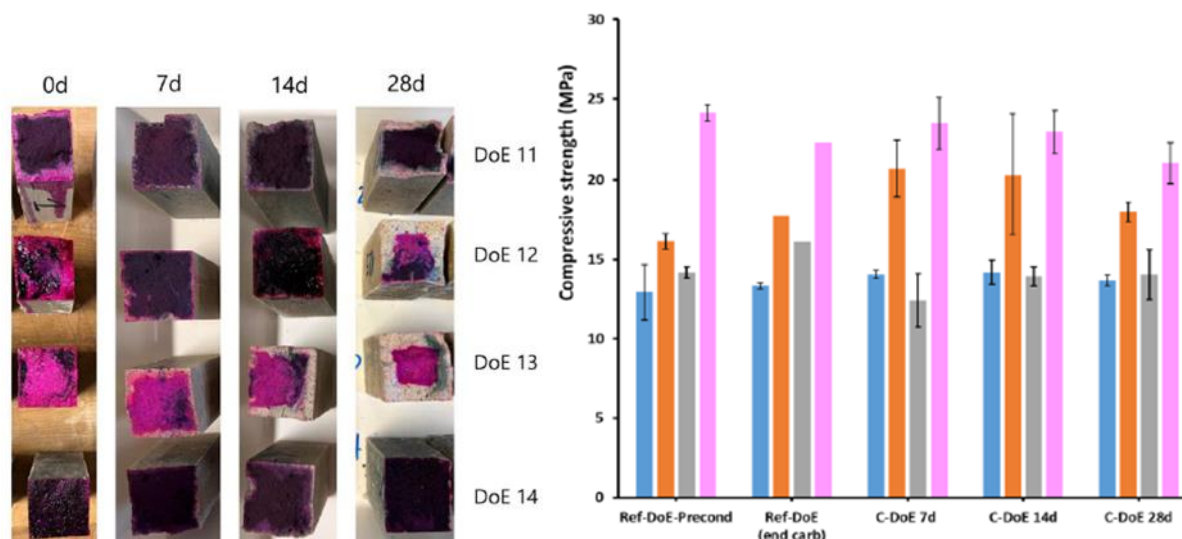
Figure 8: *Carbonation depth (left) and compressive strength (right) of the BFS-based GP with oil [20]*

Short-term leaching in NH_4NO_3 (6M, pH approx. 4.5) solution for 28 days was conducted. This method made leching faster, one sample was fully leached. It also seems to be faster for materials with a higher w/b ratio. The concentrations of leachable matrix elements were measured. The most leached elements were calcium, sodium, and potassium; no significant silicon and aluminium concentrations were observed; no significant changes were expected in the alumino-silicate framework. [20], [27], [28]

The BFS-based GP with 5 wt.% oil loading was leached also with a different protocol: the samples were cured sealed in bags or under aerated conditions. For the leaching experiment, demineralised water was used and replaced after a defined period (91 days in total). Less oil was leached from the cured matrix in a sealed bag and no more leaching was observed after 14 days (Figure 9). The total leached silicon was four to five times higher for materials cured under aerated conditions; no significant differences were observed in total calcium concentration. The conductivity of the leachates stabilised to half the initial value after 21 days. The pH value was stable in all samples. Leaching improved compressive strength. Leaching test was conducted also with higher waste loading (10 and 20 wt.%) and with the addition of surfactant. The trends were similar to those of the samples with a waste loading of 5 wt.%. Different oils were tested for immobilisation, but the compressive strength was low. [19], [20]
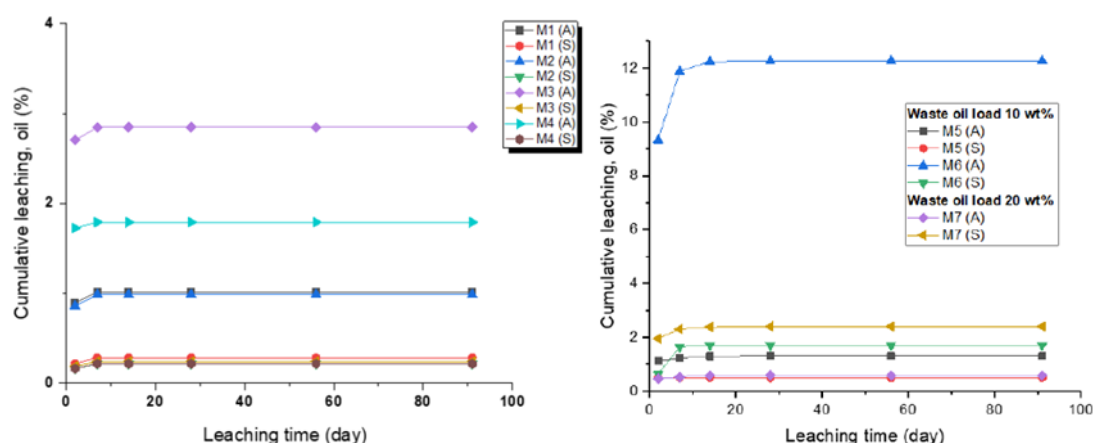
Figure 9: *Cumulative oil leaching from BFS-based GP matrix; left – 5% waste loading, right – higher waste loading; aerated (A) or sealed bag (S) curing conditions [20]*

The influence of material supply was investigated and as observed with the LSC, also with the oily waste differences were observed when changing raw materials (mainly BFS) in terms of waste loading, bleeding and mechanical strength. [19]

A volcanic tuff-BFS based GP was tested. To obtain good workability and mechanical properties, surfactant was added. The maximum waste loading was 15 wt.%. But to achieve compressive strength greater than 5 MPa (minimum value defined in PREDIS WP5), the maximum waste loading was 10 wt.%. [19]

The real waste from the decommissioning activities was immobilised in BFS-based GP. Compressive strength after curing under humid conditions, thermal cycling (30 24-hour cycles, -40 to +40 °C), immersion in water for 90 days were tested. A leaching test following the ANSI/ANS method [29] was also performed, doping the waste with ^{137}Cs.

No bleeding was observed from the MK-based GP. The compressive strength was 5.4 MPa and decreased to 5 MPa after thermal cycling. The sample broke after being immersed in water. The leachability index ^{137}Cs was 7.05 despite breaking after immersion in water. [19], [20]

MK-Based GP

The immobilisation of pump oil in MK-based GP was studied. The maximum loading of the waste in the GP was 50 vol.% with no bleeding observed. Shrinkage of samples while curing (0.03 – 0.11 %) was observed with a decreasing trend that had not stopped after 90 days.

Mechanical strength tests were performed with a waste loading 30 and 40 %, after 1, 7, 28 and 90 days of curing (Figure 10). Strength developed mainly in the first 7 days; after that, only a slight increase was observed, all samples had compressive strength greater than 10 MPa.
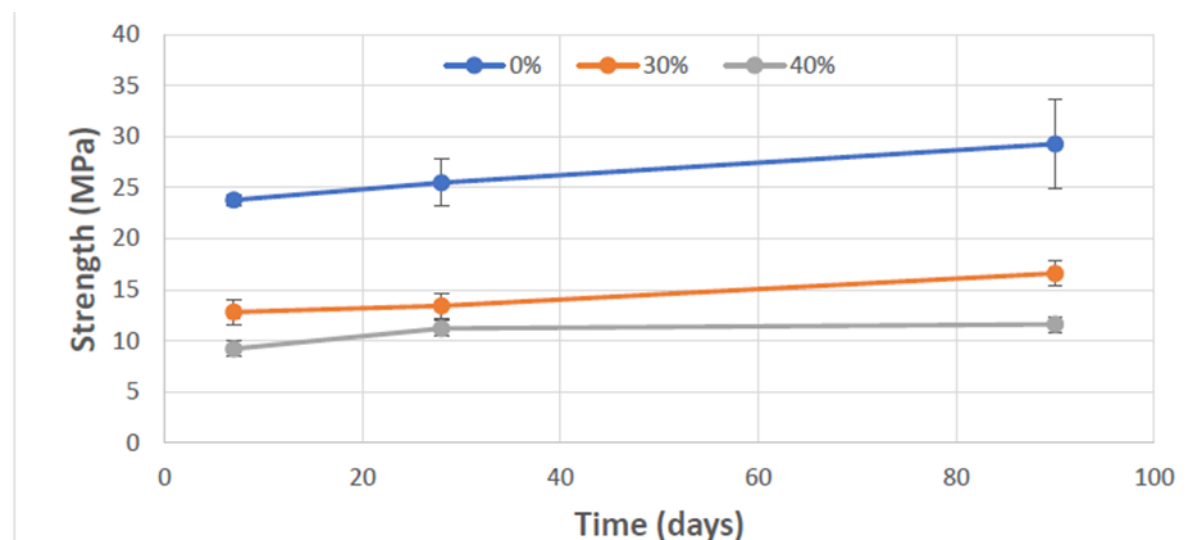
Figure 10: *Mechanical results in MK-based GP with oil [19]*

For leaching tests two protocols were tested. The first one was conducted in milliQ water and cylindrical samples were used. The leachant had to be swapped after a determined time (last for 375 days). The pH value decreased after 42 days (9 leachate replacement) from approx. 13 to approx. 10 and stabilised after around 120 days of leaching (Figure 4). No leaching was observed and the TOC values in leachate were negligible.

The second leaching protocol was based on the use of synthetic cement pore solution as leachate (Leachate replenishing: 3, 7, 14, 28, 56 and 90 days) and cylindrical samples ($V_L/S = 0.1$ m). No significant changes were observed in the compressive strength and permeability of the matrix after

leaching in water. A small oil loss (5%) was observed in 90 days. Permeability was approximately ten times higher for the samples without oil. [19], [20]

Carbonation of the MK-based GP with oil was studied under aerated conditions and in a carbonation chamber. Carbonation occurs more rapidly with increasing temperature. The oil slowed the carbonation process. But with increasing time, a decrease in compressive strength was observed (Figure 11). [20]
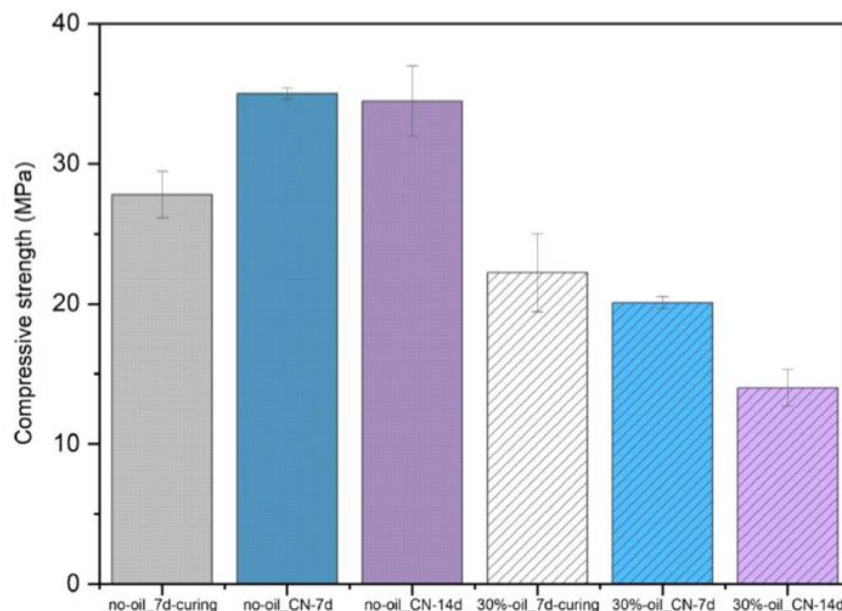
Figure 11: *Compressive strength for MK-based GP under natural carbonation* [20]

The real waste from the decommissioning activities was immobilised in MK-based GP. Compressive strength after curing under humid conditions, thermal cycling (30 24-hour cycles, -40 to +40 °C), immersion in water for 90 days were tested. A leaching test following the ANSI/ANS method [29] was also performed, doping the waste with [137]Cs.

Very slight bleeding was observed from BFS-based GP. The compressive strength was 5.5 MPa and increased to 6,3 MPa after thermal cycling, and after immersion in water it did not change. The leachability index ^{137}Cs was 7.51. [19], [20]A different approach was used by Cuccia et al [40]. Waste with bentonite was treated, that lead to sorption of Co to bentonite, or N910 was used to absorb whole oil. The new wastes were immobilised in MK-based GP. For both waste forms the compressive strength was higher than 5 MPa. For the leaching tests, the ASTM C1308 (11 days) was followed. The mechanism of cobalt release was determined to be diffusion. The average diffusion coefficient for cobalt was calculated and the value was 1.0-1.5 10^{-11} cm/s.

Irradiation

The effect of irradiation of the waste form was studied for MK-based, BSF-based and MIX-based GP. It was not possible to measure the exact gas content, so the pressure in the cell was measured instead (Figure 12). The pressure was not proportional to the total dose. No oil leakage or cracks were observed after irradiation. A smaller loss of mass after leaching was observed for the MK-based and BFS-based GP, and the trend was the opposite for the MIX-based GP. Cracks were also observed in the MK-based GP after leaching. [20]
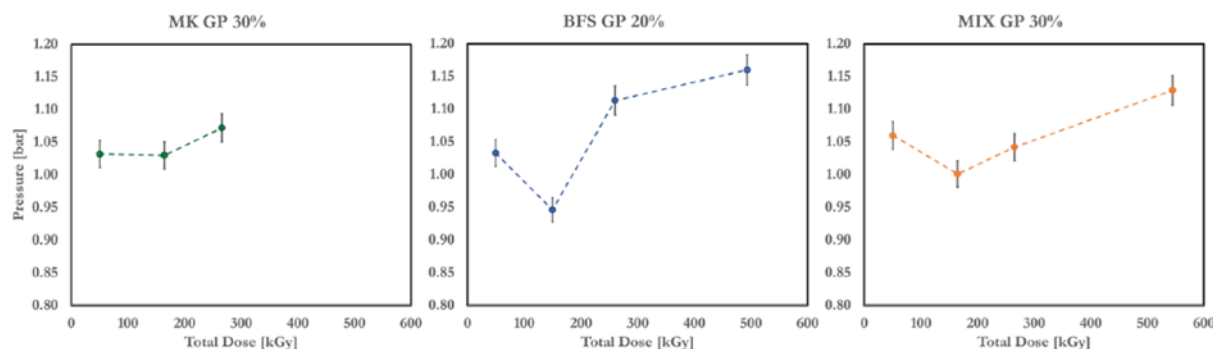
Figure 12: *Pressure as a function of the total dose* [20]

<u>Scale-up tests</u>

Scale-up experiments (50 L and 100 L drums) were performed with MK-based and BFS-based GP and oil [19]. The first set of experiments were performed with MK-based GP with a 10 wt.% loading of oil. Cracks in the matrix were observed (Figure 13), but they were suspected to be due to improper manipulation. The compressive strength was 21 MPa on the core samples. No cracks were observed in the drum with a waste loading of 20% by weight. Three samples were drilled from different height of the drum. The compressive strength was done on the core samples: 15.6 MPa (top), 12.3 MPa (middle) and 15.6 MPa (bottom).

Figure 13: *Core samples (left) from 100 L drum with oil waste (10 %) immobilised in MK-based GP, from the bottom, centre, and top of the drum (left to right); drilled hole (right)* [19]

For better immobilisation of oil in BFS-based GP, surfactant was added. The waste loading was 10 wt.%. The experiment was carried out only for 50 L drum, because the final product was soft, and separation of solid phases was observed (Figure 14).

Figure 14: *BFS-based GP with 10 wt.% oil loading inside 50 L drum* [19]

Thermal behaviour and fire hazard

The effect of high temperature was studied [20]. Cracks were observed in matrixes with or without waste after thermal cycling (from -20 to + 40 °C, 15 cycles, CEI EN 60068-2-14). Fire resistance tests were carried out by heating at 800 °C. The MK-based GP cracked (Figure 15) and the ultimate stress of other matrixes decreased after this test (Table 1).

MK Based   MIX formulation   BFS Based
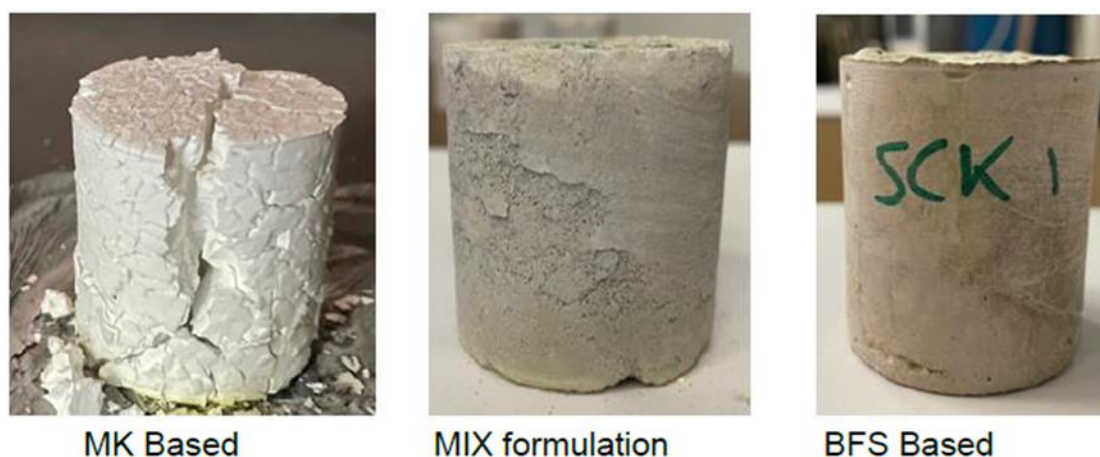
Figure 15: *Samples after fire test* [20].

Table 1: *Ultimate stress of matrices before and after fire resistance test; the test was done on two samples from each material* [20].

Formulation	Ultimate Stress [MPa]- Fresh	Ultimate Stress [MPa]- PF	Strength loss [%]
MK Based	15,36	0,00	100,00%
	8,38	0,00	100,00%
BFS Based	10,48	3,15	69,95%
	10,23	2,00	80,47%
MIX	10,24	6,02	41,19%
	14,65	4,71	67,87%

3.1.2.3 Organic liquids and solvents

As reported by IAEA [43] cement has limited efficiency for the solidification of organic liquid wastes: only 12 vol% of waste could be incorporated using the direct route, whereas up to 35 vol% could be incorporated using the pre-emulsification technique, although the latter requires a huge amount of surfactant (30 vol %).

Immobilisation of extraction liquids in MK-based GP was studied by *Watanabe et al.* [41]. The waste was dopped with copper. The waste loading was 8 %. The compressive strength was around 30 MPa (28 days of curing). Leaching tests were conducted in demineralised water for three months. No leaching of organic matter was observed, but coper leached from the waste form. The leachability index was 14.52. But the leaching did not stop.

The incorporation of organic solvents (TBP and mixtures of TBP and other solvents) has been investigated in the PREDIS project with different GP matrices.

Surrogated waste

Organic solvents (tributyl phosphate (TBP), dodecane, and their mixture) immobilisation in BFS based GP was studied. It was necessary to add surfactant because they were immiscible with water. If sodium lauryl sulfate was added, the waste loading was 15 wt.% and no bleeding was observed. In addition, tests were conducted for the immobilisation of a mixture of TBP with dodecane in MIX-based GP, but the incorporation was not good, even surfactant was added. [19], [20]

The comparison of TBP with ionic liquid immobilisation in BSF-based or MK-based GP was tested. Phase separation was observed without addition of surfactants. The maximum waste loading was 36 vol.% in the BFS-based GP, and 32.5 vol.% in the MK-based GP. The compressive strength was higher for the MK-based GP (5 MPa, after 4 days) than for the BFS-based GP (3 MPa, after 19 days). They implied a higher potential for MK-based GP. [19]

The immobilisation of pure TBP in MK-based GP was studied. The maximum loading of the waste in the GP was 20 vol.% without bleeding observed, and the samples with the higher waste loading were porous. Changes in the dimensions of the samples while curing were observed (0.06 % expansion – 0.15 % shrinkage) with a decreasing trend, which had not stopped after 90 days. For the next set of experiments, the mixture of TBP and dodecane was used with the addition of surfactant. The maximum waste loading was 30 vol.%, bleeding < 2 % was observed. The compressive strength was greater than 10 MPa after 90 days of curing. [19]

The effect of static immersion in water (for 28 days) and irradiation (200 kGy) and their combination on the compressive strength of different TBD/dodecane waste forms were tested. This was studied in the system of MK-based or BFS-based GP. The MK-based irradiated samples were not properly stored during irradiation, which caused their dehydration, and they cracked after immersion in water as a result of the rehydration. Immersion in water appears to have a greater impact than irradiation. In the next step, they dropped the waste with non-active Ce, Co, Cs, Eu, Nd, Ni, Sr, Th, and U. All contaminants had a leachability index higher than 8. No significant differences were observed in the leachability indexes determined for the sample without waste. No waste leaking was observed. [20]

Real waste

The immobilisation of the real waste sample - ionic liquid in BFS-based (sand addition) and MK-based GP was studied. This waste contained ^{14}C (25 kBq/mL) and ^{63}Ni (8 kBq/mL). The waste loading was 10 % and the compressive strength was around 20 MPa (after 28 days of curing), there was no significant difference between the inactive matrix and the matrix with real waste. In both matrixes, high sorption was observed for ^{63}Ni, but it was negligible for ^{14}C. Leaching tests were performed according to the ANSI method [29]; the last sampling day was after 90 days. The leachability index was higher than 8 for all combinations of matrixes and radionuclides. It was slightly higher for ^{14}C. [19], [20]

The real waste – TODGA in MK-based GP was studied. The waste contained Eu (^{152}Eu 3.8 Bq/g, stable 1.3 g/L), ^{241}Am (2.7 Bq/g), ^{244}Cm (3.1 Bq/g), stable Nd (0.8 g/L) and stable Ce (1.1 g/L). The waste

loading was 30 vol.% with surfactants. The samples were cured for 28 days in a humid environment or immersed in water. The compressive strength decreased by about 50 % for the waste-loaded matrix and immersion only slightly affected the compressive strength. The leaching test was carried out following ANSI/ANS16.1-2019 protocol [29]. Only non-active elements were measurable in the leachate, and the radioactive element was below the limit of detection. The leachability index was greater than 11.2 for Ce, Nd and Eu from immobilised TODGA waste. [19], [20]

3.1.2.4 SIERs and sludge

This section is focused on experiences conducted to test the durability and stability of waste forms containing non treated spent Ion exchange resins and sludges (Table 2).

Table 2: Summary of tests conducted in different countries for SIERs and sludge waste forms

Country	Waste	GP matrix	Tests conducted	Ref.
Taiwan	Surrogate doped with stable Cs and Sr	MIX-based	Compressive strength, leaching (5 days), water immersion	[35]
	Surrogate doped with stable Cs and Sr	BFS-based	Compressive strength, leaching (5 days), water immersion (90 days), thermal cycling, irradiation	[42]
Czech Republic	SIER and sludge mixture from NPP	SIAL	Compressive strength, leaching (48 hours)	[33]
Brazil	SIER surrogated doped with ^{137}Cs	MIX-based	Compressive strength, leaching (11 days)	[37]
Morocco	Surrogate doped with ^{134}Cs	MK-based	Compressive strength, immersion in water, leaching (50 days)	[34]
Slovakia	Sludges from NPP	SIAL	Compressive strength, water immersion, leaching	[33]
Canada	Metal hydroxides sludge surrogate	FA-based	Compressive strength, leaching, carbonatation	[36]

MIX-based GP for SIER immobilisation was studied by Lin et al. (Taiwan) the maximum waste loading tested was 12 wt.%. They performed a short-term leaching test according to ANSI/ANS-16.1 (5 days). No leaching of Cs was observed, but leaching of Sr was observed; leaching indexes were above 8. They immersed samples in demineralised water for 90 days, the compressive strength was about 40 % smaller for the samples after immersion. [35]

Waste form with hight waste loading (45 %) was studied by *Lee et al.* [42] . BFS-based GP was used. The compressive strength was 8.5 MPa. The SIER was doped with stable Cs and Sr. A short-term leaching test, according to the Taiwanese standard (5 days), was conducted. The cumulative leached fraction was 0.15 cm for Cs. For Sr it was much smaller 9.7 10^{-4} cm. The effect of thermal cycling, irradiation and water immersion on compressive strength was studied. The thermal cycle was with range of temperatures from -10 to + 55 °C. Each sample for the irradiation test was exposed to a cumulative dose of 1 10^6 Gy and, for immersion, was placed in water for 90 days. No significant changes in compressive strength after these tests were observed.

The mixtures of sludge and SIER from Temelin NPP and Dukovany NPP (Czech Republic) were immobilised in SIAL GP [33]. The waste loading was 17.5 wt% (dry waste). The compressive strength was 11.2-37.5 MPa. Samples were taken from 200 L drums. The leached fraction after 48 hours was 0.2-1.01 % for ^{137}Cs. The waste forms met the Czech WAC.

Different type of MIX-based GP was tested by *Casas et al.* [37] . The compressive strength was greater than 7 MPa. For the leaching test, they doped SIER with ^{137}Cs and followed ASTM C1318-21. The leaching rate slowed after the fourth day, after eleventh day the leaching rate was 3 10-5 cm/d and the caesium leaching did not stop.

Immobilisation of SIER in MK-based GP was studied by *Hamade et al.* [34]. The waste loading was 13 wt. %. No cracks in samples after being immersed for three months were observed. The compressive strength slightly increased after water immersion (from 50 to 52 MPa). The IAEA standard static leaching test[2] was followed. The leaching took place mainly in the first seven days and after that it was slow. The ^{134}Cs leaching rate was around 6 10^{-9} cm/s.

Two different sludges from the Jaslovske Bohunice NPP (Slovakia) were immobilised in SIAL GP [33]. The compressive strength was around 25 MPa. Samples were taken from 60 l drums. For ^{137}Cs leaching, the ANSI/ANS-16.1.-1986 protocol was followed. The leachability index was slightly above 8. Blank SIAL matrix was also immersed in water for 36 months, no cracks were observed. The waste forms met Slovak WAC.

FA-based GP for metal hydroxide sludges was tested by *Pandey et al.* [36] . The sludge was composed of Cd(II), Cr(III), Cr(VI), Cu(II), Pb(II) and Zn(II) salts (for each 0.029 mol per 1 kg of matrix). The solution was alkalised to form hydroxides. Carbonatation (50 vol.% CO_2, room temperature), compressive strength and leaching (following US EPA - TCPL and SPLP) were tested. Samples after carbonatation had slightly lower compressive strength. GP was effective in immobilising Cr and Cu, to a lesser degree Zn, Cd and Pb.

Immobilisation of dried borate waste surrogate in MK-based GP was studied by *Kim et al.* [38]. The incorporation of boron in the GP structure (boron replaced silicon) was observed. The compressive strength was around 15 MPa for 15% waste loading. The cumulative leached fraction was about 30 % (for cement waste it was approx. 50 %). The leching slowed after 96 hours, but did not stop after 11 days.

During the PREDIS project additional studies were conducted on the immobilisation of treated RSOW (SIERs) with geopolymers .

MIX-based matrix usage for SIERs ashes immobilization was tested. Ashes were doped with nonactive elements (B, Cs, Sr, Fe, Co, Cr, Mn, Ni, Zn, and Ag). Long-term leaching following the PREDIS leaching protocol[3] was performed [30]. Different types of water (Synthetic Cement Water - SCW, Deionized Water - DW and Disposal Site Water (from El Cabril facility) - DSW) were used. Materials immersed in SCW

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[2] Samples: cylindrical, V_L/S = 0.1 m; Leachate: demineralised water; Leachate replenishing: 1, 3, 7, 14, 21, 30 and 50 days

[3] Samples: cylindrical, V_L/S = 0.1 m; Leachate: synthetic cementitious water; Leachate replenishing: 7, 14, 21 and 28 days, then mothly for the rest of the first year, then 12, 16, 18 and 24 months

or DSW slightly lost compression strength, but it was still high (Figure 16). The porosity of the submerged materials (6 months) increased by 2 – 4 %. Negligible microstructural changes were observed after 1 year of immersion. The zone affected by leaching was approximately 450 μm after 1 year. Silicon and aluminium had a higher normalised loss of leached material in SCW (Figure 17). The leaching indexes were lower for the leached material in the DSW, but all were greater than 6. Under alkaline conditions, the matrix elements leached faster. [21]
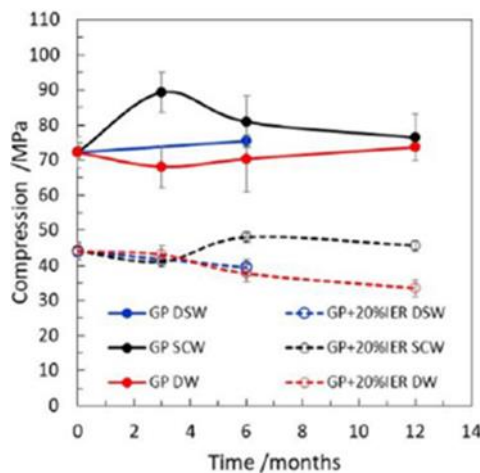
Figure 16: *Compression strength as a function of leaching time [21]*
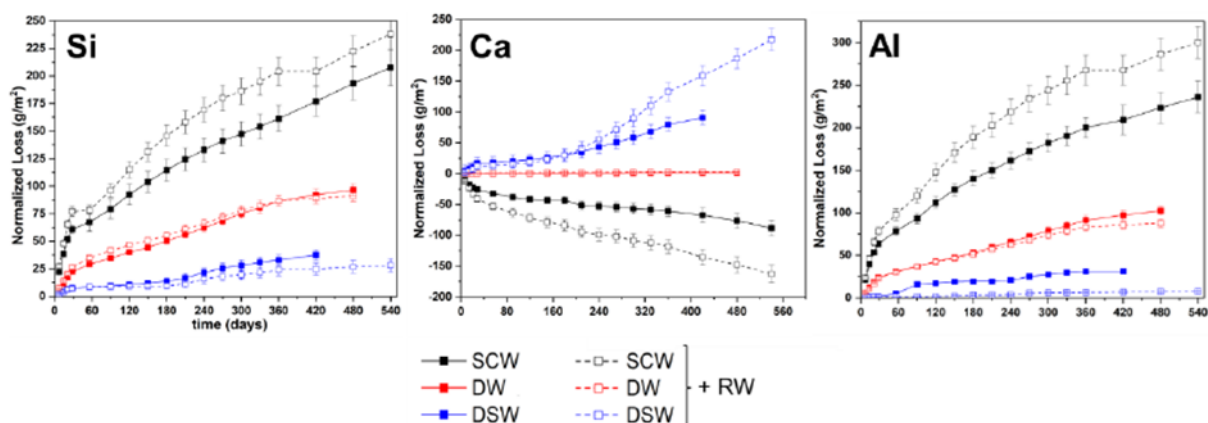
Figure 17: *Normalised losses calculated for Si, Ca, and Al for leaching test [21]*

Different MIX-based GPs with different treated SIERs (ashes, wet-oxidation, MSO) and IRIS ashes were tested. The effect of thermal cycling, long-term immersion in water, and leaching was tested. No significant changes in compressive strength were observed after 3 months of leaching. The lowest leachability index was for Cs from IRIS waste form. The leachability indexes were above 10 for the rest of the tracers. [21], [31]

The immobilisation of SIERs MSO in MIX-based GP was studied. The carbonation process was accelerated in the climate chamber. The carbonation depth was lower for material with higher waste loading. No changes in compressive strength were observed for the materials after carbonation. For leaching tests, the PREDIS leaching protocol (3 months) was used. The leachability indexes were around 6 for the alkali elements (Table 3). This high leaching of these elements was compensated by incorporating calcium into the matrix from the leachate. The microstructure of the matrix seemed to be unaffected by 3 months of leaching. [21]

Table 3: Leachability indexes for all monitored elements [21]

	Na	Ca	K	Al	SO$_4$	Si
BFS – 10%	6	10	6	8	7	8
BFS – 20%	6	10	4	8	7	8
Reference	7	8	6	9	7	7

Usage of different MK-based GPs for SIERs ashes immobilisation was studied. For leaching experiments, the PREDIS leaching protocol was used. Leaching of aluminium and silicate from the matrix was observed, but calcium was absorbed by the matrix from the leaching solution. The leaching of the trace element stabilised after 30 days. It was suggested the exchange of sodium or potassium for calcium cations. [21]

3.1.3. Process of geopolymer matrix approval in the Czech Republic

The Czech Republic is one of the first countries to have industry and regulatory approval for the use of geopolymers for radioactive waste conditioning. This section provides a summary of the process to reach this achievement, to raise awareness for other countries.

The initiation points in the process of developing a new matrix for solidification the liquid and semi-liquid radioactive waste was cumulating the significant volumes of problematic RAW (spent resins, sludge, sludge/resins, liquid or crystalline borates, oils, other organic liquids, concentrate and ashes) as a part of special category of operational radioactive waste arising at the operated NPP´s in the Czech Republic. The operational RAW is understand as a waste stream of radioactive waste originating in the relation to the operation of NPP and energy production.

At the beginning, as a conditioning technology of spent resins and sludges the bituminization technology was expected to be used. This technology was already successfully applied at both operated NPPs. The standard liquid RAW is processed by the evaporation technology to enhance volume reduction and the originated concentrate is conditioned by the bitumen matrix according to the waste acceptance criteria (WAC) individually developed for the disposal site for operational RAW (the LLW), the Repository Dukovany.

The technical issues during bituminization when the resins or sludge stuck in the pipes or bitumen product, the motivation for developing different solidification matrix was rising.

The process steps were as follows:

1. Expression of interest by the producer of RAW to develop new matrix for selected type of waste and prepare the preliminary request addressed to the Regulator
2. Agreement of involved parties (Regulator (SÚJB), Producer (ČEZ a.s.), RAWRA (SÚRAO) and owner of technology on the matrix performance testing (number of samples, solidification of samples under supervision, of involved parties, agreement on parameters to be tested and measured, approval of applied methodologies (standards), part-scale and full-scale experiments, time schedule and independent verification on real RAW streams.

The basic parameters were tested as compression strength, leachability, diffusion coefficients, radiation stability, biodegradability of matrix. And the additional tests were performed to obtain following parameters such as distribution and partition coefficients, influence of frost and water presence to the product stability, long term physical stability in water, dustiness, time dependence of compression strength and water reduction.

The next step in approval process was preparing the Safety analysis for final product acceptability to the Dukovany repository performed by RAWRA (SÚRAO). This document was based on the Safety analysis of Dukovany Repository, the data of geopolymer matrix testing and data of final report. This document evaluates the normal development scenario, the residential scenario and the scenario of

intrusion on the site while the RAW is solidified in the geopolymer matrix. And the waste acceptance criteria were derived from.

Then the approval form Regulator (SÚJB) was received for the technical specification for Repository Dukovany, including the updated Waste acceptance criteria for RAW solidified into geopolymer matrix.

There is also necessary to note, that the geopolymer matrix is able to ensure the basic WAC requirements as the leachability and mechanical strength, also the effective immobilization of radionuclides, especially ^{137}Cs, but comparing to the bitumen matrix the filling is lower (bitumen up to 35%, GP 20%). On the other hand, processing and conditioning RAW in GP is in some aspects easier, e.g. it´s not thermal process and the fire risk is significantly lower but still there is heat generation during the polymerization process. The individual composition of GP matrix is needed to define not only due to the characteristics of processed waste stream but also due to the different quality of GP matrix components. There is always needed to perform the laboratory tests ahead the technology run.

The International mission WANO (the WORLD Association of Nuclear Operators) and OSART (the Operational Safety Review Team) evaluated the used geopolymer matrix technology (SIAL) at Dukovany NPP as an example of good practice in 2010.

3.1.4. Conclusions

As reported in the previous sub-sections, different waste forms were prepared based on different alumino-silicates. The same wastes had not shown good compatibility with GP (e.g. LSC), for others surfactant had to be added (e.g. Lubricant oils). There is still a gap if the release rate of waste corresponds with the release rate of contaminant, or the radionuclides are strongly absorbed on the matrix. More experiments should be performed with real waste or surrogate doped with radionuclides or stable element.

For wet conditions, shorth-term experiments were done in most cases. Some process had not reached equilibrium (leaching, dimension changes, etc.) For better understanding of long-term behaviour and confirmation of models based on short-term experiment, it is necessary to study long-term behaviour of the waste forms. A good example of this approach was work done in the PREDIS project with the PREDIS leaching protocol.

The stability of dimensions during curing or immersion in water was studied thoroughly only in one case and did not stabilise in 90 days. In this field there is still a gap, this should be investigated for more waste forms, because it could lead to damage of repository barriers. Barriers could also be damaged by gas release. This gas can be produced by irradiation of waste forms, there is a gap in this area for many waste forms.

In many cases, the waste forms meet the compressive strength criteria defined by each country WAC. But when the waste form was not properly stored, the matrix dried out and cracks occurred (mainly MK-based). In the surface repository, water is not expected to be there for the first hundreds of years after closure. More research should be done in the field of dry condition, if the liquid waste will migrate to the matrix or if SIER will bound water from the matrix and destroy it. In the near-surface repository temperature can change, the thermal cycling experiments can provide us with how will waste forms behave under these conditions. From the results, there is no significant impact of thermal cycling, but it should be further investigated in tandem with saturation and desaturation. This could lead to damage of matrix and faster radionuclide release.

Geopolymers can be prepared from a variety of aluminosilicate materials, allowing their properties to be tailored to the properties of the immobilised waste. However, this advantage is also their main disadvantage because using a material from another manufacturer will significantly affect the properties of the matrix. Therefore, it is important to optimise the waste matrices before use.

3.2 Magnesium potassium phosphate cements (MKPC)

3.2.1. Nature of the matrix and immobilised waste

3.2.1.1 Magnesium potassium phosphate cement characterisation and properties

Magnesium phosphate cements (MPC) are based on the chemical reaction between a solid basic magnesia powder and a soluble acidic phosphate salt. Early formulations used ammonium dihydrogen phosphate ($NH_4H_2PO_4$ or NDP) as a source of phosphate generating the precipitation of a low-solubility mineral called struvite ($MgNH_4PO_4 \cdot 6H_2O$). Due to generation of noxious ammonia gas during the setting process, monopotassium dihydrogen phosphate (KH_2PO_4 or KDP) became extensively used instead. In addition, KH_2PO_4 has lower dissociation constant (pKa) and lower molar solubility than $NH_4H_2PO_4$, thus, lower reaction rate and less amount of heat is generated in the acid-base reaction.

The chemical reaction between magnesia and monopotassium phosphate in presence of water produces K-struvite, according to equation 1:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O \qquad \text{(eq. 1)}$$
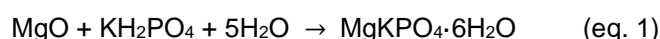
To retard the fast setting and decrease the heat of the highly exothermic reaction, a chemical retarder and an inert filler is normally added. The cement formed by this system is called magnesium potassium phosphate cement (MKPC).

MKPC pastes preparation is a simple process. Usually, MgO, KH_2PO_4 and the filler are mixed as solid powder materials while the retarder is first dissolved in water and the solution is then added to the solid mixture. Precursors are mixed until a homogeneous paste is generated. MKPC mortars can also be prepared by the addition of sand to the mixture.

The reaction mechanisms for the formation of K-struvite proceed through dissolution/precipitation processes. Dissolution reactions include partial dissolution of MgO aggregates and subsequent hydration to form the octahedrally coordinated aqueous species $[Mg(H_2O)_6]^{2+}$ and complete dissolution of KDP in the aqueous medium. Precipitation processes are described through different mechanisms in literature. Since the reaction rates are fast, which makes inconvenient to study the reaction sequence experimentally, a consensus has not been achieved. It is important, however, to unravel the hydration process of the system $MgO-KH_2PO_4-H_2O$ because it directly influences on the rheological properties of the resulting MKPC.

Some recent studies have evaluated the *in situ* MKPC hydration using different analytical techniques, such as electrical conductivity [44] , pH [45] and [46] and isothermal calorimetry [47]. As reported by Le Rouzic *et al.* [48] and Wang *et al.* [49], the pH increases gradually from 4 to 6, due to the continuous dissolution of MgO; in the range 6-7, newberyite ($MgHPO_4 \cdot 3H_2O$), a metastable intermediate mineral phase, forms and starts its transformation to different morphologies of K-struvite, to finally dissolve completely at pH above 7. Depending on the water/binder and Mg/PO_4 (M/P) ratios, other intermediates or co-precipitations have been observed, including cattiite [$Mg_3(PO_4)_2 \cdot 22H_2O$], phosphorrösslerite ($MgHPO_4 \cdot 7H_2O$), $Mg_2KH(PO_4)_2 \cdot 15H_2O$ and other amorphous phases [45], [46], [50], [53]. Additional intermediates form during hydration when the retarder is included. Lünebergite $\{Mg_3(H_2O)_6[B_2(OH)_6(PO_4)_2]\}$ and other magnesium borates [$Mg_7B_4O_{13} \cdot 7H_2O$; $MgB_3O_3(OH)_2 \cdot 5H_2O$] have been detected when borax ($Na_2B_4O_7 \cdot 10H_2O$) or boric acid (H_3BO_3) were added as retarders [54], [55].

In addition to the type of materials, the mix design to formulate a MKPC is defined by the M/P ratio (normally expressed as a molar ratio), the water/binder or water/solid ratio, the filler/binder or filler/MgO replacement ratio, the percentage of retarder used and, in case of a mortar formulation, the sand/binder ratio. The binder or cement accounts for the sum of MgO and KH_2PO_4.

Several key parameters were identified to control the reactivity and performance of MKPC [56]:

- The nature of MgO
- The role of retarders

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- The filler nature and ratio
- The water content
- The role of the M/P ratio
- The MKPC curing conditions and temperature

The nature of KH_2PO_4 is, however, not considered as a key parameter since the bottleneck lies on the MgO and its partial dissolution. In terms of functionality, KDP is marketed as a high-grade water-soluble fertilizer. The cost and availability of KDP are the main causes for concern. In 2014, the European Union added phosphate rocks to the list of critical raw materials. Morocco supplies 27% of the demand in the European Union, whereas China supplies 48% of the global demand [57]. The cost of KDP is significantly higher than that of MgO and other components used in the production of MKPC, yet other phosphate sources have not been shown to achieve comparable yields. Consequently, in order to decrease the cost impact of KDP, efforts should be concentrated on estimating the final hydration degree to produce K-struvite by modifying the M/P ratio, minimising the amount of KDP used.

Thermal treatment of magnesite is the main via to obtain MgO. Reserves of magnesite are geographically limited and randomly distributed worldwide. Due to its relevance, the European Union included magnesite in the list of critical raw materials in 2014, which remains present in 2023 [57]. At low calcination temperature, MgO is classified as light-burnt or reactive magnesia (700–1000 °C). Hard-burnt MgO is calcined within the range of 1000–1500 °C, although several authors consider temperatures above 1300 ºC. Well-crystallised periclase crystals are formed, without amorphous coating, achieving a narrow range of reactivity. Dead-burnt MgO is obtained at temperatures ranging from 1500 to 2000 °C, which yields a high purity material with very little reactivity. Needless to say, the temperature applied has a direct impact on the energy consumption for production and material cost.

Most of the research studies use dead- or hard-burnt magnesia as source of MgO. Reactive magnesia exhibits lower MgO content and larger particles' surface area and generates a larger exothermic reaction to produce MKPC. The larger the specific surface of magnesia, the shorter the setting time of the cement paste. Therefore, MKPC prepared with reactive MgO must have an effective retarder to be workable, and that excludes the commonly used boric acid, as it has been observed that does not work efficiently with reactive MgO. Sodium thiosulphate ($Na_2S_2O_3$) has been proposed instead, as it can effectively delay the hydration reaction for a sufficient time to allow industrial use of the cement [58]. Other studied retarders used for MKPC production include sodium triphosphate ($Na_5P_3O_{10}$) [60], $Zn(NO_3)_2$ [60], aluminium nitrate [$Al(NO_3)_3 \cdot 9H_2O$] [61], sodium alginate [$(C_6H_7O_6Na)_n$] [62], sodium gluconate [63], acetic acid [64], citric acid [65].

In 1978, Stierli *et al.* [66] patented a method for controlling the setting of MPC using soluble oxy-boron compounds such as boric acid or borax. These chemicals were discovered to successfully retard the setting time and reduce the severity of the exothermal reactions; thus, they were included in the formulation as key components, but the retarding mechanism was still under debate. Sarkar [67] investigated the kinetics of retardation of the reaction between MgO and NDP with boric acid. It was hypothesized that a surface film of magnesium borate compounds might form and cover the magnesia particles, and the film was slowly destroyed by magnesium ions dissociated from magnesia, thereby delaying the setting reaction to form lünebergite, that prevented the grains from dissolving in the acid solution. Subsequently, as the pH of the solution rose, the coating dissolved slowly, and the grains were exposed back to the acid solution. Because the dissolution of MgO was delayed, the acid-base reaction rate decreased.

Other retarders may work through a different route. Physical adsorption on MgO crystal nuclei was proposed for the use of sodium triphosphate, thereby inhibiting crystal nucleation and growth, and or chelating magnesium ions in a soluble complex [59]. Therefore, the microstructural characteristics are very dependent on the type and amount of retarder employed.

The addition of mineral admixtures, either natural minerals, rocks or industrial by-products, not only contributes to delay the setting time of MKPC but also contributes to reduce the heat generated during

the early hydration, may enhance the workability of the fresh cement pastes and improve the mechanical strength and, definitively, decrease the material productions costs.

The main principle considers replacement of MgO and KH_2PO_4 by an inert filler material that should not participate in the acid-base reaction and has none or low interaction with the precursors. The addition of inert mineral admixtures impedes the contact between MgO particles and phosphate, extending the setting time, although some studies observed that some oxides, included as filler's components, such as MgO, CaO, ZnO, Al_2O_3 and Fe_2O_3, can compete with MgO in the reaction with phosphate, changing the original M/P and the accelerating reaction rate [68].

Xu *et al.* [69] studied the incorporation of fly ash (FA) and proposed a filler replacement ratio for MgO only, maintaining the filler plus MgO to KH_2PO_4 ratio constant, as it was suggested that the replacement of MgO by fly ash led to higher strength and denser microstructure. Other authors express the filler content as filler to MgO + KH_2PO_4 + water [70], or as filler to MgO + KH_2PO_4. An effort to standardise the different expressions reported in literature should be accomplished.

Due to their morphology and small particles' size, coal FA and blast furnace slag (BFS) are the most used fillers in MKPC formulations. However, since FA is produced as a by-product of coal-based thermal power plants that are closing globally to reduce carbon emissions and achieve climate commitments, its availability has recently decreased. Similarly, as the iron and steel industry shifts to low-carbon steelmaking, the amount of BFS available would drastically decrease on a worldwide scale. As alternatives to FA and BFS, other materials have been incorporated in MKPC, such as metakaolin [71], silica fume [72], wollastonite ($CaSiO_3$) [73][74], volcanic ash [75], steel slag [76], red mud [77], [78]and glass powder [79], [80] among others.

Several studies have evaluated MKPC formulations according to a three-phase system, considering that the M/P and the water to binder (W/C) are the most important ratios that influence on the MKPC performance [45], [81]. As MgO is often in excess, the theoretical minimum water content must comply with the stoichiometric molar ratio presented in eq. 1 in relation to phosphate (5:1) to produce K-struvite, which is more stable and has higher mechanical strength than other hydration products. This theoretically water to phosphate ratio (W/P), expressed in mass ratio, is equal to 0.662. An increase in the water content, however, may increase the workability of the cement paste and retard the setting but decrease considerably the mechanical strength, as the excess of water is not chemically bound within the hardened cement, leaving a porous structure during curing [82]. The relationship between the W/P mass ratio and compressive strength achieved after 1 day, in MKPC formulations without filler, showed maximum strength at W/P values slightly lower than the theoretically calculated, in a narrow range closer to 0.6 [83]. The reason for this difference might be attributed to the dosage of MgO and retarder affecting the reaction degree of phosphate. Larger W/P ratios decrease the mechanical strength.

The M/P ratio highly influences on microstructural properties, including the porosity and pore size distribution, the mechanical properties and the volume stability. Ideally, if all MgO could dissolve and react with phosphate, a M/P molar ratio equal to 1 would be adequate to produce K-struvite. An excess of magnesia has been proved to be more beneficial in practice, considering the fraction of MgO that will remain in aggregates within the MKPC matrix. For construction applications or as a repair material, high M/P molar ratios (≥4) have been frequently used.

Conversely, low M/P molar ratios (< 4) are preferred for immobilizing radioactive aluminium metal and heavy elements, as neutral pH conditions are required to preserve their passivation domain (i.e. pH in the range of 4–9 for aluminium) [84], [85]. An excess of KH_2PO_4, that might be produced at low M/P ratios, has been shown to be detrimental due to efflorescence formation [86], that may lead to the expansion and cracking of samples. Yue *et al.* [87] observed numerous cracks on the surface of MKPC specimens prepared with a M/P molar ratio equal to 3, but hardly any cracks on samples prepared with the same materials but with M/P ratios of 4 and 6. This resulted in significantly higher flexural and compressive strength.

There are questions, however, regarding the long-term evolution of MKPC-based materials containing unreacted MgO in humid environments of low and intermediate level radioactive waste (LILW) repositories, since it is well known that the hydration of MgO into brucite [Mg(OH)$_2$] is accompanied by a significant increase in volume [88]. This is why the maximum allowable MgO content in standard Portland cements in Europe is limited to 5 wt.%, according to the EN 197-1 standard. Therefore, most MKPC formulations with application for immobilisation of LILW reported in literature consider low M/P molar ratios, usually within the range 1–2 [51], [70], [89], [90], [91], although more recent studies consider M/P molar ratios of 3 as a better choice for this purpose since it has been demonstrated good stability and durability [92].

In addition, the nature of the filler used contributes to regulate the pore pH in MKPC matrices. Measuring the pH of MKPC pastes in water suspensions, Dieguez *et al.*[74] observed an increase of one order of magnitude, from around 7.3 to 8.3, by replacing the filler FA, metakaolin or pumice for wollastonite in MKPC formulations with a M/P molar ratio equal 1. When the M/P molar ratio increased from 2 to 3 and 4, Padilla-Encinas *et al.* [75] observed an increment in pH after 90 days, also measured in water suspensions, from 8 to 9.5 using wollastonite and from 8 to 9.2 using volcanic ash as fillers. Fernández-García *et al.* [85] observed an increase in pH, on MKPC samples cured at 100% of relative humidity (RH), from approximately 7.5 to 10.5 after 90 days when the M/P molar ratio increased from 1 up to 3, using FA as filler. Lower pH was observed in cement pastes compared to cement mortars, attributed to the higher water/solid ratios of the latter.

Curing conditions of MKPC specimens significantly influence on the chemical and physical properties. It has been observed larger instability, showing efflorescence, volumetric changes and lower mechanical strength in samples cured under high moisture conditions, particularly immersed in water, followed by curing at 100% of RH, and better stability in samples cured under endogenous conditions [32].

3.2.1.2 MKPC for immobilisation of LILW

Low and intermediate radioactive waste comprises materials of various compositions and natures, such as organic (solid and liquid) and metallic.

- LILW may contain radioactively-contaminated metals originating from the decommissioning of nuclear power plants and other industrial activities [93]. Aluminium, beryllium, land Magnox (a magnesium alloy) are the primary sources of radioactive metal waste that must be immobilised before final disposal in surface/near-surface or geological repositories.

- Spent ion-exchange resins (SIERs) are produced during nuclear facility operations, including nuclear fuel recycling, demineralization of wastewater, decontamination of nuclear installations, and decommissioning activities. These resins are considered some of the most significant radioactive low- and intermediate-level wastes and are typically loaded with small amounts of radionuclides (^{137}Cs, ^{90}Sr…). Since spent IERs cannot be regenerated or reused, they must be properly treated and disposed of to minimize their environmental impact. These resins make up a large portion of the solid radioactive waste generated by the nuclear industry, and the treatment and disposal of spent IERs have become critical concerns in some countries in the development of nuclear power plants.

MKPC is considered as an alternative matrix to immobilise these types of LILW. The suitability and long-term durability must be demonstrated and the stability of the waste form must be ensured.

3.2.2. Waste form durability and stability

3.2.2.1 Radioactive metals immobilisation in MKPC matrixes

Radioactive metals can chemically interact with ions dissolved in the pore water of the cementitious matrix, leading to instability and potentially compromising the long-term integrity of the waste form. A key factor in the immobilisation of radioactive metals is the pH of the cement pore solution. The stability pH range (passive state) varies for each metal: for aluminium, it ranges from pH 4 to 9; for beryllium, from pH 3 to 13.5; and for activated Magnox metal, above pH 10.5.

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The primary concern in radioactive metal confinement is minimising the risks associated with hydrogen gas generation due to corrosion. This gas can accumulate, leading to pressure build-up, stress-related issues, and the potential transport of radionuclides out of the waste package [4]. Two key challenges must be addressed to ensure the successful encapsulation of radioactive metals: (i) the high volumes of hydrogen generated during cement grout curing when water is readily available for reaction, and (ii) the long-term effects of continued but slower corrosion on the encapsulated product.

Portland-based matrices have commonly been used for the immobilisation of radioactive metals, often incorporating mineral additions. One example is the grout mix of Ordinary Portland cement (OPC) blended with BFS, which has been used for Magnox encapsulation [4]. However, the chemical composition and pH of available binders vary significantly and must be tailored to the specific metal being encapsulated. Notably, MKPCs have shown to effectively reduce uranium corrosion rates by half [94], and have demonstrated promising results for the encapsulation of Al and Be.

Performance of Beryllium encapsulation in MKPC matrices

Beryllium is highly toxic and, in its powdered form, is classified as a carcinogen that can cause an incurable respiratory disease. In atmospheric conditions, the metal is protected by a thin oxide layer, typically composed of beryllium oxide (BeO) or beryllium hydroxide [$Be(OH)_2$]. The reactivity of beryllium in a given environment is primarily influenced by the stability of this protective layer. Beryllium undergoes corrosion, producing hydrogen and beryllium hydroxide and/or oxide, as described by the equation 2:

$$Be + 2H_2O \rightarrow Be(OH)_2 + H_2 \qquad (eq.\ 2).$$

Studies using simulated pore solutions with pH ranging from 12.5 to 14 have shown that the corrosion rate of beryllium increases exponentially with pH. In contrast, under near-neutral pH conditions, pure beryllium corrodes at a significantly slower rate [95]. The available literature on the behaviour of beryllium in cementitious systems is limited. Beryllium reactivity has been studied in cement matrices with varying pore solution pH levels [95], [96], including brushite cement (pH 1.75–6.44), MKPC (pH 5.6–8.4), calcium sulfoaluminate cement (pH 10.9–12.3), OPC (pH 12.5–12.9), and activated slag (pH 12.9–13.8). Beryllium nuclear waste can be conditioned using Portland cement, calcium sulfoaluminate cement, or magnesium phosphate cement with acceptable stability. However, corrosion rates are excessively high in brushite cement and alkali-activated slag, leading to significant hydrogen production. In contrast, when beryllium is embedded in cementitious materials such as OPC and MKPC, corrosion rates are significantly lower [95]. Corrosion rates of beryllium in cement pastes at 7 days under 100% RH conditions have been reported as 0.34 and 0.89 µm/year for OPC and 0.035 and 0.81 µm/year for MKPC, using electrochemical methods and gas chromatography to assess hydrogen generation, respectively. These results reveal significant discrepancies between the two measurement methods, emphasising the need for further research to improve accuracy.

Aluminium encapsulation in MKPC matrices

Aluminium metal forms a stable, protective amphoteric alumina oxide layer (Al_2O_3) within a pH range of 4 to 9. However, outside this range, the natural Al_2O_3 layer dissolves, promoting aluminium corrosion in aqueous media and leading to hydrogen generation, as described in equation 3:

$$2Al + 6H_2O \rightarrow Al_2O_3 \cdot 3H_2O + 3H_2 \qquad (eq.\ 3).$$
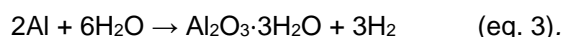
In strongly alkaline environments, such as those found in Portland cement matrices, aluminium undergoes active corrosion, continuously producing hydrogen. Consequently, ordinary Portland cement (CEM I) has demonstrated significant limitations in immobilising radioactive aluminium due to the high pH of its pore solution (ranging from 12 to 13.7) [84], [97].

Laboratory studies have reported hydrogen release volumes (per unit of embedded metal surface) generated by aluminium corrosion in OPC matrices, both with and without mineral additions, as well as

in MKPC systems. Two methodologies have been used: direct measurement via gas composition analysis using gas chromatography (GC) and indirect estimation based on corrosion rate measurements [84], [97], [98].

A review of literature data on hydrogen release volumes reveals significant variability across studies [97]. One factor contributing to these discrepancies is the measurement technique employed. In general, direct measurement methods yield lower H_2 volumes under the same age and test conditions compared to indirect estimations (electrochemical methods) [84]. The exact cause of this difference remains unclear, though possible explanations include gas retention within the matrix or inaccuracies in direct gas volume measurements, underscoring the need for further investigation. Despite this variability, certain trends can be identified from electrochemical data by analysing different parameters that kinetically influence the volume of H_2 gas generated during the corrosion process of Al alloys immobilised in MKPC, as observed in Figure 18 and through comparisons between different studies.
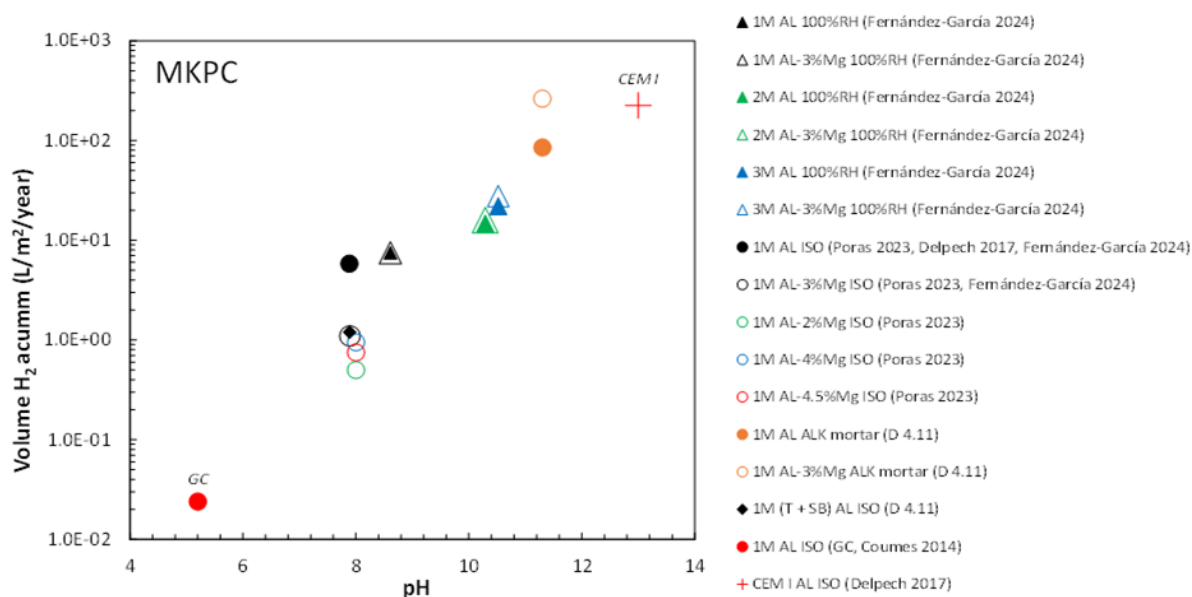
Figure 18: Volume of H_2 gas release (in $L \cdot m^{-2} \cdot year^{-1}$) from Al alloy immobilised in MKPC matrices [99]

Different parameters influencing the corrosion rate of aluminium are explained below.

- *Influence of type of binder:* Previous studies indicate a general consensus among authors regarding the advantageous properties of MKPC over Portland cementitious matrices for aluminium immobilisation [84], [97], [98], [100]. In CEM I mortars cured under isolated conditions, significant H_2 gas production has been reported, reaching approximately 225 $L \cdot m^{-2} \cdot year^{-1}$ [98]. In contrast, much lower H_2 volumes have been observed in MKPC systems with a 1M magnesia-to-phosphate (M/P) ratio, with reported values of 0.026 $L \cdot m^{-2} \cdot year^{-1}$ in pastes [84], and approximately 5 $L \cdot m^{-2} \cdot year^{-1}$ in mortar over the same period [98]. Additionally, some studies have estimated H_2 release after one year of water immersion at approximately 30 $L \cdot m^{-2} \cdot year^{-1}$ for OPC (pH = 12.7), 25 $L \cdot m^{-2} \cdot year^{-1}$ for CEM IV (OPC blended with FA and BFS) (pH = 12.6), and 7 $L \cdot m^{-2} \cdot year^{-1}$ for OPC with 50% silica fume (pH = 10.8), whereas MKPC 1M recorded only 0.03 $L \cdot m^{-2} \cdot year^{-1}$ [97], [100].

  In addition to the significant differences in aluminium corrosion kinetics, notable alterations in the OPC matrix have been observed at the interface region [97]. A highly porous domain develops near the Al/OPC paste interface due to the large volume of H_2 gas released, even under isolated curing conditions with low pore-water content. Furthermore, the high corrosion rate of aluminium results in the release of Al ions, which can diffuse into the cement matrix due

to the highly alkaline pore solution. This process promotes the formation of expansive ettringite at the matrix interface, potentially compromising the long-term integrity of the waste form.

Therefore, the use of CEM I is not recommended for aluminium immobilisation. The lowest corrosion rates and minimal H_2 gas production are observed in the 1M MKPC matrix, followed by OPC + 50% SF, as the gradual decrease in pore pH during hydration enhances their long-term stability. These matrices are considered optimal alternatives for the immobilisation of Al and Al–Mg alloys compared to the commonly used CEM I system [97].

- *Effect of M/P ratio:* The MKPC dosage, defined by the M/P ratio, also influences the aluminium corrosion rate and H_2 release [85]. The corrosion process of Al alloys in MKPC matrices is affected by both, pH and ion content in the pore solution. An increase in pH from 7–8 in a 1M M/P ratio to 9 and 10 in 2M and 3M M/P ratios, respectively, leads to doubling and tripling the initial Al corrosion rate. Over one year, the accumulated average H_2 release under 100% RH conditions was 7.5 $L \cdot m^{-2} \cdot year^{-1}$ for 1M M/P, 14.7 $L \cdot m^{-2} \cdot year^{-1}$ for 2M M/P, and 16 $L \cdot m^{-2} \cdot year^{-1}$ for 3M M/P. These differences were primarily attributed to variations in pore pH, but also to differences in phosphate ion content in the pore solution. The presence of phosphate ions inhibits the Al corrosion process, while borates, introduced as retarders in the mix, have also been shown to reduce the Al corrosion rate in MKPC. Most hydrogen release occurs within the first 15 days of aluminium interaction with the MKPC matrix and then attenuates over time, provided that the surrounding conditions are not changed.

  According to previous results, MKPC exhibits the highest chemical compatibility with aluminium at a 1M M/P ratio. However, the physicochemical instabilities of this matrix, particularly regarding microstructural properties and volume changes, suggest that an M/P ratio greater than 1 may be more suitable [85].

- *Influence of water content in pores:* The type of curing and moisture content in the pores also influence aluminium corrosion. Under endogenous (isolated) curing, the corrosion kinetics are significantly reduced. Hydrogen release values, calculated from corrosion rate measurements, range from 1 to 5 $L \cdot m^{-2} \cdot year^{-1}$ [85], [98] while under 100% RH conditions, pure Al releases 7.5 $L \cdot m^{-2} \cdot year^{-1}$. These differences are primarily attributed to variations in pore solution pH (ranging from 7 to 8.5) and phosphate content, which result from the incomplete progression of the acid-based reaction between MgO and KH_2PO_4 under isolated curing conditions.

- *Influence of Mg content in Al:* The presence of magnesium in aluminium (Al-Mg alloys) also influences corrosion behaviour. When the Mg content is <3%, higher corrosion rates and increased H_2 release are observed [85], [101]. However, if the Mg content is >3%, both the corrosion rate and hydrogen release decrease due to the protective effect of magnesium on aluminium. The influence of Mg content in the alloy becomes more pronounced as the M/P ratio increases, since higher M/P ratios lead to increased pore solution pH, which, in turn, accelerates aluminium corrosion.

- *Influence of MgO reactivity:* Although there is a clear lack of information regarding the effect of MgO microstructure as a consequence of the calcination temperature, most studies on aluminium corrosion in MKPC have been conducted using hard-burnt MgO. However, a comparison with light- or soft-burnt MgO indicates lower H_2 release in the latter system, attributed to differences in MgO reactivity [102], [103]. Additionally, the type of retarder used also influences this reduction, with thiosulphate proving more effectiveness in soft-burnt systems compared to borate in hard-burnt systems.

- *Effect of MKPC alkalisation:* In the long term, water interacting with the concrete containment cell can generate an alkaline plume, potentially affecting both, the microstructure of the MKPC

waste form and increasing its pore pH. There is a significant lack of information on this aspect. Studies conducted within the PREDIS project have shown that the passivity of aluminium in MKPC can be compromised if alkalinisation of the MKPC matrix occurs [99], [102]. When the pH increases from 7 (MKPC 1M) to 11.3, hydrogen release can rise by more than two orders of magnitude, from 5 $L \cdot m^{-2} \cdot year^{-1}$ to 100 $L \cdot m^{-2} \cdot year^{-1}$, reaching levels comparable to those observed in OPC [98]. As illustrated in Figure 18, this process could compromise the long-term performance of the repository and the encapsulated radioactive metal.

Corrosion of steel in MKPC:

- It is well known and widely accepted that steel is naturally protected from corrosion in an alkaline environment (pH 12–13) by a thin oxide layer that passivates the metal. However, the pore solution pH in MKPC matrices is significantly lower depending on the M/P ratio used, ranging from 7 to 10 (1 to 3 molar M/P ratio) [85]. In this lower pH environment, the effectiveness of the MKPC matrix in providing corrosion protection for steel is uncertain, below the level of the passivity of steel. Experimental studies have shown that MKPC can provide a high level of protection when used as coating for steel, achieving a passive state [104], [105], [106]. The presence of certain pore ions, such as phosphate and borate, may contribute to this protective effect. These ions have been identified in MKPC matrices, with their concentration varying over time in a manner similar to pH, depending on the M/P ratio and matrix ageing [85]. However, the exact mechanism behind this protection remains unclear and requires further investigation.

- The protective effect of MKPC paste (mass ratio of MgO/Phosphate: 4/1) covering steel reinforcement in contact with NaCl demonstrated excellent corrosion protection, attributed to the formation of an insoluble iron phosphate-based protective film, along with other composite products [104]. The characteristics of this film were largely influenced by the type of phosphate used (ammonium or potassium). The protective mechanism of MKPC was considered to occur in two stages: (1) the formation and evolution of the protective film and (2) the re-passivation and inhibition of corrosion. Yin et al. [105] investigated MKPC coatings (dead-burned MgO to KH_2PO_4 = 5 molar ratio slurry) for protecting mild steel. Their findings highlighted the role of magnesia as a key factor in corrosion resistance, providing a barrier effect while dissolved phosphate ions further enhanced protection. The coating significantly improved the corrosion resistance of steel in salt spray environments. Similarly, Zang et al. [106] confirmed that an MKPC paste coating applied to steel reinforcement effectively delays corrosion onset and suppresses corrosion reactions. However, the presence of boric acid as a retarder (5% by weight of MgO) was found to interfere with the protective response of MKPC, significantly reducing the time required for passivation.

- The reactivity of steel in various MKPC mortar formulations was investigated and compared with OPC to better understand and estimate corrosion rates and hydrogen generation [102]. Both hard-burnt and soft-burnt MgO were used in a 1M M/P formulation, with boric acid and sodium thiosulphate as retarders. The study found that steel corrosion was more pronounced in sodium thiosulphate, while boric acid did not provide sufficient protection for steel drums. Moreover, their combined use appeared to exacerbate the corrosion process. Higher steel corrosion was observed in soft-burned MKPC formulations compared to hard-burned ones. The behaviour of carbon steel in MKPC matrices was similar to that in OPC, with the key difference being that, although the initial corrosion rate was higher in MKPC, it decreased more rapidly over time. However, hydrogen release from carbon steel in MKPC was found to be higher than in OPC matrices.

3.2.2.2 Spent ion-exchange resins encapsulation in MKPC matrices

Promising alternative cement binders under consideration for encapsulating reactive secondary wastes (including SIERs) include alkali-activated cements [110], calcium aluminate phosphate-modified cements (CAP) [111], and MPCs [112]. Among these options, MKPCs stand out as a particularly promising choice for immobilizing ^{137}Cs, a challenging isotope to contain. The main reaction product generated in this system is the K-struvite, and this could chemically fix the ^{137}Cs in the event of release of this radionuclide from the resin.

However, there are not many works in the literature that consider the encapsulation of SIERs in MKPC. Garcia-Lodeiro *et al*. [113] analysed the effect of the incorporation of a surrogate waste, a nuclear grade Purolite resin (doped with Cs) in different proportions (from 0 to 20 wt.% of the dry mass of resin) in MKPCs specially designed with a secondary product obtained from the calcination of magnesite, a low-grade MgO. The results obtained showed that the incorporation of the resin retards the kinetic of reaction, decreases the mechanical strength development and affects the microstructure (increasing the total porosity values). However, all systems, including those with the highest proportion of SIERs (20%), overpass the 10 MPa waste acceptance criteria (WAC) after 28 days of curing. The presence of resin did not seem to affect the formation of the main reaction product, the K-struvite. Unpublished results from the same authors showed that MKPC systems designed with a M/P ratio of 3 and containing up to 15% resin perform well under leaching in deionized water [114]. After 28 days of immersion, MKPC systems with 15% resin, showed slight decreases in the mechanical strength values and an increase in total porosity and pore size was detected. Despite this, the cementitious matrices still show adequate strengths, making their use entirely feasible. The study of the leachates showed that the system with 15% resin was perfectly capable of immobilising Cs (Leaching index, $L_i > 6$). However, a high leaching rate of Sr and B was detected, indicating that is necessary to take measurements to improve this aspect. Although the results shown are promising, there are still important gaps in knowledge that need to be addressed.

3.2.2.3 Leaching resistance of MKPC matrices and waste immobilisation

The response of magnesium phosphate matrices in contact with water or water after interaction with repository barriers is a very relevant issue to determine their confinement properties, but also to understand the degradation mechanisms involved under leaching, which is of great importance to ensure the long-term durability of the waste form. Neutral and alkaline waters are the two most common scenarios expected in a LILW repository. WAC for evaluation of LILW typically considers deionised water for leaching resistance characterisation. However, a common or standardised leaching protocol has not been found, that is of relevant interest to obtain comparative results and better interpret the processes involved in leaching.

MKPC leaching in deionised water: Several studies evidenced a reduction in the compressive strength of magnesium phosphate cement-based materials exposed to water [115], [116], [117] Yang *et al*. [115] studied the water resistance of MPC mortars (prepared with $NH_4H_2PO_4$ and a M/P molar ratio of 3), cured for 28 days under endogenous conditions, exhibiting a strength decrease of about 11% and 18% after 30 and 90 days of immersion, respectively. Lahalle *et al*. [118] investigated the evolution of MKPC paste samples (M/P molar ratio of 1 and w/c of 0.56) immersed in deionized water (pH 6.8) for 6 months. X-ray diffraction (XRD) analyses revealed a decrease in crystalline K-struvite content and an increase in amorphous, likely due to the formation of poorly crystalline K-struvite. Pore solution analyses indicated the release of ions into the immersion solution, particularly K^+ ions. In more recent studies, the leaching response of MKPC pastes with 1M M/P and semi-dynamic leaching tests concluded that leaching is governed by diffusion transport combined with chemical reactions (dissolution/precipitation fronts) [119], [120]. A linear evolution of cumulative leached element concentrations versus the square root of time was found. Three main zones were observed in the matrix leached solids: (i) a poorly cohesive residual layer, where K-struvite was fully depleted, (ii) an intermediate zone where K-struvite coexisted with cattiite [$Mg_3(PO_4)_2 \cdot 22H_2O$], and (iii) a third zone without any cattiite. Reactive transport modelling was proposed to predict the extent of degradation and the phase evolution of the MKPC matrix. The effect

of the filler in MKPC has also been studied through leaching tests carried out on MKPC mortars prepared with FA and BFS [120], [121]. The leachability indices (L_i) and diffusivities were analysed. Whatever the filler used, the L_i of main MKPC components, K, Mg, P and B were >9, largely exceeding the threshold of 6 defined by the US Nuclear Regulatory Commission.

Stability of MKPC in an alkaline environment: The alkaline plume generated by the interaction of groundwater with the concrete cell container can affect the stability of the MKPC immobilisation matrix. Several studies have been conducted to analyse this interaction [102], [103], [118], [120], [122], [123].

Lahalle *et al.*[118] investigated the evolution of the mineralogy, pore solution, and porosity of MKPC over time in basic environments. Their findings indicated an amorphisation of MKPC pastes, potentially linked to structural changes in the K-struvite phase. In alkaline solutions, a substitution of potassium ions by sodium ions may occur, along with changes in pore size distribution. Additionally, a loss of compressive strength is expected for MKPC pastes exposed to basic conditions. Zhong *et al.* [122] examined the influence of alkaline curing systems (pH 10–14) on the physico-mechanical and microstructural properties of MPC composites. High alkalinity (pH 14) negatively affected compressive strength, with higher M/P ratios leading to reduced resistance of MPC in alkaline environments. Although no changes were detected in the types of reaction products, variations were observed in their quantity. Increased porosity, a coarser microstructure, and product dissolution were noted, with the dissolution of K-struvite under highly alkaline conditions identified as a key factor contributing to the reduction in compressive strength. In more recent studies, such as those carried out under the frame of the PREDIS project, MKPC paste samples with FA as a filler were subjected to semi-dynamic leaching tests using an alkaline solution [120], [123]. Under these conditions, K-struvite tended to dissolve, while other phases precipitated. A decrease in crystalline K-struvite content was observed, along with the formation of calcium-deficient hydroxyapatite, brucite, and possibly magnesium silicate hydrates and calcium phosphate phases. The glassy fraction of the fly ash filler was also found to undergo a partial reaction. Additionally, the chemical and microstructural alterations in 1M M/P MKPCs exposed to simulated pore alkaline water (SPAW) and direct contact with OPC mortar, alkaline mortar, [102], [103]. The authors confirmed that alkalinisation significantly modified MKPC, although K-struvite remained as the primary phase. Both exposure conditions increased porosity and raised the pH from 7.9 to >11. Under SPAW exposure, Si, Ca, and S accumulated at the MKPC surface, likely due to external ion precipitation and reaction with FA, forming an outer layer. In contrast, alkaline mortar exposure led to more pronounced compositional changes, with P depletion in MKPC and enrichment in alkaline mortar, indicating K-struvite dissolution and interfacial ion exchange, ultimately forming amorphous calcium-phosphate phases. These changes slightly reduced the alkaline mortar pH from 13 to 12.8, while increasing its porosity. These findings highlight the long-term impact of OPC exposure on MKPC stability and its implications for waste immobilisation in concrete cells.

Capacity of retention of waste in MKPC: Little information is available about the retention of hazardous metals and radionuclides by MKPC matrices [124], [125]. Buj *et al.* [124] incorporated different heavy metals in nitrate solutions containing Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) or Zn(II)) in MKPC (M/P=1) pastes. The retention capacity was evaluated through different leaching tests: batch test, equilibrium leaching test and acid neutralization capacity test. The authors conclude that short-term heavy metal retention by MKPC is very effective, especially regarding Ni(II), Pb(II), Cu(II) and Zn(II), when compared with the disposal criteria under the current regulations. When more aggressive leaching agents were employed, such as nitric acid, the release of Pb(II) and Cr(III) was especially low under acidic or neutral conditions.

The retention of radionuclides incorporated into ion exchange resins, such as Cs and Sr, is practically unexplored except for the study mentioned in [114] (unpublished results) which found that MKPC was a suitable matrix for immobilising Cs ($L_i > 6$). The leachability of MKPC mortars polluted with contaminants (Co, Sr, Cs, Eu) and exposed to irradiation at 200, 500, and 1000 kGy were studied in deionised water [126]. The leachability indices of Eu were consistent with the non-irradiated. Cs exhibited the poorest

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leaching behaviour. The immobilisation of Cs and Co, both strong beta/gamma emitters, is particularly important. The mobility of ^{137}Cs and the abundance of ^{60}Co in metal alloys make their successful containment significant accomplishments in terms of radioactive waste management.

3.2.2.4 MKPC performance under irradiation

The effect of γ-radiation on the chemical transformations and stability of phosphate cement has been investigated in several studies. Various cement types have been tested for their irradiation performance, including OPC, calcium aluminate cement, calcium sulphoaluminate cement, and MKPC. A compilation of hydrogen production values, normalised by the total water content of cement-based materials, is summarised in [13]. However, discrepancies exist among different studies regarding cement formulations, and the implications for the stability and durability of cement matrices remain unclear, necessitating further research. MPC-based materials have been shown to produce significantly less H_2 than other binders under gamma and, to a lesser extent, alpha irradiation. MPC materials with minimal residual pore water (where most of the mixing water is consumed in K-struvite formation) are expected to produce very little hydrogen [126], [12], [13], [127].

Chartier *et al.* [13] evaluates the potential of MKPC compared to Portland cement (PC) pastes and mortars under γ-irradiation. The H_2 radiolytic yield of MKPC materials was found to be 2 to 3 times lower than that of OPC. Furthermore, γ-irradiation of an MKPC mortar up to an integrated dose of 10 MGy with dose rate of 2500 Gy/h had no significant effect on its mechanical properties or mineralogy. However, other radiolytic gases, such as O_2, were also produced, raising concerns about pressure build-up within the cemented waste package, which could make MKPC a less attractive solution in certain scenarios.

Bykov *et al.* [12] investigated MPC under ^{60}Co γ-radiation and detected hydrogen formation from water radiolysis, with a yield of approximately 0.055 ± 0.005 molecules/100 eV at absorbed doses of 4–5 MGy. At higher doses, hydrogen accumulation reached a stationary level, with no swelling of the MPC matrix or significant changes in mechanical strength, even at elevated radiation doses. In a more recent study, Bykov *et al.* [127] examined the radiation stability of OPC and MPC under γ-irradiation at absorbed doses of up to 100 MGy, typical of high-level waste. The radiation-induced decomposition of water in the cements was accompanied by hydrogen evolution, but the rate of gas release decreased as the dose increased. The limiting gas concentration was approximately 2.6 L/kg for OPC and 0.7 L/kg for MPC, with equilibrium reached at ~20 MGy. Unlike OPC, oxygen was not released into free volume in MPC but it reacted with some components of the cement. Additionally, in MPC, the formation of MgO_2 was observed. Notably, hydrogen formation did not cause swelling or degradation of either cement type, confirming their stability under very high-dose γ-irradiation.

Recent research has been published on the behaviour of MPC under irradiation [126], [128]. Gamma irradiation was selected to evaluate the durability of this matrix, as it is the most penetrating form of radiation. This choice is taken not only for practical reasons, but especially because it provides the most conservative results. Mortars were prepared containing four contaminants, representing radionuclides commonly found in nuclear waste, added as analytical-grade nitrates of cobalt, strontium, europium and caesium. Samples were irradiated up to 1000 kGy, with no significant radiation-induced effects observed in the mineralogical or microstructural properties of the mortars. The mortars exhibited excellent leaching resistance and maintained high mechanical strength, even after exposure to irradiation, freeze-thaw cycles, and water immersion.

Additionally, gamma irradiation using ^{137}Cs was conducted at an estimated dose rate of 400 ± 80 Gy/h [128]. Irradiation was applied at different MPC curing ages, with samples irradiated up to 200 kGy. XRD analysis showed no major changes in the mineralogical composition, regardless of curing time (up to 28 days) or total dose (up to 200 kGy), when compared to non-irradiated samples. However, in irradiated samples, certain morphological changes in K-struvite were observed, including the formation of needle-like or tabular crystals, suggesting alterations induced by gamma irradiation. Leaching tests in ultrapure

water indicated that higher total doses correlated with reduced element release. Specifically, cumulative Mg concentrations showed an inverse relationship with dose rate, suggesting that higher dose rates lead to lower element release.

3.2.2.5 Thermal performance of MKPC

MKPC resistance at high temperatures: It has been reported that magnesium phosphate compounds historically were ever used as refractory material due to its excellent thermal expansion coefficient and higher flexural strength, whilst current MKPC interests have evolved to include fire-retardant coatings or composites due to high-level of fire resistance [131][132].

Moreover, MKPC binders are often blended up to 50% by weight with additives (such as FA, metakaolin, or silica fume, etc.) to minimise the exothermic production of the acid-base reaction, improve compressive strength, reduce material costs, ensure sufficient workability and improve water resistance, but also to improve their performance at elevated temperatures. Gao *et al.* [133] observed that both, magnesium ammonium phosphate cement (MAPC) and MKPC mixtures containing 10% wollastonite at elevated temperatures showed higher compressive strength values as well as better high-temperature resistance with a refined microstructure. Zhang *et al.* [134] studied the mechanical properties of MKPC and calcium aluminate cement (CAC)-MKPC samples in water and high temperatures. After the exposure to temperature above 1000 ºC, the compressive strength of CAC-MKPC samples increased especially for the samples with 30% of CAC (up to 20 MPa). The improvement was attributed to the hydration products coating the particles and the formation of $MgAl_2O$ spinel. Yu *et al.* [135] introduced sulphoaluminate cement (CSA) into MPC to improve its thermal properties at elevated temperatures. In consideration of strength retention of the pastes, 30% CSA were recommended to replace dead-burnt MgO in MPC pastes at exposure temperature below 400 ºC, while 10% CSA were recommended to replace MgO at exposure temperature above 800 ºC.

Furthermore, it has been reported that MPC with FA or ground granulated blast furnace slag (GBFS) could meet the fire performance requirements for waste storage. Gardner *et al.* [130] observed that although the phase assemblage and microstructure of FA/MKPC and GBFS/MKPC binders were considerably altered at high temperatures, they formed stable products whilst retaining physical stability with no evidence of spalling/cracking. In addition, Li *et al.* [136] studied the performance of MPCs formed by potassium phosphate with FA or sand after exposure to high temperatures. For the MPC specimens with FA, the cracks became more pronounced and extensively increased with the increase of FA. Meanwhile, for the MPC specimens with sand, the volume deformation of specimens became more pronounced gradually with increasing of sand. The strength of MPC specimens decreased significantly when the temperature passed 130 ºC. At 1000 ºC, residual strength was about 30%.

However, it is worth mentioning that little attention has been paid to the high temperature resistance of MKPC for the stabilization of hazardous and radioactive wastes and this will be addressed in WP7 of the EURAD-2 project.

Alteration of MKPC under thermal cycling:

Previous studies have indicated that magnesium phosphate cement (MPC) mortar has good freeze-thaw resistance, almost no change on the surface of samples after freeze-thaw cycles, and a very low degree of decrease in compressive strength [8], [10], [11]. Feng *et al.* [11] investigated the frost resistance of ultra-high ductility magnesium phosphate cement-based composites (UHDMC) with different FA substitutions, including 0, 10, 20, 30, 40, and 50% under different freeze-thaw cycles (from 0 to 600). After 600 freeze-thaw cycles, UHDMC specimens with FA substitution below 30% showed excellent freeze-thaw resistance, presenting the values of the dynamic elastic modulus and mass loss rate above 81.1% and less than 1.38%, respectively. Their appearance presented no visible damage. The increase in the proportion of gel pores, transition pores, and capillary pores in the specimens with FA content below 30% showed good frost resistance.

In a surface disposal facility, the waste packages, in addition to being subjected to thermal cycling, can also be exposed to salts, being sulfate attacks the most common. When environmental water infiltrates

the concrete, SO_4^{2-} reacts with $Ca(OH)_2$ and calcium aluminate hydrate to produce insoluble salts. Those salts absorb many water molecules and expand in volume. When the internal expansion stress exceeds the tensile strength of the concrete, the concrete is eventually destroyed. Chong *et al.* [137] observed that at the end of 400 freeze-thaw cycles in water, 3.5% NaCl solution and 5% Na_2SO_4 solution, the minimum flexural strength and compressive strength residual rates of MKPC paste without any admixture were around 75.4% and 64.5%, respectively, reflecting its high resistance on freeze-thaw cycles. Zhang *et al.* [8] investigated the compressive strength loss of wollastonite-modified MAPC and MKPC paste after exposure to NaCl freeze-thaw cycles, alternation of dry-wet (water medium and 3% NaCl medium), H_2SO_4 and NaOH corrosion. MKPC showed lower compressive strength loss when the samples were exposed to NaCl freeze-thaw cycles and dry-wet cycles in NaCl solution. While, in the condition of dry-wet cycles in water, MAPC behaved with a lower compressive strength loss. Yang *et al.* [10] studied the sulfate freeze-thaw resistance of MKPC and Portland cement mortar specimens of the same strength grade prepared with river sand. The results showed that the Portland cement mortar specimen completely lost its strength after 75 cycles of rapid water freezing and thawing and 50 cycles of sodium sulfate solution (5%) freezing and thawing. However, the residual strength rating of the MKPC mortar specimen after 75 cycles of water freezing and thawing and 100 cycles of sodium sulfate solution freezing and thawing was higher than 75%.

3.2.3. Conclusions

Since magnesium potassium phosphate cements have only been explored in the last decade for immobilisation of low and intermediate level radioactive waste, significant uncertainties and gaps remain.

Regarding the nature of the matrix:

- Different types of MgO exhibit varying degrees of reactivity, necessitating the use of a suitable retarder, which precise mechanism is still under debate.
- Many different materials have been considered as mineral admixtures. Although their contribution in optimised proportions is recognised to decrease the reaction temperature and increase the mechanical strength, their participation in the hydration reaction is hardly observed and largely disregarded. Their impact on the long-term durability of the matrices have not yet been assessed.
- The M/P molar ratio has been identified as a key parameter in the formulation as it controls the pH in the pore solution and the effective stoichiometry of the acid-base reaction. However, isolated aggregates of MgO remain within the matrix of optimised formulations, which may hydrate under humid environments, inducing the formation of brucite and causing a significant increase in volume. To our knowledge, no experimental investigation has evaluated this risk and only a few studies have evaluated the reactivity of MPKC matrices under the repository environment.

Regarding the immobilisation of LILW:

- Radioactive metal encapsulation, such as Al, is mainly controlled by the pore pH. Increasing the M/P ratio from 1 to 2 is necessary for waste form stability reasons but affects the hydrogen release at early ages. The composition of MgO, the chemical retarder and the ambient humidity have consequence on H_2 release that must be identified. Further research is needed to clarify the short- and long-term H_2 assessment by the change of environmental conditions due to alkalisation of the MKPC matrix and study the durability of MPC containing Al.
- The encapsulation of spent resins in MKPC is unexplored, although preliminary investigations indicate promising option for immobilizing Cs.

Regarding the durability of the matrix:

- MKPC exposed to deionised water or alkaline environments leads to amorphisation of K-struvite and reduction of the compressive strength. The alkalization of the MKPC matrix may cause the filler to begin reacting, changing the waste form's characteristics. To guarantee the waste form's long-term durability, it is essential to comprehend the leaching-

      related degradation mechanisms. A common or standardised leaching protocol is missing to obtain comparative results and better interpret the processes involved in leaching.

- The radiolysis of water produces hydrogen, but it does not cause swelling or degradation of the MKPC matrix, showing its stability under high-dose γ-irradiation. However, there is a lack of knowledge about the irradiation dosage and its long-term performance.
- MKPC has demonstrated acceptable resistance to temperature cycling, like freeze-thaw in dry conditions. However, the response at different saturation levels remains unexplored. Furthermore, the combination of environmental actions, such as irradiation, temperature cycling in aqueous environments has not yet been investigated.

All these relevant points are intended to be addressed in WP7: L'OPERA, in order to contribute to filling these knowledge gaps.

3.3 Nochar

3.3.1. Nature of the matrix and immobilised waste

The Nochar Petrobond® "N" Series Polymer Technology consists of a range of granulated polymer products which act to immobilise a variety of liquid waste streams via absorption and an inter-molecular bonding process. In particular Nochar N910 is suitable for the immobilization of oils, organics, solvents and other hydrocarbon waste streams, N960 can be used for the immobilization of acid, alkali and aqueous waste streams and N935 is suitable for the immobilization of alcohol-based and water-based waste streams. These polymer systems can be blended in the event that a mixed hydrocarbon/aqueous waste stream is encountered.

Some basic data on the polymer's characteristics are available from the producer website [138]. The primary characteristics of N910 and N960 (the most commonly used for liquid waste streams) are summarised in the following Table 4.

Table 4: Nochar (N910 and N960) characteristics

		N910	N960
Composition		Polymer (Thermoplastic elastomer)	Polymer (Acrylic polymer)
Physical chemistry characteristics	Aspect	Granular	Granular
	Colour	White	White
	Density (g/cm³)	0.3	0.8

Of particular interest is Nochar N910 that can be used to solidify/immobilized RLOW. It is a thermoplastic elastomer which consists of a copolymer made of styrenic blocks playing the role of physical crosslinks while the central macromolecules confer the elastic properties. It is found as a white porous powder with very low density (300-400 kg/m³).

Applications of Nochar Polymer Technology to immobilise liquid waste of various nature have been conducted in different countries [139].

Different liquid wastes were considered:

- Mixed sludge types; oil, oil-water with other contaminants such as high salt content, sand, dirt
- Pump and machine oil, various types of synthetic and standard oil
- Organic liquids including scintillation cocktails, TBP
- Aqueous liquids; water, low pH acid, high pH alkaline solutions
- Light alcohols; glycol, methanol, ethanol

In some cases, real waste containing radiological contaminants including heavy metal, isotopes, tritium and Low level (LLW) and intermediate level waste (ILW) have been treated.

Mechanism of immobilization

The mechanism of immobilization of liquid waste streams with the Nochar Polymer is not encapsulation. The process converts the liquid material into a solid material via absorption and an inter-molecular bonding [140]. This material has been shown to be able to immobilize liquid waste streams with a volumetric increase of typically 5%. The solidification process has shown to be simple and safe to apply,

it does not create an endothermic or exothermic heat reaction, no harmful chemical reaction, with little/no airborne particles [140].

The solidification process is generally implemented in 2 main steps [141]: (i) mixing waste/polymer (with a slow and constant addition of the waste on the polymer) and (ii) curing.

The process parameters may be different for the different polymer used and liquid waste to be immobilised. With the N910 polymer,as the organic liquid moves through the polymer layer, the polymer swell and immobilise the liquid. With the N960 aqueous waste can be absorbed up to 100 times its own weight. It creates a strong mechanical bond which permanently traps the contamination imbedded in the aqueous liquids [141].

3.3.2. Waste form durability and stability

The application of Nochar's engineered polymer technology has been implemented in some countries for the solidification of a range of highly complex oil, organic, aqueous, acidic and basic low-level (LLW) and intermediate-level waste (ILW) [139].

3.3.2.1 Liquid Waste immobilised in Nochar Polymer

Bench-scale tests for solidification

Experiences conducted with different oils and aqueous and organic liquids [140], [141] showed that bench tests are needed to determine the best polymer for solidification (depending on the composition of the waste solution), and to determine the appropriate and safe solidification procedure, based on liquid/polymer ratios by weight.

The effectiveness of solidification was tested with simple compression testing, to assess the degree of liquid immobilization, and with manual exudation tests

It was highlighted that the rate of addition and the mixing protocol have the greatest impact on the solidification process. Also, the nature of the polymer bed was considered another parameter which has an impact on the success of the solidification.

Age of the waste stream was shown to influence the curing time as the oils were demonstrated to cure more quickly than the older one [140]. The results demonstrate that the polymer products selectively bond with the hydrocarbon elements of the material.

Bench-scale tests for durability and stability

Some tests have been conducted to assess the liquid waste immobilised in Nochar polymer degradation and durability.

Radiation and thermal stability of polymer matrixes after solidification of aqueous and organic solutions and mixed waste were investigated by Khlopin Radium Institute in Russia [144], [145].

Experiments were conducted to analyse the composition of the gaseous phase arisen under the impact of radiation during the long-term storage of waste in the polymer matrix. In addition, the differential thermal analysis was carried out to assess the thermal stability.

Radiation stability was tested using a [60]Cobalt gamma source irradiator.

The irradiation tests were carried out under static conditions in sealed glass ampoules and samples were exposed to an integrated gamma dose of 2.7 MGy over 103 days. After irradiation the samples were checked to visually evaluate waste volume reduction, brittleness and the presence of any liquid release. The released gas in the ampoules was then measured.

Gas generation tests have been conducted on the polymers (pure N910 and N960) and on the solidified samples with nitric acid and samples with oil and TBP.

The composition of gases formed under irradiation was determined by sampling gases from the ampoules containing the irradiated samples. Results have shown that there is small gas release from

the polymers under irradiation. A very small percentage, less than 1%, of hydrogen gas was detected from the oil / TBP sample and no gas generation was detected from the nitric sample.

Thermal stability of the polymers was tested with differential thermal analysis (Figure 19) [144], [145].

Additional DTA tests were conducted using polymer N960 with HNO_3 solutions with similar results. It can be concluded from these experiments that the polymers possess rather high thermal stability with decomposition occurring at 300°C.
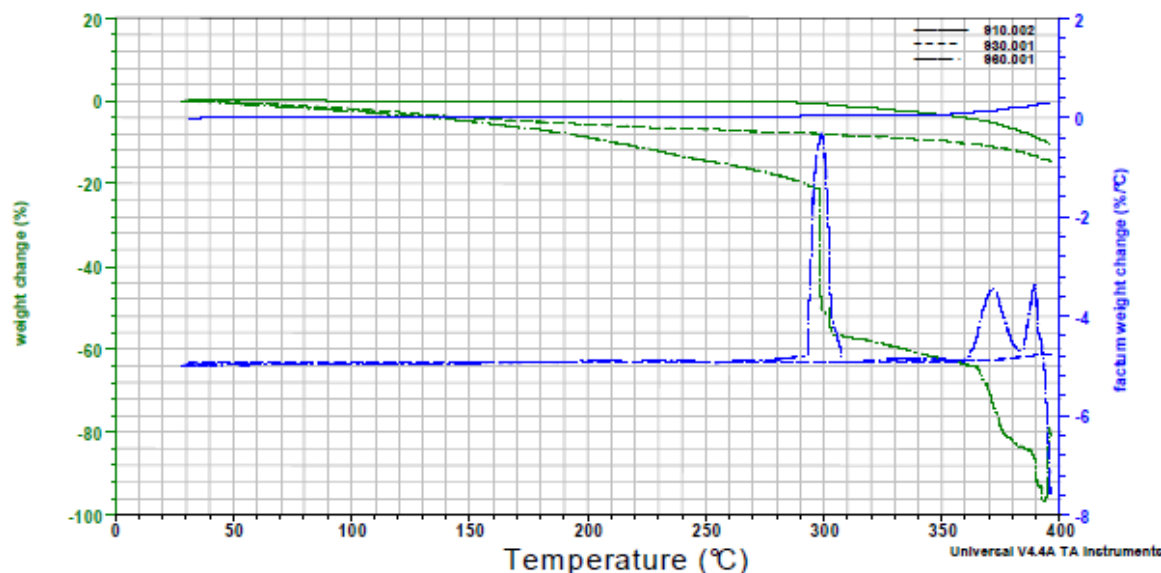
Figure 19: *DTA – curves for polymers, N910, N930 and N960 [145]*

Irradiation tests were conducted also by the China Institute of Atomic Energy, in order to evaluate degradation of waste form and polymers [149].

Six simulant waste streams were tested:

- Tri-butyl phosphate and kerosene: 30% TBP / 70% kerosene
- Acidic (nitric) solution: near to 0 pH
- Alkaline solution: 14+ pH
- Ion exchange resin: anion to cation – 2:1
- Sodium type-beads, chlorine type-beads and 50% water
- Vacuum pump oil
- Scintillation fluid

Polymers used were N 910, for oil and organic liquid and N960, for aqueous solutions. A premium blend of polymers for oil / organic liquid and 20% or less of aqueous content (N990) was also used.

Solidification ratios of waste to polymer were defined with bench-scale tests (Figure 20) and they varied between 1:1 and 3:1 for all tests except ion exchange resin which was performed at 5:1.

Figure 20: *Solidification of TBP/OK after 6 weeks (waste/polymer ratio 1:1 (left); waste/polymer ratio 3:1 (right))* [149]

The solidified waste streams were sealed in individual ampoules and irradiated with a ^{60}Cobalt gamma source irradiator up to an integrated gamma dose of 0,1 MGy (Figure 21). After irradiation the samples were checked to visually evaluate any significant variation in the appearance and the presence of any liquid release.
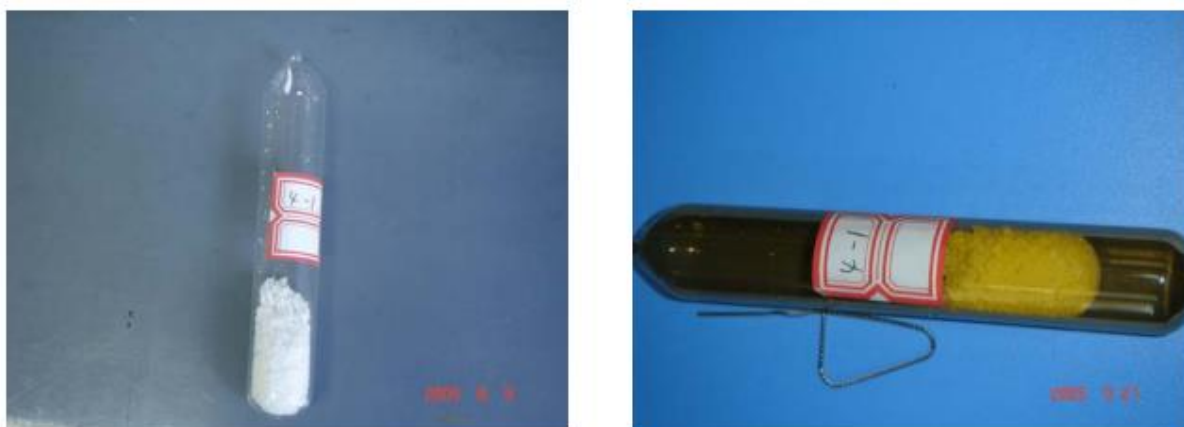
Figure 21: *Vacuum Pump Oil before Irradiation (left) and after Irradiation (right)* [149]

An IR spectra-graph analysis was performed on the two pure polymers N910 and N960 before and after irradiation to check their degradation. Results (Figure 22 and Figure 23) doesn't seems indicate polymers modification under irradiation to 0,1 MGy.
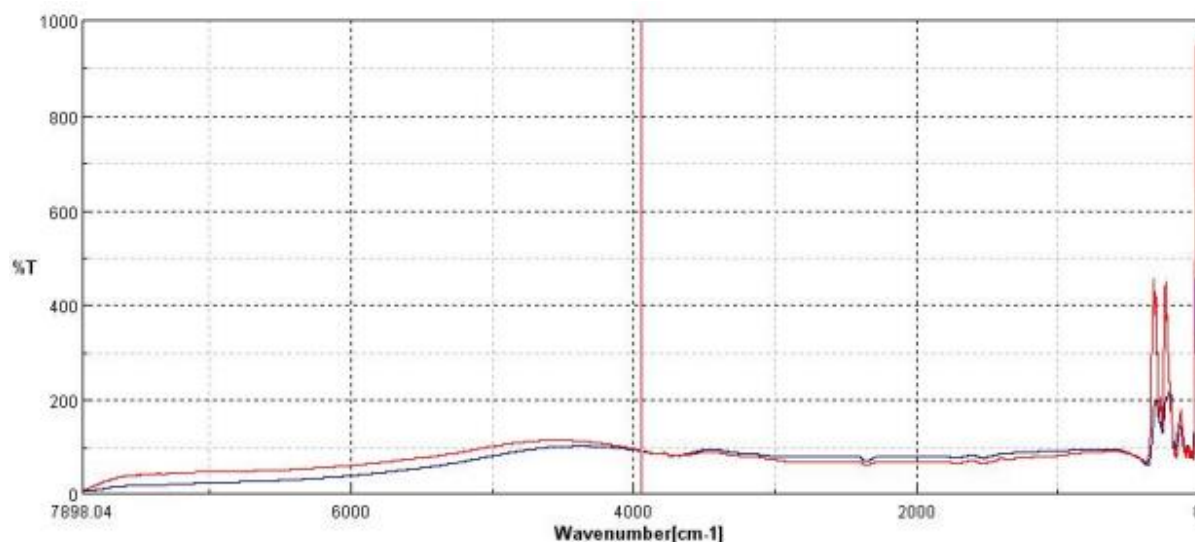
Figure 22: *IR Spectra-graph of Polymer N910 before (blue) and after (red) irradiation [149]*
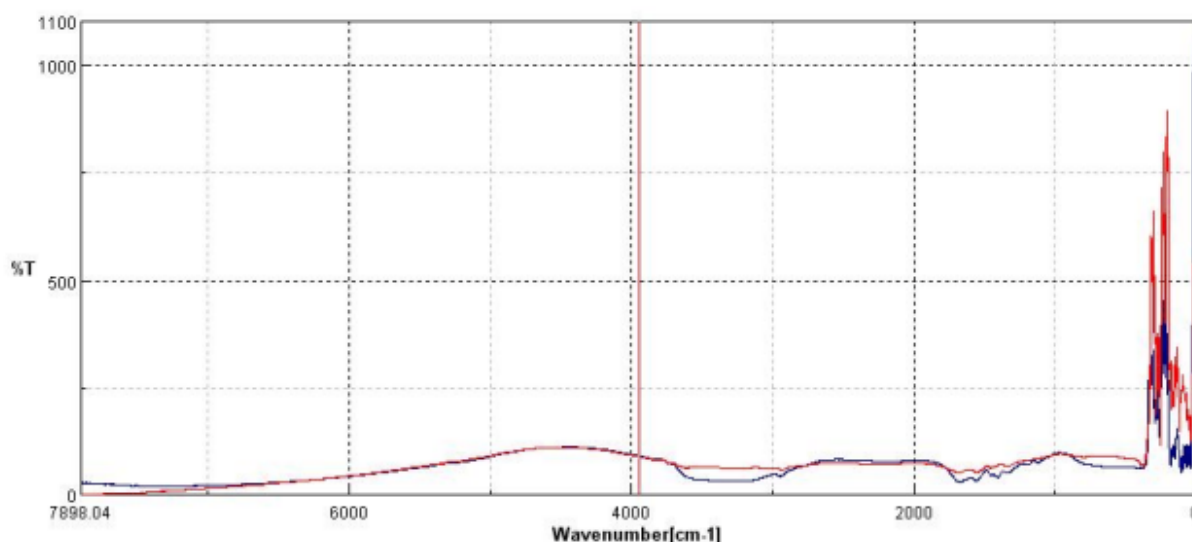
Figure 23: *IR Spectra-graph of Polymer N960 before (blue) and after (red) irradiation [149]*

Real waste solidification experiences

Experiences in solidification of real waste have been conducted in USA, Romania, Slovenia and Russia.

In 1997, the U.S. Department of Energy (DOE) approached Nochar regarding its solidification technology used for commercial oil spill control and other liquid spill applications. In 1999, tests were conducted on tritiated mixed waste oil and the tests required for final disposal at DOE's Nevada Test Site repository passed intense examination. In 2000, full scale solidification of tritiated vacuum pump oil commenced under the EM-50 program [146].

Nochar's absorbent technology became the baseline technology for the treatment of Mound's LLW and MLLW oils. Solidified waste was packaged in special polyethylene containers with a standard steel drum overpack.

At the Rocky Flats Technology Site, Nochar polymers addressed orphan liquid waste streams.

Solidified material was loaded directly into a standard 55 gallon (about 208 L) carbon steel drums with plastic liners and delivered to the Waste Isolation Pilot Plant (WIPP) for final disposal.

In 2009, Nochar polymers (N910 and N960) were employed to solidify various organic waste streams (pump oil, oil contaminated with tritium, scintillation liquids, organic solvents) in the Cernavoda Nuclear Power Plant [142], [143].

The large-scale solidification method (Figure 24) was developed after a bench scale testing campaign, and it included the following steps:

- Pre-weighting of the contaminated organic liquid waste and polymer, to obtain the proper bonding ratio (depending on the waste composition)
- Mixing of the materials (organic liquid and polymer) at a predetermined slow speed in order to avoid polymer breaking
- Packaging of the solidified organic liquid into drums and curing for 24-48 hours.

The procedure has been applied not to produce a waste form intended for final disposal but just to immobilise the waste in a solid form. The solidified material was collected into Polyethylene bags (10-12 kg) and re-packed in 220 L drums, type A containers, to be sent to an incineration facility abroad.
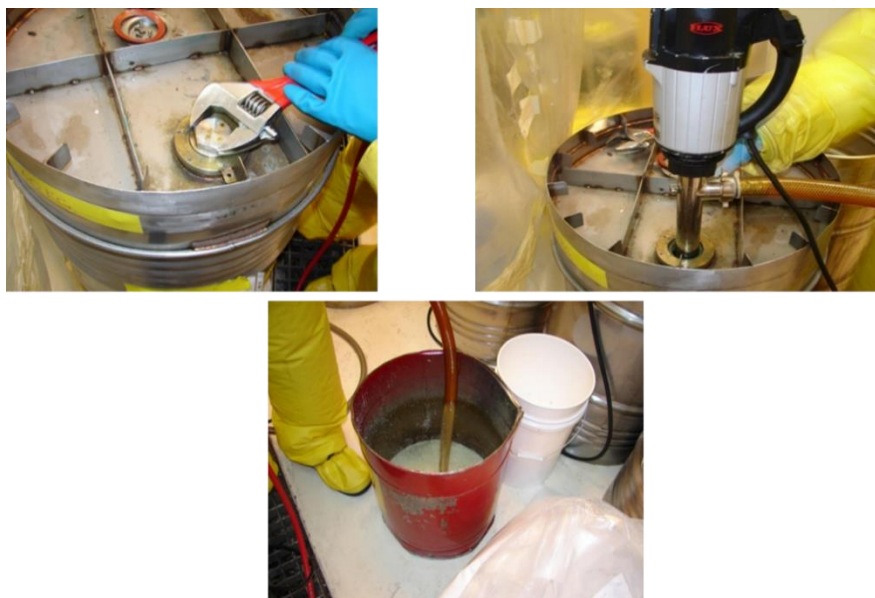
Figure 24: Solidification at large scale [143]

Nochar polymers were used in the same site also for organic liquid separation from solid-liquid mixture [142]. Flammable solids were treated with a mixture of Nochar polymer N910 (applied to organic liquids) and polymer N960 (applied to aqueous liquids). The liquid was absorbed on the polymer and the remaining solids (plastics and textiles or mixture) were completely free from organic liquid and treated and classified as "normal" solid waste.

In 2013 the Agency for Radioactive Waste Management, ARAO, in Slovenia, implemented the Nochar technology to treat small volume of complex waste streams (mixture of liquid scintillation fluids, solvents, organic and aqueous solutions) with the aim of reducing their potential hazard by producing a solid material that can be safely handled during transportation, storage and possible final disposal [152].

Three Nochar polymers were applied, N935 for light alcohols, N910 for organic toluene, and N960 for aqueous streams. Because of the waste stream complexity, a 1:1 solidification ratio resulted in a good solid mass and safe for interim disposal. Preliminary bench-scale tests were performed to determine the polymer formulas prior to the addition of each waste from many containers. The solidification process was limited to small batches to ensure that each batch was successfully solidified with no loose liquid.

At the end of the solidification process, the solidified materials were packaged according to the waste acceptance criteria for the storage facility. 200 liters of liquid radioactive waste was stabilized by solidification process in 400 liters of solid radioactive waste.Nochar polymer technology is the first foreign absorbent technology to be formally certified by ROSATOM, for use at Russian sites [139].

After the testing program previously described a solution of TBP in hexachlorobutadiene (HCBD) was solidified with N910 at 5:1 ratio and then encapsulated in cement The solution was capped by paraffin wax to prohibit gas emission, and the solidified waste was packaged to be sent to the Final Storage at RADON SosNovvy Bor Site.

3.3.2.2 Liquid Waste pre-impregnated in Nochar Polymer and solidified with other matrices

Experiences have been conducted in some countries to study the properties of a waste form obtained with the use of Nochar polymer and other solidifying matrices: cement, geopolymer, geocement and composite matrices [147], [148], [150], [151], [153].

N910 Polymer and cement

A combination of N910 polymer and cement has been tested in some countries for the immobilisation of mixed aqueous/organic waste streams.

In Italy [147] a multiphase very low level (VLLW) radioactive liquid waste, characterized by the presence of three different stratified phases (oil, water and sludge), was solidified by using N910 polymer (to absorb the oily phase of the liquid waste stream) and cement powder (to solidify the aqueous phase).

Bench scale tests, with surrogated oily waste and oily-water mixture, were conducted to define the optimum waste/polymer ratio and to verify the degree of liquid immobilization. In order to determine the optimal ratio between oil and polymer N910 some release tests were carried out during time, applying a vertical pressure of 2 kg on an aliquot of polymerized product placed on a substrate of absorbent material (Figure 25).
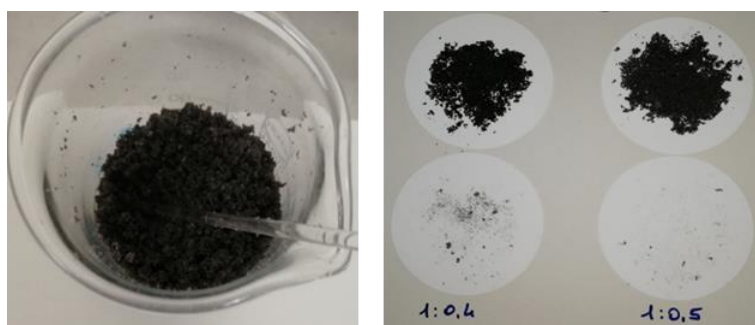
Figure 25: Release tests at different Oil/polymer ratios [147]

Cementation tests were carried out on polymerized water-oil mixtures using Composite Portland 42.5 R cement (Figure 26).

Figure 26: Cementation tests [147]

Compact and not friable specimens were obtained with a weight ratio Oil:Polymer N910 equal to 1:0.5 and a weight ratio Water/Cement equal to 0,5.

The optimised formulation was tested at bench scale with the real waste (Figure 27).
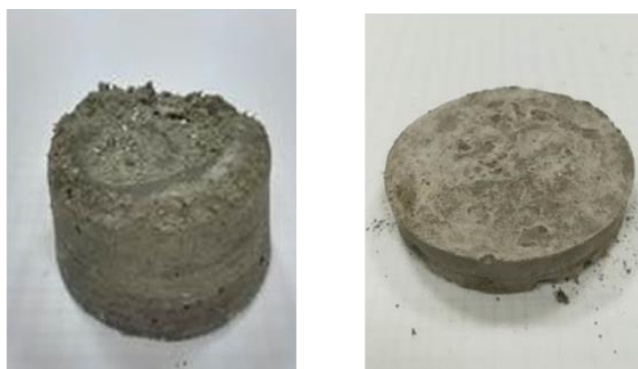
Figure 27: Real waste bench scale cementation [147]

The results obtained with the simulated waste and the real waste demonstrated the feasibility of the polymerization and cementation process to solidify both the oily and aqueous phases providing a monolithic solid product.

A full-scale mixing system was designed and realized to provide the solidification process directly into 220 litres drums preloaded with a fixed amount of liquid waste by using a removable impeller (Figure 28).

Figure 28: *Full-scale solidification system (left) and removable impeller (right) [147]*

Some trials were performed to test the system and to verify the solidification procedure and the characteristics of the solidified product (Figure 29)

Figure 29: *Full-scale trials – solidification procedure and final product [147]*

The product obtained at the end of the solidification process is a solid and stable (monolithic) matrix having homogeneously distributed inside the particles of polymeric material, but it doesn't comply itself with the Italian acceptance criteria for VLLW final disposal.

To meet the disposal requirement a further cement encapsulation of the solidified waste is needed. The final waste package is composed by a 380 L drum with inside the solidified waste (collected into 220 L drum) surrounded by a cement matrix (Figure 30).
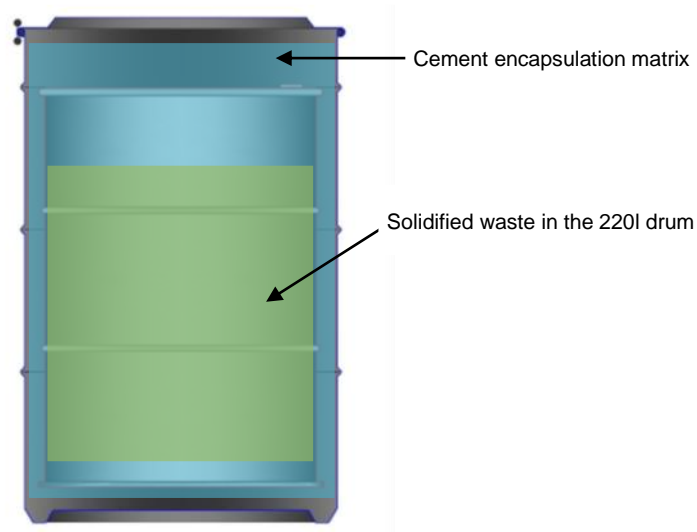
Figure 30: *Final Package characteristics*

To comply the acceptance criteria for the final disposal to the National Repository in Italy (ISIN Technical Guide n. 33), the solidified waste (into 220 litres drum) needs to be embedded in cement inside an overpack.

In Slovakia [153], the possibility of immobilising intermediate level radioactive waste sludge containing dowtherm (organic aromatic waste) was studied. The dowtherm presented in sludge was pre-treated with Nochar N910 (ratio Nochar to downtherm = 0,5) and the sludge was then immobilized into Pozzolanic cement CEM II/B-P 32.5R.

Bench-scale tests were conducted to determine the optimal formulation: the content of the (dry) sludge varied from 5.0 to 10.5% and dowtherm content varied from 8 to 35% and the procedure was designed for lost stirrer immobilisation.

Durability and stability tests on *N910 Polymer and cement*

Some durability and stability tests have been conducted on the solidified sludge containing dowtherm samples [153].

Compressive strength was measured, and leaching tests were conducted according to ANSI ANS 16.1 (91 days). The following data were analysed:

- leaching for ^{137}Cs (after 91 days and after 2 years)
- Alpha spectrometric determination of the % of leached gross alpha (over 2 years)
- HPLC determination of the % of leached downterm
- pH and conductivity in leachates

Results demonstrated that:

- Compressive strength depends on waste loading and downtherm content. Downtherm absorbed onto Nochar N910 makes product plastic but not brittle.
- The index of leachability (^{137}Cs) depends on W/S (Waste/Solid) ratio and not on the content of immobilised downtherm.
- Downtherm is not leached from the matrix (mixture of cement + Nochar N910): no peacks were detected by means of HPLC determination and extraction to n-hexane.

- Leachability of limited alpha radionuclide is lower than 0.1% of total fixed activity. Alpha radionuclides leachability depends on W/S ratio and waste loading.

In case of the Italian experience [147], some stability and durability tests were conducted on the final waste package (Figure 30) to assess the effect of <u>gas generated by radiolysis</u> and the behaviour of the package if exposed to <u>high temperatures</u>. Both were needed to confirm the acceptance of the package to the final disposal.

The contribution of gases generated by radiolysis can come from both the water present in the cement matrix and the organic content present in the waste. An analytical procedure was developed to estimate the total amount of gas, and some basic assumptions were set:

- The waste is uniformly distributed in the package
- Energy emitted from the radioisotopes is completely absorbed by the final package (for water radiolysis) or by the organic material (for organic radiolysis)
- All the organic material (oil and polymer N910) present has been assimilated to lubricating oil

The maximum gas flow rate from the radiolysis of the embedding cement matrix and from the radiolysis of the organic content have been calculated and, considering the decay over a period of 300 years, the production of H_2 and O_2 form radiolysis of water and organic materials has been estimated around 3.68 litres.

Some gases can also be generated by the corrosion of the metals present in the package: the total surface area of 220 L inside drum (internal and external) plus the internal surface of the 380 L overpack. The gas generation reaction takes place only in the case of contact between the metal and the free water present. The calculated generation of gas due to metal corrosion is equal to $3.47 \cdot 10^{-4}$ L/h and it is about 3 orders of magnitude higher than the contribution given by the radiolysis of water and of the organic material contained in the waste.

Based on those data, the maximum overpressure generated inside the package, intended as a solicitation on the solidified cement matrix, was calculated. The obtained value of $6.33 \cdot 10^{-4}$ MPa was compared with the tensile strength of the embedding cement matrix (3.2 MPa) to assess the absence of any mechanical criticality linked to gas generation.

The fire and high temperatures resistance checks were performed according to the IAEA SSR-6 (Rev01), using the Finite Element software Comsol Multiphysics (Heat Transfer module version 5.3) and a 2D transient axisymmetric model (see Figure 31 and Figure 32).
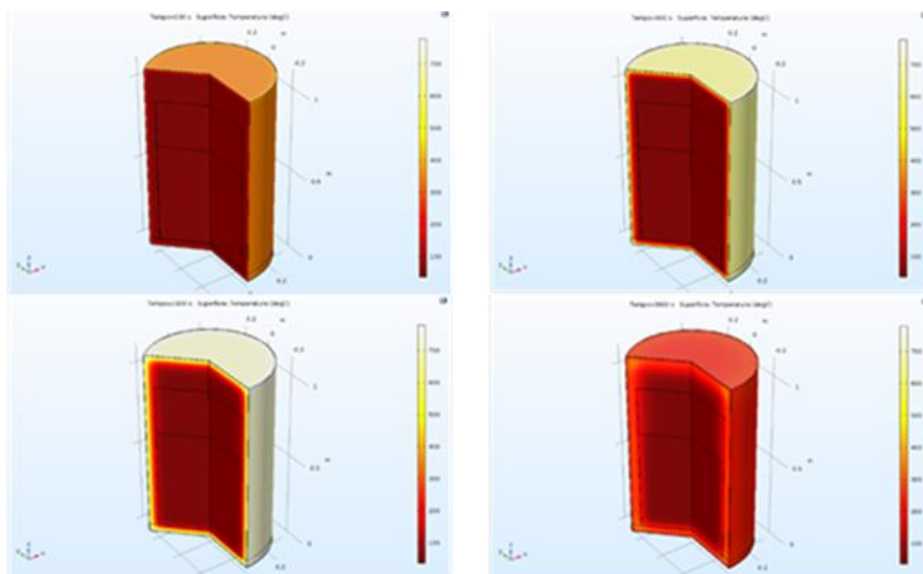
Figure 31: *Trend of the thermal field inside the package as function of time (clockwise starting from the top left: t = 100s, t = 600 s, t = 1800 s and t = 3600s) [147]*
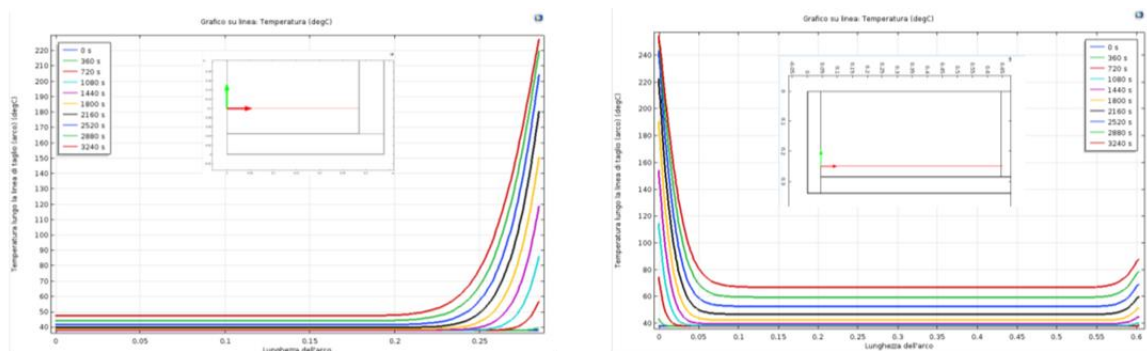
Figure 32: *Temperature profile inside the waste as function of time [147]*

The data were used to verify that the temperature inside the package did not raise up to value that could generate any degradation on the solidified waste: an upper limit for the temperature close to the waste was fixed to 200°C. It was demonstrated that an increase of 5 cm of the cement filler in the bottom of the package (the total thickness was raised to 9.5 cm) would overcome any anomalous behaviours of the package that may compromise its stability and therefore the qualification of the conditioning process.

Real waste solidification experiences with *N910 Polymer and cement*

Following the bench-scale and full-scale testing campaign and the additional assessment conducted on the final waste package, the Italian Safety Authority approved the project and in 2021 about 800 L of very low level mixed oily waste were successfully solidified and finally conditioned with cement encapsulation.

Figure 33: *Real waste in the drum before (left) and after (middle) the solidification with Nochar N910 and cement inside a 220 L drum (right)*

N910/N960 Polymer and geopolymer, geocement or other composite matrices

A combination of N910 (or N960) polymer and geopolymer, geocement or other composite matrices has been tested in some countries for the immobilisation of organic (solvent, scintillation liquid and oils) and aqueous (alkali, high content salt solutions and slurry) waste streams.

RLOW impregnation on absorbing materials, followed by encapsulation in a stable geopolymeric matrix have been studied by POLIMI [148] . Nochar N910 polymer was pre impregnated with 10%wt. of RLOW surrogated: liquid scintillation cocktail (LSC) or PUREX solvent (kerosene + 30%v. TBP).

Pre-impregnation was followed by encapsulation in geopolymer matrix based on the use of natural and recycled aluminosilicate precursor materials: micronized volcanic tuff, fly ash (FA) and ground-granulated blast furnace slag (BFS).

No organic liquid bleeding was observed after mixing with the geopolymeric grout nor during curing, meaning that the impregnated N910 polymer is stable in the alkaline environment.

Compressive strength tests have been performed. The addition of 5%wt. of N910 polymer causes a reduction of the compression (from 17,3 to 13,4 MPa). With the addition of 10%wt. of organic liquid the compressive strength is further reduced to 10,4 MPa (with LSC) and 5,9 MPa (with solvent).

Water immersion tests were conducted on cylindrical samples containing N910. The leachates deriving from the water immersion experiments were limpid and homogeneous, without apparent signs of organic liquid release. In addition, the specimens seemed to preserve their integrity after water immersion. Regardless of the RLOW surrogate content, the geopolymer constituents are released from all specimens following water immersion. The outcomes of the work showed that N910 polymer seems to successfully meet the requirement of stable organic liquid retention without excessively compromising the mechanical and water immersion stability of the resulting waste form, nevertheless additional studies (mechanical, thermal, fire, radiolytic, leaching, and biodegradability resistance tests) are needed to verify the long-term durability of the waste form and ascertain its safe disposability.

Extensive testing campaign for the solidification of contaminated pump oil, alkali, high content salt solutions and slurry have been conducted by the Mangystau Atomic Energy Combine (MAEC-Kazatomprom) located in Aktau (Shevchenko), Kazakhstan [150], [151].

Solidification tests with Nochar N910 and N960 were conducted on four waste streams: machine oil (Figure 34), sodium hydroxide (Figure 35) and 2 saline solutions containing sodium nitrate, sodium oxalate and sodium chloride with different salt content (Figure 36).
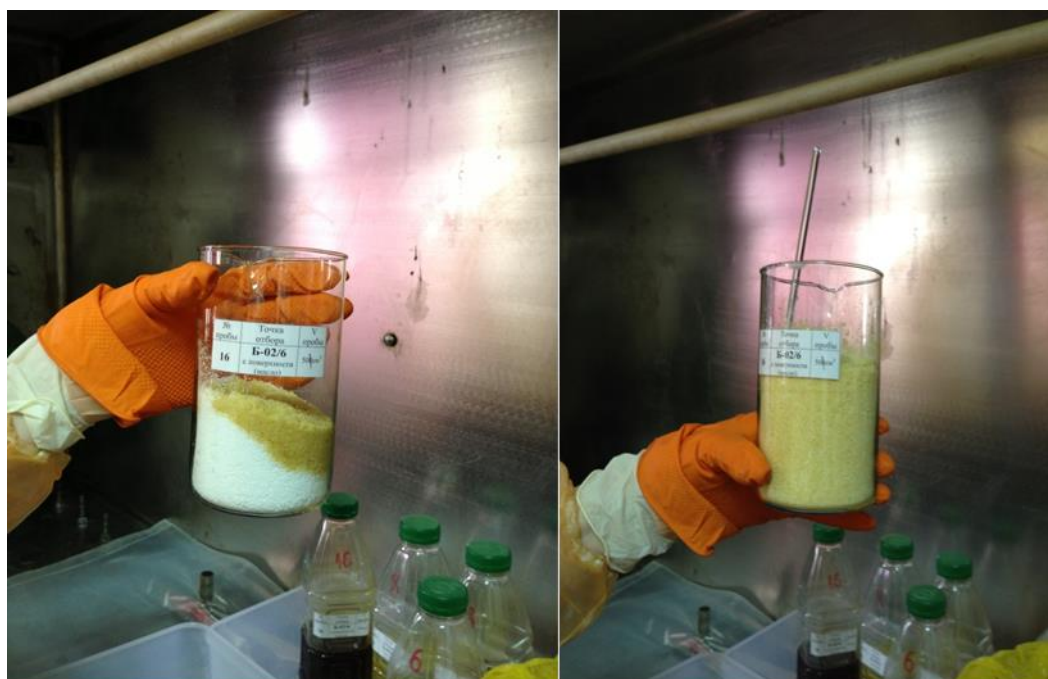
Figure 34: *Machine oil solidification process (left) and solidified oil with N910 at 3:1 ratio (right) [150]*
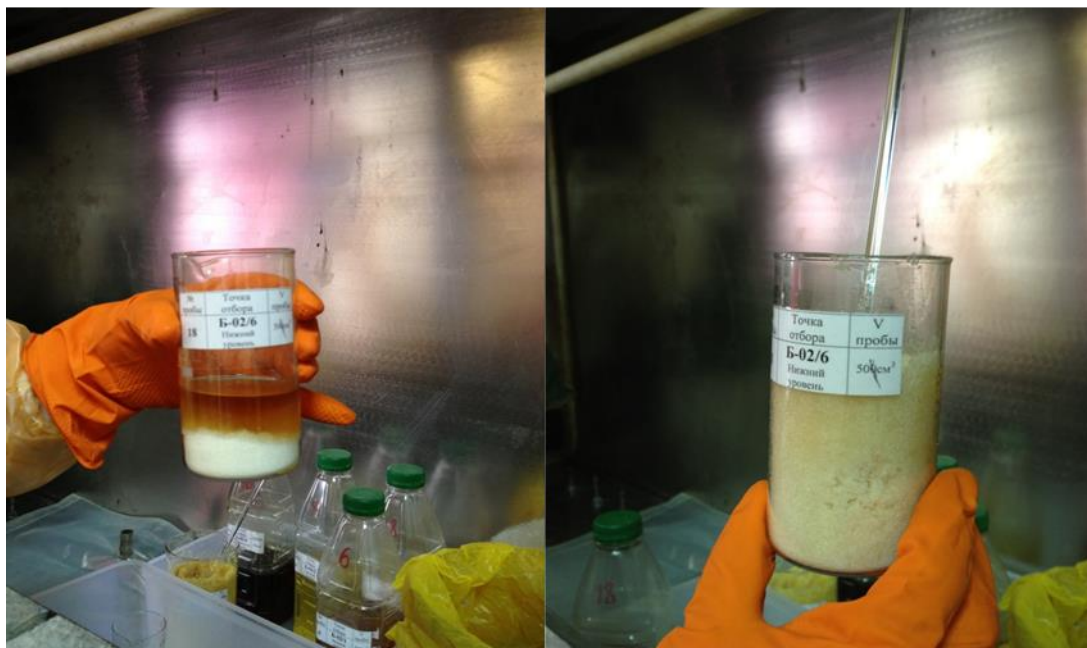
Figure 35: *Sodium hydroxide in liquid form (left) and solidified sodium hydroxide with N960 at 3:1 ratio (right)* [150]

Figure 36: *Saline solution (left) and saline solution with N960 at 2:1 ratio (right)* [150]

The polymers saturated with liquid waste do not meet the requirements for hardened waste as they represent hydrophilic gels (jelly) with zero strength.Therefore, to accommodate long-term storage, these polymers shall be immobilized into a solid and water-resistant matrix.

Different tests have been conducted to evaluate two newly designed techniques capable of immobilizing the polymer with liquid waste and creating a final matrix that will comply with requirements for long term storage and/or disposal summarised in the following Table 5.

Table 5: Requirements to materials for LRW immobilization and encapsulation

Requirement to material	Value	Method of testing
Leaching rate (for Cs-137), g/(cm^2 day), (not more than)	$1 \cdot 10^{-3}$	Pursuant to GOST 29114
Mechanical strength (ultimate limit under compression), MPa (kg/cm^2), not less than	4,9(50)	Pursuant to GOST 310.4
Radiation stability under irradiation, (Gr)	$1 \cdot 10^{6}$	Variation of strength
Frost resistance (number of freezing /melting cycles), not less than$^)$	30	Pursuant to GOST10060.1
Resistance to durable stay in water, days	90	Variation of strength

The tested immobilization and encapsulation technologies are:

    a. geocement with components of diatomite, kaolin clay, and blast furnace slag
    b. sulphur composite that is a new, innovative design.

Experimental results on the immobilization of liquid radioactive waste with polymers into the geocement and sulfur composite matrices showed that:

- the samples obtained with liquid radioactive waste (pump oil) and Nochar N910 polymer have shown good results on mechanical strength, leaching and water resistance, meeting all of the regulatory requirements for long term storage and or final disposal
- the samples obtained with liquid radioactive waste (salt and alkaline solutions) and Nochar N960 didn't sustain the leaching and water resistance tests.

To solve this problem with Nochar N960 additional tests were performed [151], and they were based on:

- Selection of advanced materials for encapsulation that comply with regulatory requirements
- Burning at moderate temperatures to avoid the thermal sublimation of Cs-137 and Sr-90 followed by immobilization into geocement and sulfur composite matrices.

In order to investigate the possibility to use sulfur as a binding agent for immobilization of LRW there were conducted experiments with the purpose to develop compositions, in which the sulfur is the binder.

Due to the fact that sulfur binding properties are exhibited only in the transition from melt into crystalline state in the absence of liquid, the work procedure involved the preparation of mixtures of diatomite and liquid radioactive waste solutions that were evaporated to dry state, milled and used in experiments together with Nochar polymers (N960 and N910), saturated with liquid waste, and natural sulfur was used as the binder.

It was demonstrated that the samples with polymer N910 saturated with real radioactive liquid waste (oil) and solidified in sulfur composite matrix showed high water and leaching resistance meeting the requirements for long term storage and/or disposal.

For Polymer N960 saturated with liquid radioactive waste (high concentration salt solutions) it was necessary to preliminary burn at temperature 300°C to obtain a successfully immobilisation into sulfur composite matrix or geocement, that meets regulatory requirements.

In addition, containers made of sulfur composite (Figure 37) have been developed and tested to encapsulate polymer N960 saturated with liquid waste (high concentration salt solutions). In order to reduce the volume of encapsulated mixtures of polymer and liquid waste, the mixture has to be preliminary dried at temperature 150°C and burned at temperature 250-300°C before encapsulation.

Figure 37: *Sulfur composite container of laboratory scale [150]*

3.3.3. Conclusions

As previously reported, experiences in the use of Nochar's engineered polymer technology have been implemented in some countries for the solidification of a range of highly complex oil, organic, aqueous, acidic and basic low-level (LLW) and intermediate-level waste (ILW).

A summary of those experiences is reported in the Table 6 where the waste types considered, the polymers or other materials used, and the main tests performed on the specific waste form are reported. Additionally, some basic information on further treatment/conditioning activities assumed in the different countries to meet the final disposal requirements are included.

Most of the bench scale tests have been performed on the solidified product obtained after the absorption of the liquid waste in the Nochar polymer to check the ability of the technology to retain the liquid and to properly define the type and quantity of polymer to use.

In general:

- Mixing may be required, especially if aqueous liquids are present
- Polymers may be blended into the formula, to capture mixed organic and aqueous liquids
- Solidification ratios will vary, depending upon the chemical composition of the waste
  - o Oil, generally 1:1 – 3:1 (liquid : polymer)
  - o Mixed sludge types, generally 2:1 – 4:1
  - o Aqueous solutions, generally 2:1 – 5:1

In some cases, the solidified product (liquid waste + polymer) has been considered suitable for interim or final storage or for direct disposal, into stainless or carbon steel drums or into highly integrated containers.

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In most of the cases additional treatment and conditioning steps are needed to comply with the final disposal requirement:

- Incineration of the solidified waste
- Encapsulation in cement for homogeneous or non-homogeneous encapsulation
- Encapsulation in other inorganic filler: geopolymer, geocement or sulfur composite matrices

The complexity of LLW and ILW generated across nuclear operations necessitates reliable and economical treatment solutions. As reported in the above-mentioned case studies, Nochar's polymer technology provides a flexible and effective means to solidify diverse waste streams, including those containing tritium, thus facilitating compliance with varying national waste acceptance criteria. The demonstrated success across multiple international sites underscores the potential of these polymers as a key solution in managing radioactive waste, particularly in the face of limited characterization and economic feasibility for small volume waste streams. The results suggest a promising pathway toward enhanced safety and environmental protection in the nuclear sector.

Nevertheless, as the polymer technology is relatively new to prospective users, additional test work may be required to validate its use in certain countries.

In particular it has been recognised that the waste polymer formulation is fully dependent on the chemical composition of the waste and additional studies may be required to properly understand the bonding process with different waste streams.

Regarding the durability of the matrix, some radiation and thermal stability tests have been conducted on the solidified liquid waste with polymers, but additional work is needed to better understand how ageing affects the polymer sorption properties under various conditions (i.e. radiation exposure, temperature fluctuations, and water presence). Previous studies about organic degradation wastes have showed that coupled effect of irradiation and water presence, can lead to organic degradation and release of soluble species that could modify radionuclide mobility **Errore. L'origine riferimento non è stata trovata.**. The degradation mechanism of Nochar/waste forms has to be investigated regarding the durability/lifetime of encapsulation properties.

Moreover, it has been recognised that the polymers saturated with liquid waste has no adequate mechanical strength value to comply with the requirements (existing in most of the countries) for hardened waste and additional treatment/conditioning steps are needed. Further work is necessary in the area of solidification / cement encapsulation to assess the mechanical resistance of the final waste form and to acquire data on the long-term durability and on the effect of cement composition.

Leaching experiments are needed to understand the leaching-related degradation mechanisms and the radionuclide mobility in the presence of organics both considering radionuclide adsorption and the potential effect of organic degradation products on radionuclide retention.

Table 6: Summary of experiences and applications of Nochar Polymer Technology

Country	Waste type	Polymer and other materials used	Waste form	Tests conducted	Further treatment/conditioning to meet disposal requirements	Ref.
UK	mineral oils, hydraulic oils, mineral/hydraulic mixes and oil/glycol mixes	N910, N960	Liquid Waste immobilised in Nochar Polymer	Bench scale / Qualitative observations: Polymer/waste compatibility and ratio, process parameters (e.g. mixing, curing time)	Cement encapsulation	[140]
France	Aqueous and organic liquids (solvent, oil, solvent/oil mixing etc)	N910, N960	Liquid Waste immobilised in Nochar Polymer	Bench scale / Qualitative observations: Polymer/waste compatibility, and ratio, process parameters (e.g. mixing, curing time)	Cement encapsulation	[141]
Romania	Oils contaminated with tritium	N910, N960	Liquid Waste immobilised in Nochar Polymer	Bench scale + real waste: Waste absorption	Incineration	[142], [143]
Russia	Nitric acid, oil, TBP	N960, N910	Liquid Waste immobilised in Nochar Polymer	Bench scale: Waste/polymer + radiolytic gases after irradiation	Cement encapsulation	[144], [145]
USA	Methanol-based solution, Mixed organic, Spent pump oil	N910, N960	Liquid Waste immobilised in Nochar Polymer	Real waste solidification process	Packaging in carbon steel drums for disposal	[146]
Italy	Oil+water+sludge	N910 + cement	Liquid Waste immobilised in Nochar Polymer and Cement	Bench scale + full-scale + real waste: Polymer/waste compatibility, and ratio, cement/waste ratio, process parameters (e.g. mixing, curing time). On the final package: analytical evaluation of gas generated by radiolysis and metallic corrosion + fire and high temperatures resistance	Cement encapsulation	[147]
Italy	TBP/Kerosene (30/70), scintillation liquid	N910 + geopolymer	Liquid Waste immobilised in	Bench scale:	No additional treatment/conditioning is assumed	[148]

Country	Waste type	Polymer and other materials used	Waste form	Tests conducted	Further treatment/conditioning to meet disposal requirements	Ref.
			Nochar Polymer and Geopolymer	Liquid retention, compressive strength, leaching before and after the immersion tests		
China	TBP/Kerosene (30/70), Acidic solution, Alkaline solution, Ion exchange resin (with 50% water), oil, scintillation liquid	N910, N960	Liquid Waste immobilised in Nochar Polymer	Bench scale: Polymer/waste compatibility, and ratio, 6 week observations for degradation, effects of irradiation on the solidified samples	Packaging of the solidified waste is assumed as a possibility	[149]
Kazakhstan	Contaminated pump oil, alkali, high content salt solutions and slurry	N910, N960 + geocement or sulfur composite matrices	Liquid Waste immobilised in Nochar Polymer and geocement or sulfur composite matrices	Bench scale on polymer and polymer + waste: Thermal analysis by differential thermal analysis (DTA) + Cs137 release with temperature. Bench scale on the sulfur and geocement materials: Specific surface of fillers, average density, compressive and bend strengths, water resistance	No additional treatment/conditioning is assumed	[150], [151]
Slovenia	liquid scintillation fluids, solvents, organic and aqueous solutions	N910, N960, N935	Liquid Waste immobilised in Nochar Polymer	Bench scale: blending of three components of polymers and waste/polymer ratio. Real waste solidified to reduce its potential hazard	Packaging for interim storage	[152]
Slovakia	sludge with dowtherm (organic aromatic waste)	N910 + cement	Liquid Waste immobilised in Nochar Polymer and Cement	Bench scale: visual evaluation, leaching index for ^{137}Cs, leachability of Am + Pu, determination of dowtherm in leaching water, pH and conductivity in leachates, compressive strength, long-term testing of products for three years	No additional treatment/conditioning is assumed	[153]

4.   Summary of identified gaps to be addressed in L'OPERA

As reported before, direct conditioning of RLOW, RSOW and metallic materials with traditional cementitious matrix, pose significant challenges.

Direct immobilization of <u>liquid and solid organic wastes</u> in a cement matrix is affected by the interference of the organic components with the hydration reactions of the cementitious matrix which leads to retardation in the setting of the cementitious paste and creation of porous matrix. The retention of the organic components is mainly dependent on physical entrapment (i.e. encapsulation in cavities) and not the chemical bonds with cement, which will make them vulnerable to leaching. Organic wastes are susceptible to radiolysis, thermal and microbial degradation, which is associated with gas releases that can initiate cracking and affect radionuclide retention. These challenges limit the full-scale practice of organic liquid wastes immobilization into conventional cementitious matrices to low waste loading.

Portland-based matrices have commonly been used for the immobilisation of <u>radioactive metals</u>, often incorporating mineral additions, but radioactive metals can chemically interact with ions dissolved in the pore water of the cementitious matrix, leading to instability and potentially compromising the long-term integrity of the waste form. The primary concern in radioactive metal confinement is minimising the risks associated with hydrogen gas generation due to corrosion. The chemical composition and pH of available binders vary significantly and must be tailored to the specific metal being encapsulated.

Novel matrices (geopolymer, magnesium potassium phosphate cement (MKPC), Nochar and alkali-activated materials) showed promising results in terms of waste encapsulation and short-term performances, but there are still some identified gaps to be addressed for assessing their long-term behaviour under disposal conditions.

Geopolymers and alkali activated materials

Geopolymers and alkali activated materials can be prepared from a variety of aluminosilicate materials, allowing their properties to be tailored to the properties of the immobilised waste. However, it has been recognised that different raw materials significantly affect the properties of the matrix. It is therefore important to assess the influence of raw materials and optimise the waste matrices before use.

Some waste types showed good compatibility with geopolymer, but further work is needed to assess the release of contaminant or radionuclide from the matrix (experiments with real waste or surrogated waste doped with radionuclides or stable element).

Some matrix properties have already been investigated, but these have mainly been short-term tests, usually lasting three months, and in some cases (e.g. leaching, dimension changes) it seemed not to have reached equilibrium. Long-term stability under various conditions: long-term leaching in water (including experiments with contaminants), exposure to irradiation (and related gas generation), thermal ageing, and mechanical ageing, needs to be assessed. Moreover, models to extrapolate the long-term performances of the waste forms should be developed.

Magnesium potassium phosphate cements (MKPC)

The identified uncertainties and gaps with regards to the MKPC system are mainly linked with the nature of the matrix, as different types of MgO have varying reactivity and requiring suitable retarders and many different materials have been considered as mineral admixtures. Moreover, the M/P Molar Ratio has been demonstrated to be crucial for controlling pH and the acid-base reaction. It has been highlighted that isolated MgO aggregates may hydrate and cause volume increase under humid conditions. Further investigations are needed to assess the impact of mineral admixtures and M/P molar ratio on long-term durability.

In terms of waste encapsulation, it has been already demonstrated that encapsulation of radioactive metals is influenced by pore pH and M/P ratio and H2 release must be assessed. Further research is

needed to clarify the short- and long-term H_2 assessment by the change of environmental conditions. Moreover, encapsulation of SIERs has not yet explored.

Finally in terms of waste form durability:

- it is known that waste form durability is affected by exposure to water and alkaline environments, leading to amorphization and strength reduction. It is essential to comprehend the leaching-related degradation mechanisms, and a standardised leaching protocol is missing to obtain comparative results and better interpret the processes involved in leaching
- there is a lack of knowledge about the irradiation dosage and waste form long-term performance
- acceptable resistance to temperature cycling has been demonstrated but further studies are needed to better understand the response at different saturation levels.
- furthermore, the combination of environmental actions, such as irradiation, temperature cycling in aqueous environments has not yet been investigated.

Nochar

It has been recognised that the waste polymer formulation is fully dependent on the chemical composition of the waste and additional studies may be required to properly understand the bonding process with different waste streams.

Regarding the durability of the matrix, some radiation and thermal stability tests have been conducted on the solidified liquid waste with polymers, but additional work is needed to better understand how ageing affects the polymer sorption properties under various conditions (i.e. radiation exposure, temperature fluctuations, and water presence). Moreover, the degradation mechanism of Nochar/waste forms needs to be investigated regarding the durability/lifetime of encapsulation properties.

Further work is necessary in the area of solidification / cement encapsulation to assess the mechanical resistance of the final waste form and to acquire data on the long-term durability and on the effect of cement composition.

Leaching experiments are needed to understand the leaching-related degradation mechanisms and the radionuclide mobility in the presence of organics both considering radionuclide adsorption and the potential effect of organic degradation products on radionuclide retention.

L'OPERA Work Package aims to contribute to filling these knowledge gaps by conducting R&D activities to evaluate the long-term behaviour of the matrices and waste forms.

In the following Figure 38, a schematic summary of the identified uncertainties/gaps linked with the three systems that will be studied in L'OPERA is summarised together with the R&D activities that will be conducted in L'OPERA.

As reported in the figure, before moving to the experimental work in the scope of Task 4 (Inventory of the conditioned materials and complete characterisation), Task 5 (Waste forms durability and stability testing) and Task 6 (Implementation), a preliminary work aimed to identify and characterise the key parameters influencing the durability and the stability of the different waste matrices is expected and included in Task 3 (Boundary conditions). The outcomes of Task 3 will be used to establish experimental protocols to be used in the other tasks.

eurad **2**
European Partnership
on Radioactive Waste Management

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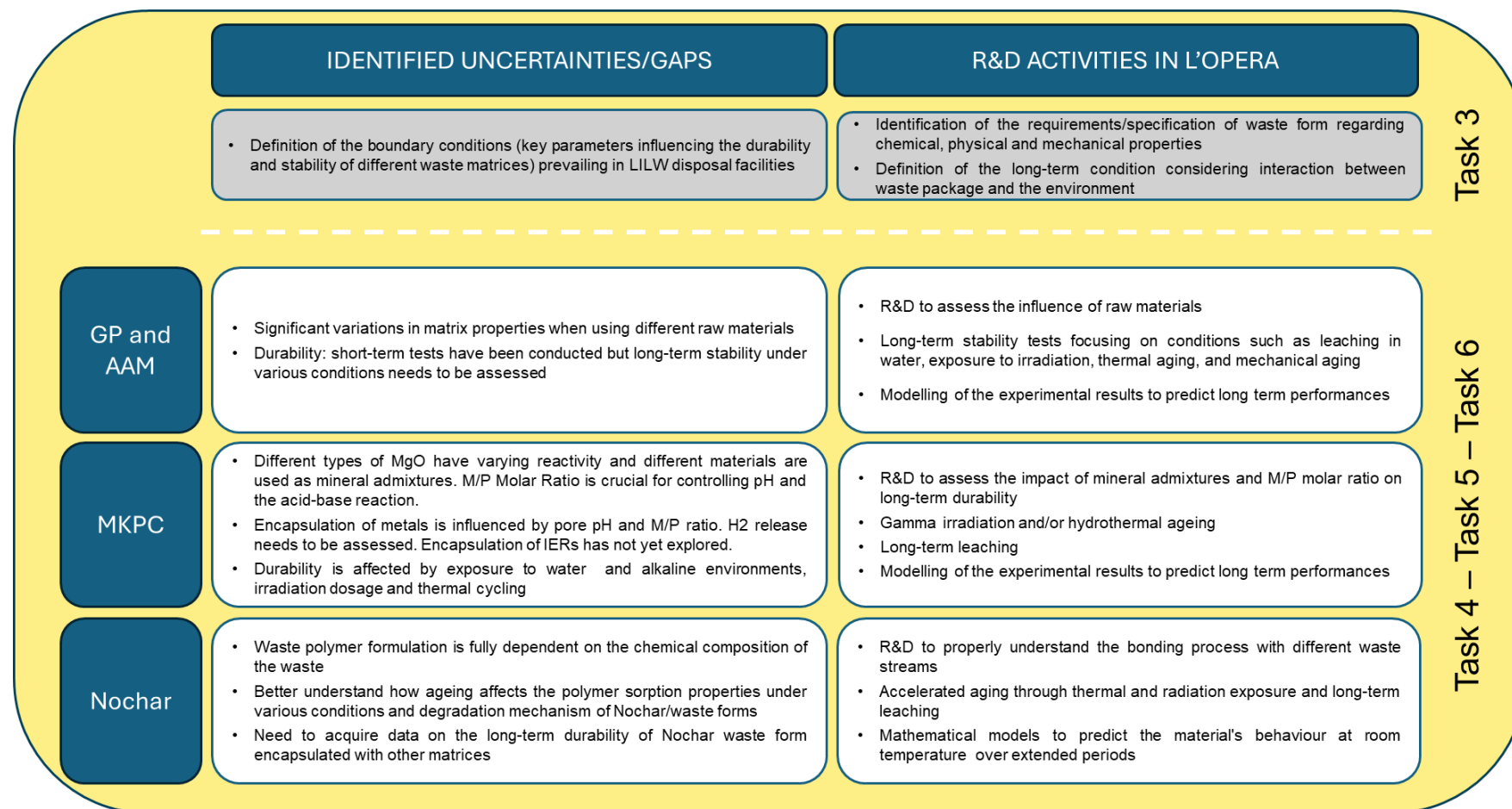| IDENTIFIED UNCERTAINTIES/GAPS	R&D ACTIVITIES IN L'OPERA	
• Definition of the boundary conditions (key parameters influencing the durability and stability of different waste matrices) prevailing in LILW disposal facilities	• Identification of the requirements/specification of waste form regarding chemical, physical and mechanical properties • Definition of the long-term condition considering interaction between waste package and the environment	Task 3
GP and AAM • Significant variations in matrix properties when using different raw materials • Durability: short-term tests have been conducted but long-term stability under various conditions needs to be assessed	• R&D to assess the influence of raw materials • Long-term stability tests focusing on conditions such as leaching in water, exposure to irradiation, thermal aging, and mechanical aging • Modelling of the experimental results to predict long term performances	Task 4 – Task 5 – Task 6
MKPC • Different types of MgO have varying reactivity and different materials are used as mineral admixtures. M/P Molar Ratio is crucial for controlling pH and the acid-base reaction. • Encapsulation of metals is influenced by pore pH and M/P ratio. H_2 release needs to be assessed. Encapsulation of IERs has not yet explored. • Durability is affected by exposure to water and alkaline environments, irradiation dosage and thermal cycling	• R&D to assess the impact of mineral admixtures and M/P molar ratio on long-term durability • Gamma irradiation and/or hydrothermal ageing • Long-term leaching • Modelling of the experimental results to predict long term performances	
Nochar • Waste polymer formulation is fully dependent on the chemical composition of the waste • Better understand how ageing affects the polymer sorption properties under various conditions and degradation mechanism of Nochar/waste forms • Need to acquire data on the long-term durability of Nochar waste form encapsulated with other matrices	• R&D to properly understand the bonding process with different waste streams • Accelerated aging through thermal and radiation exposure and long-term leaching • Mathematical models to predict the material's behaviour at room temperature over extended periods	

Figure 38: *Summary of identified gaps and activities to be performed in L'OPERA*

5.   References

[1].   (2021): EURAD Roadmap, extended with Competence Matrix. Final version as of 27.09.2021 deliverable D1.7 of the HORIZON 2020 project EURAD. EC Grant agreement no: 847593 https://www.ejp-eurad.eu/roadmap

[2].   EURAD Bureau. (2023): Update of the EURAD Strategic Research and Knowledge Management Agenda (SRA), of deliverable D1.9 of the HORIZON 2020 project EURAD. EC Grant agreement no: 847593 https://www.ejp-eurad.eu/publications/eurad-sra

[3].   EU-project PREDIS "Predisposal Management of Radioactive Waste" project https://predis-h2020.eu/

[4].   IAEA TECDOC-1397 - Long term behaviour of low and intermediate level waste packages under repository conditions (2004) https://www-pub.iaea.org/MTCD/Publications/PDF/te_1397_web.pdf

[5].   IAEA TECDOC-1177 - Extrapolation of short term observations to time periods relevant to the isolation of long lived radioactive waste (2000)

[6].   IAEA TECDOC-1701 - The Behaviours of Cementitious Materials in Long Term Storage and Disposal of Radioactive Waste (2013)

[7].   L. Nachmilner and L. Karásková-Nenadálová, "PREDIS D.2.4 International approaches to establishing a waste acceptance system (2021).

[8].   S. Konopásková, H. Vojtěchová, J. Mikšová PREDIS Deliverable 2.6 Guidance on waste form qualification (2024)

[9].   L. Zhang, A. Zhang, Q. Wang, Y. Han, K. Li, X. Gao, Z. Tang, Corrosion resistance of wollastonite modified magnesium phosphate cement paste exposed to freeze-thaw cycles and acid-base corrosion, Case Studies in Construction Materials 13 (2020) e00421. https://doi.org/10.1016/j.cscm.2020.e00421.

[10].   Y. Yang, J. Han, R. Liu, Understanding hydration properties of magnesium potassium phosphate cement with low magnesium-to-phosphate ratio, Construction and Building Materials 416 (2024) 135221. https://doi.org/10.1016/j.conbuildmat.2024.135221.

[11].   H. Feng, L. Wang, Z. Yu, A. Guo, J. Liang, Freeze-thaw resistance and service life prediction of fly ash incorporated ultra-high ductility magnesium phosphate cement-based composites, Construction and Building Materials 449 (2024) 138330. https://doi.org/10.1016/j.conbuildmat.2024.138330.

[12].   G.L. Bykov, V.A. Ershov, B.G. Ershov, Radiolysis of the magnesium phosphate cement on γ-irradiation, Construction and Building Materials 252 (2020) 119156. https://doi.org/10.1016/j.conbuildmat.2020.119156.

[13].   D. Chartier, J. Sanchez-Canet, P. Antonucci, S. Esnouf, J.-P. Renault, O. Farcy, D. Lambertin, S. Parraud, H. Lamotte, C.C.D. Coumes, Behaviour of magnesium phosphate cement-based materials under gamma and alpha irradiation, Journal of Nuclear Materials 541 (2020) 152411. https://doi.org/10.1016/j.jnucmat.2020.152411.

[14].   Nuclear Decommissioning Authority, Geological disposal. Guidance on the application of the Waste Package Specifications for unshielded waste packages, Harwell Oxford, 2014.

[15].   L.J. Gardner, S.A. Walling, C.L. Corkhill, S.A. Bernal, V. Lejeune, M.C. Stennett, J.L. Provis, N.C. Hyatt, Temperature transformation of blended magnesium potassium phosphate cement binders, Cement and Concrete Research 141 (2021). https://doi.org/10.1016/j.cemconres.2020.106332.

[16].   J. L. Provis: Alkali-activated materials. Cement and Concrete Research, 114. pp. 40-48. ISSN 0008-8846 (2018) https://doi.org/10.1016/j.cemconres.2017.02.009.

[17].   J. Davidovits: Geopolymer Chemistry and Applications, 5th edition, Saint-Quentin: Institut Géopolymère, 2020.

[18].   Ch. Reeb, Ch. Pierlot, C. Davy and D. Lambertin: Incorporation of organic liquids into geopolymer materials - A review of processing, properties and applications, Ceramics International, 2020.

[19].   F. Pancotti, C. Bucur, PREDIS Deliverable 5.2: Report on Synthesis of formulation & process studies results, 2024. https://ejp-eurad.eu/sites/default/files/2024-12/PREDIS_D5.2-Synthesis-report_vF-9.2.2024.pdf

[20].   M. Briffaut PREDIS Deliverable 5.3: Report on Synthesis of conditioning matrix performances studies, 2024. file:///C:/Users/a264289/Downloads/PREDIS_D5.3_Synthesis-of-conditioning-matrix-performances_vF-August-2024_0.pdf

[21]. E. Myllykylä PREDIS Deliverable 6.6: Final Report on the Physico-chemical characterization of reconditioned waste for and stability testing, 2024. https://www.ejp-eurad.eu/sites/default/files/2024-12/PREDIS_D6.6-Physico-chemical-characterization_vF-30.8.2024.pdf

[22]. A. Hasnaoui, C. Reeb, M. De Campos, C.A. Davy, D.Lambertin: Controlling the properties of metakaolin-based geopolymer/liquid organic waste emulsions: A rheological approach, Applied Clay Science, 2023

[23]. J.L. Provis, J.S.J. van Deventer, Geopolymers: Structure, Processing, Properties and Industrial Applications, 2009, ISBN 978-1-4398-0970-9.

[24]. M. Houhou, · N. Leklou, · H. Ranaivomanana, · JD. Penot, · S. de Barros: Geopolymers in nuclear waste storage and immobilization: mechanisms, applications, and challenges

[25]. A. Wanga, Y. Zheng, Z. Zhang, K. Liu, Y. Li, L. Shi, D. Sun: The Durability of Alkali-Activated Materials in Comparison with Ordinary Portland Cements and Concretes: A Review

[26]. T. N. Nguyen, Q. T. Phung, Z. Yu, L. Frederickx, D. Jacques, D. Sakalleriou, A. Dauzeres, J. Elsen and Y. Pontikes: Alteration in molecular structure of alkali activated slag with various water to binder ratios under accelerated carbonation, Scientific reports, 2022.

[27]. T. N. Nguyen, Q. T. Phung, D. Jacques, J. Elsen and Y. Pontikes: Microstructure and transport properties of metakaolin-based geopolymers subjected to accelerated leaching, Construction and Building Materials, 2024.

[28]. T. N. Nguyen, Q. T. Phung, D. Jacques, M. Nedi, A. Dauzeres, J. Elsen and Y. Pontikes: Microstructure, water permeability and micromechanical properties of alkali activated slag subjected to accelerated leaching, Materials & Design, 2024.

[29]. ANSI/ANS-16.1-2019: Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure, 2019.

[30]. PREDIS Milestone 39: Definition of the leaching procedure for the short-term experiments and the long-term durability experiments, 2021.

[31]. A. Santi, E. Mossini, G. Magugliani, F. Galluccio, E. Macerata, P. Lotti, G. D. Gatta, D. Vadivel, D. Dondi, D. Cori, H. Nonnet and M. Mariani: Design of sustainable geopolymeric matrices for encapsulation of treated radioactive solid organic waste, Frontiers in Materials, 2022.

[32]. Sayenko S., Svitlychnyi Y., Shkuropatenko V., Pancotti F., Sandalova S., Poulesquen A., Giboire I., Hasnaoui A., Cori D., Magugliani G. and Mossini E.: Incorporation of organic liquid waste in alkali activated mixed fly ash/blast furnace slag/metakaolin-based geopolymers, NUCL ENG DES, 2024.

[33]. Lichavr P., Rozloznik M. and Sekely S.: Behaviour of Aluminosilicate Inorganic Matrix Sial During and After Solidification of Radioactive Sludge And Radioactive Spent Resins and Their Mixtures, 2013.

[34]. Hamdane, H., Oumam, H. H.-M., Chailassi, A. B.-T. E. and Boulif, B. M.-R: An Efficient and Environmentally Friendly Geopolymer Package for Encapsulation of Nuclear Grade Resins Loaded with 134Cs Radionuclide, RADIOACTIVE WASTE MANAGEMENT (s. p. 194–203). IAEA (2023).

[35]. Lin W., Chen H. and Huang Ch.: Performance study of ion exchange resins solidification using metakaolin-based geopolymer binder, Prog. Nucl. Energy, 2020.

[36]. Pandey B., Kinrade S. D. and Catalan L. J. J.: Effects of carbonation on the leachability and compressive strength of cement-solidified and geopolymer-solidified synthetic metal wastes, JEM, 2012.

[37]. Casas A. L., Araujo L. D., Vincente R. and Marumo J. T.: Toward Sustainable Radioactive Waste Management: Geopolymerization of Sewage Sludge Ash as a Viable Solution, ACS Omega, 2025.

[38]. Kim B., Lee J., Kang J. and Um W.: Development of geopolymer waste form for immobilization of radioactive borate waste, J. Hazard. Mater., 2021.

[39]. El-Naggar M. R., El-Sherief E. A. and Mekhemar H. S.: Performance of geopolymers for direct immobilization of solvent extraction liquids: Metakaolin/LIX-84 formulations, J. Hazard. Mater., 2018.

[40]. Cuccia V., Freire C. B. and Ladeira A. C. Q.: Radwaste oil immobilization in geopolymer after non-destructive treatment, Prog. Nuclear Energy, 2020.

[41]. Watanabe S., Takahatake Y., Ogi H., Osugi T., Taniguchi T., Sato J., Arai T. and Kajinami A.: Decontamination and solidification treatment on spent liquid scintillation cocktail, J. Nucl. Mater., 2023.

[42]. Lee W.H., Ch. T.W., Ding Y.Ch., Lin K.L., Tsai S.W. and Huang Ch.P.: Geopolymer technology for the solidification of simulated ion exchange resins with radionuclides, JEM, 2019.

[43]. IAEA TECDOC-656 - Treatment and conditioning of radioactive organic liquids (1992)

[44]. S. Hong, J. Zhang, H. Liang, J. Xiao, C. Huang, G. Wang, H. Hu, Y. Liu, Y. Xu, F. Xing, B. Dong, Investigation on early hydration features of magnesium potassium phosphate cementitious material with the electrodeless resistivity method, Cement and Concrete Composites 90 (2018) 235–240. https://doi.org/10.1016/j.cemconcomp.2018.04.005.

[45]. B. Xu, B. Lothenbach, A. Leemann, F. Winnefeld, Reaction mechanism of magnesium potassium phosphate cement with high magnesium-to-phosphate ratio, Cement and Concrete Research 108 (2018) 140–151. https://doi.org/10.1016/j.cemconres.2018.03.013.

[46]. H. Lahalle, C. Cau Dit Coumes, A. Mesbah, D. Lambertin, C. Cannes, S. Delpech, S. Gauffinet, Investigation of magnesium phosphate cement hydration in diluted suspension and its retardation by boric acid, Cement and Concrete Research 87 (2016) 77–86. https://doi.org/10.1016/j.cemconres.2016.04.010.

[47]. A. Viani, P. Mácová, Polyamorphism and frustrated crystallization in the acid–base reaction of magnesium potassium phosphate cements, CrystEngComm 20 (2018) 4600–4613. https://doi.org/10.1039/C8CE00670A.

[48]. M. Le Rouzic, T. Chaussadent, G. Platret, L. Stefan, Mechanisms of k-struvite formation in magnesium phosphate cements, Cement and Concrete Research 91 (2017) 117–122. https://doi.org/10.1016/j.cemconres.2016.11.008.

[49]. Y. Wang, B. Lin, F. He, J. Zhou, C. Chen, Z. He, L. Wang, Understanding hydration process and paste viscosity evolution of magnesium potassium phosphate cement, Cement and Concrete Research 169 (2023) 107177. https://doi.org/10.1016/j.cemconres.2023.107177.

[50]. B. Xu, F. Winnefeld, J. Kaufmann, B. Lothenbach, Influence of magnesium-to-phosphate ratio and water-to-cement ratio on hydration and properties of magnesium potassium phosphate cements, Cement and Concrete Research 123 (2019) 105781. https://doi.org/10.1016/j.cemconres.2019.105781.

[51]. H. Lahalle, C. Cau Dit Coumes, C. Mercier, D. Lambertin, C. Cannes, S. Delpech, S. Gauffinet, Influence of the w/c ratio on the hydration process of a magnesium phosphate cement and on its retardation by boric acid, Cement and Concrete Research 109 (2018) 159–174. https://doi.org/10.1016/j.cemconres.2018.04.010.

[52]. E. Qoku, M. Scheibel, T. Bier, A. Gerz, Phase development of different magnesium phosphate cements at room temperature and elevated temperatures, Construction and Building Materials 272 (2021) 121654. https://doi.org/10.1016/j.conbuildmat.2020.121654.

[53]. T. Zhang, H. Chen, X. Li, Z. Zhu, Hydration behavior of magnesium potassium phosphate cement and stability analysis of its hydration products through thermodynamic modeling, Cement and Concrete Research 98 (2017) 101–110. https://doi.org/10.1016/j.cemconres.2017.03.015.

[54]. A.S. Wagh, D. Singh, S.Y. Jeong, Stabilization of hazardous ash waste with newberyite-rich chemically bonded magnesium phosphate ceramic, Argonne National Lab., IL, United States, 1995. https://inis.iaea.org/records/excz7-0db83.

[55]. K. Sasaki, S. Moriyama, Effect of calcination temperature for magnesite on interaction of MgO-rich phases with boric acid, Ceramics International 40 (2014) 1651–1660. https://doi.org/10.1016/j.ceramint.2013.07.056.

[56]. R. Fernandez PREDIS, Deliverable 4.8 Characterization of magnesium phosphate cement and low-cost magnesium phosphate cement, 2024. https://www.ejp-eurad.eu/sites/default/files/2024-12/PREDIS_D4.8-Characterisation-of-MPC_vFinal-28.6.2024.pdf.

[57]. European Commission, Study on the critical raw materials for the EU 2023 - Final Report, 2023.

[58]. L. Stefan, T. Chaussadent, H. Bessaies-Bey, Thiosulphates for use as set retarders in phosphomagnesium cement pastes, WO/2021/123564, 2021.

[59]. D.A. Hall, R. Stevens, B. El-Jazairi, The effect of retarders on the microstructure and mechanical properties of magnesia–phosphate cement mortar, Cement and Concrete Research 31 (2001) 455–465. https://doi.org/10.1016/S0008-8846(00)00501-9.

[60]. Z. Lai, X. Lai, J. Shi, Z. Lu, Effect of Zn2+ on the early hydration behavior of potassium phosphate based magnesium phosphate cement, Construction and Building Materials 129 (2016) 70–78. https://doi.org/10.1016/j.conbuildmat.2016.11.002.

[61]. C. Cau Dit Coumes, A. Rousselet, B. Xu, C.A. Mercier, S. Gauffinet, Investigation of aluminum nitrate as a set retarder of magnesium potassium phosphate cement: Mechanisms involved in diluted suspension, Cement and Concrete Research 150 (2021) 106608. https://doi.org/10.1016/j.cemconres.2021.106608.

[62]. Y. Yang, B. Fang, G. Zhang, J. Guo, R. Liu, Hydration Performance of Magnesium Potassium Phosphate Cement Using Sodium Alginate as a Candidate Retarder, Materials 15 (2022). https://doi.org/10.3390/ma15030943.

[63]. Z. Luo, Y. Wang, X. Liu, C. Tian, Y. Wang, Y. Mu, M. Zhang, Y. Hao, Comparative Investigation of Effect of Borax and Sodium Gluconate Retarders on Properties of Magnesium Phosphate Cement, Arabian Journal for Science and Engineering 47 (2022) 13187–13198. https://doi.org/10.1007/s13369-022-06762-0.

[64]. L. Jun, J. Yong-sheng, H. Guodong, J. Cheng, Retardation and reaction mechanisms of magnesium phosphate cement mixed with glacial acetic acid, RSC Adv. 7 (2017) 46852–46857. https://doi.org/10.1039/C7RA08383A.

[65]. A. Viani, P. Mácová, R. Ševčík, L. Zárybnická, Mechanism of magnesium phosphate cement retardation by citric acid, Ceramics International 49 (2023) 11112–11122. https://doi.org/10.1016/j.ceramint.2022.11.308.

[66]. F.R. Stierli, J.M. Gaidis, C.T. Clayton, Control of setting time in magnesia-phosphate cement, UK Patent 1,512,275, 1978.

[67]. A.K. Sarkar, Hydration/dehydration characteristics of struvite and dittmarite pertaining to magnesium ammonium phosphate cement systems, Journal of Materials Science 26 (1991) 2514–2518. https://doi.org/10.1007/BF01130204.

[68]. A.S. Wagh, Chapter 3 - Raw Materials, in: A.S. Wagh (Ed.), Chemically Bonded Phosphate Ceramics, Elsevier, Oxford, 2004: pp. 29–41. https://doi.org/10.1016/B978-008044505-2/50007-7.

[69]. B. Xu, B. Lothenbach, H. Ma, Properties of fly ash blended magnesium potassium phosphate mortars: Effect of the ratio between fly ash and magnesia, Cement and Concrete Composites 90 (2018) 169–177. https://doi.org/10.1016/j.cemconcomp.2018.04.002.

[70]. L.J. Gardner, S.A. Bernal, S.A. Walling, C.L. Corkhill, J.L. Provis, N.C. Hyatt, Characterisation of magnesium potassium phosphate cements blended with fly ash and ground granulated blast furnace slag, Cement and Concrete Research 74 (2015) 78–87. https://doi.org/10.1016/j.cemconres.2015.01.015.

[71]. X. Lu, B. Chen, Experimental study of magnesium phosphate cements modified by metakaolin, Construction and Building Materials 123 (2016) 719–726. https://doi.org/10.1016/j.conbuildmat.2016.07.092.

[72]. X. Xu, X. Lin, X. Pan, T. Ji, Y. Liang, H. Zhang, Influence of silica fume on the setting time and mechanical properties of a new magnesium phosphate cement, Construction and Building Materials 235 (2020) 117544. https://doi.org/10.1016/j.conbuildmat.2019.117544.

[73]. B. Xu, B. Lothenbach, F. Winnefeld, Influence of wollastonite on hydration and properties of magnesium potassium phosphate cements, Cement and Concrete Research 131 (2020) 106012. https://doi.org/10.1016/j.cemconres.2020.106012.

[74]. M. Dieguez, A.I. Ruiz, J. Cuevas, M.C. Alonso, I. García-Lodeiro, R. Fernández, Evaluation of Fillers for Magnesium Potassium Phosphate Cement (MKPC) for the Encapsulation of Low and Intermediate Level Metallic Radioactive Wastes, Materials 16 (2023) 679. https://doi.org/10.3390/ma16020679.

[75]. P. Padilla-Encinas, M. Dieguez, J. Cuevas, A.I. Ruiz, R. Fernández, The Influence of the Magnesium-to-Phosphate Molar Ratio on Magnesium Potassium Phosphate Cement Properties Using Either Wollastonite or Volcanic Ash as Fillers, Minerals 14 (2024) 103. https://doi.org/10.3390/min14010103.

[76]. J. Yang, J. Lu, Q. Wu, M.F. Xia, X. Li, Influence of steel slag powders on the properties of MKPC paste, Construction and Building Materials 159 (2018) 137–146. https://doi.org/10.1016/j.conbuildmat.2017.10.081.

[77]. M. Nicu, L. Ionascu, F. Dragolici, G.H. Dogaru, Effect of magnesium oxide particle size and the filler content on magnesium potassium phosphate cement properties, Romanian Journal of Physics 61 (2016) 543–552.

[78]. S. Ma, Z. Zhang, X. Liu, Y. Li, Q. Zeng, W. Zhang, Reuse of red mud in magnesium potassium phosphate cement: Reaction mechanism and performance optimization, Journal of Building Engineering 61 (2022) 105290. https://doi.org/10.1016/j.jobe.2022.105290.

[79]. A. Sadji, M.R. Boudchicha, Addition of Glass Powder to Magnesium Potassium Phosphate Cement Based on MgO Brick, Journal of Materials in Civil Engineering 35 (2023). https://doi.org/10.1061/(ASCE)MT.1943-5533.0004743.

[80]. Q. Deng, Z. Lai, R. Xiao, J. Wu, M. Liu, Z. Lu, S. Lv, Effect of Waste Glass on the Properties and Microstructure of Magnesium Potassium Phosphate Cement, Materials 14 (2021) 2073. https://doi.org/10.3390/ma14082073.

[81]. J. Qin, J. Qian, X. Dai, C. You, H. Ma, Z. Li, Effect of water content on microstructure and properties of magnesium potassium phosphate cement pastes with different magnesia-to-phosphate ratios, Journal of the American Ceramic Society 104 (2021) 2799–2819. https://doi.org/10.1111/jace.17695.

[82]. D.A. Hall, R. Stevens, B.E. Jazairi, Effect of Water Content on the Structure and Mechanical Properties of Magnesia-Phosphate Cement Mortar, Journal of the American Ceramic Society 81 (2005) 1550–1556.

[83]. Y. Zheng, Y. Zhou, X. Huang, H. Luo, Effect of raw materials and proportion on mechanical properties of magnesium phosphate cement, Journal of Road Engineering 2 (2022) 243–251. https://doi.org/10.1016/j.jreng.2022.06.001.

[84]. C. Cau Dit Coumes, D. Lambertin, H. Lahalle, P. Antonucci, C. Cannes, S. Delpech, Selection of a mineral binder with potentialities for the stabilization/solidification of aluminum metal, Journal of Nuclear Materials 453 (2014) 31–40. https://doi.org/10.1016/j.jnucmat.2014.06.032.

[85]. C. Fernández-García, M.C. Alonso, J.M. Bastidas, I. García-Lodeiro, R. Fernández, MgO/KH2PO4 and Curing Moisture Content in MKPC Matrices to Optimize the Immobilization of Pure Al and Al-Mg Alloys, Materials 17 (2024) 1263. https://doi.org/10.3390/ma17061263.

[86]. M. Le Rouzic, T. Chaussadent, L. Stefan, M. Saillio, On the influence of Mg/P ratio on the properties and durability of magnesium potassium phosphate cement pastes, Cement and Concrete Research 96 (2017) 27–41. https://doi.org/10.1016/j.cemconres.2017.02.033.

[87]. L. Yue, S. Jia, C. Bing, Experimental study of magnesia and M/P ratio influencing properties of magnesium phosphate cement, Construction and Building Materials 65 (2014) 177–183. https://doi.org/10.1016/j.conbuildmat.2014.04.136.

[88]. M. Xue, H. Wang, X. Xiao, J. Cao, Influence of m(P)/m(M) mass ratio on properties of magnesium phosphate cement and its mechanism analysis, Gongneng Cailiao/Journal of Functional Materials 46 (2015) 23090–23095. https://doi.org/10.3969/j.issn.1001-9731.2015.23.019.

[89]. A. Covill, N.C. Hyatt, J. Hill, N.C. Collier, Development of magnesium phosphate cements for encapsulation of radioactive waste, Advances in Applied Ceramics 110 (2011) 151–156. https://doi.org/10.1179/1743676110Y.0000000008.

[90]. L. Ionascu, M. Nicu, C. Turcanu, F. Dragolici, G.H. Rotarescu, Study of the conditioning matrices for aluminium radioactive wastes, Romanian Journal of Physics 59 (2014) 360–368.

[91]. W. Montague, L. Vandeperre, M. Hayes, Processing Characteristics and Strength of Magnesium Phosphate Cement Formulations Compatible with UK Nuclear Waste Treatment Plants, MRS Online Proceedings Library 1475 (2012) 287–292. https://doi.org/10.1557/opl.2012.588.

[92]. S. Chhaiba, S. Martinez-Sanchez, N. Husillos-Rodriguez, Á. Palomo, H. Kinoshita, I. Garcia-Lodeiro, Durability of Magnesium Potassium Phosphate Cements (MKPCs) under Chemical Attack, Materials 17 (2024). https://doi.org/10.3390/ma17174252.

[93]. IAEA-TECDOC-1325, Management of low and intermediate level radioactive wastes with regard to their chemical toxicity, 2002. https://www-pub.iaea.org/MTCD/Publications/PDF/te_1325_web.pdf.

[94]. L.J. Gardner, C.L. Corkhill, S.A. Walling, J.E. Vigor, C.A. Murray, C.C. Tang, J.L. Provis, N.C. Hyatt, Early age hydration and application of blended magnesium potassium phosphate cements for reduced corrosion of reactive metals, Cement and Concrete Research 143 (2021) 106375. https://doi.org/10.1016/j.cemconres.2021.106375.

[95]. S. Caes, A. Bukaemskiy, G. Deissmann, G. Modolo, V. de Souza, B. Kursten PREDIS, Deliverable 4.12 Beryllium reactivity in magnesium phosphate cement, 2024. https://www.ejp-eurad.eu/sites/default/files/2024-12/PREDIS_D4.12-Beryllium_vFinal-28.6.2024.pdf.

[96]. P. Bouhier, C. Cannes, D. Lambertin, C. Grisolia, D. Rodrigues, S. Delpech, Evaluation of several conditioning matrices for the management of radioactive metal beryllium wastes,

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on Radioactive Waste Management

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Date of issue of this report: **19/06/2025**

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Journal of Nuclear Materials 559 (2022) 153464. https://doi.org/10.1016/j.jnucmat.2021.153464.

[97].   C. Fernández-García, P. Padilla-Encinas, R. Fernández, M.C. Alonso, Interaction of aluminum alloys with MKPC and Portland-based cements on the metal-matrix interface, Applied Geochemistry 172 (2024) 106105. https://doi.org/10.1016/j.apgeochem.2024.106105.

[98].   S. Delpech, C. Cannes, N. Barré, Q.T. Tran, C. Sanchez, H. Lahalle, D. Lambertin, S. Gauffinet, C. Cau Dit Coumes, Kinetic Model of Aluminum Behavior in Cement-Based Matrices Analyzed by Impedance Spectroscopy, Journal of The Electrochemical Society 164 (2017) C717–C727. https://doi.org/10.1149/2.0211713jes.

[99].   C. Fernández-García, M.C. Alonso, Aluminium corrosion reactivation in MKPC and Portland-based waste-forms under simulated alkaline alkaline repository conditions, Journal of Nuclear Materials under review (2025).

[100]. R. Perona, C. Fernández-García, I. García-Lodeiro, M. Criado, J.M. Bastidas, M.C. Alonso, Corrosion behavior and immobilization of pure aluminum and Al−Mg alloy LLRW in magnesium potassium phosphate cements, Journal of Nuclear Materials 582 (2023) 154501. https://doi.org/10.1016/j.jnucmat.2023.154501.

[101]. G. Poras, C. Cau Dit Coumes, P. Antonucci, C. Cannes, S. Delpech, S. Perrin, Electrochemical Behavior of Al/Mg Alloys Immobilized in a Magnesium Potassium Phosphate Cement-Based Mortar, Materials 16 (2023). https://doi.org/10.3390/ma16155415.

[102]. C. Bucur, M.C. Alonso PREDIS, Deliverable 4.11 Aluminium and steel reactivity in magnesium phosphate cement, 2024. https://www.ejp-eurad.eu/sites/default/files/2024-12/PREDIS_D4.11-Al-and-steel-reactivity-in-MPC_vFinal-28.6.2024.pdf.

[103]. C. Fernández-García, K.K. Le, M.C. Alonso, C. Cannes, S. Delpech, Passivation of aluminium A1050 in MKPC matrices: effect of MgO type and chemical retarder composition, Electrochimica Acta accepted (2025).

[104]. H. Tang, J. Qian, Z. Ji, X. Dai, Z. Li, The protective effect of magnesium phosphate cement on steel corrosion, Construction and Building Materials 255 (2020) 119422. https://doi.org/10.1016/j.conbuildmat.2020.119422.

[105]. S. Yin, H. Yang, Y. Dong, C. Qu, J. Liu, T. Guo, K. Duan, Environmentally favorable magnesium phosphate anti-corrosive coating on carbon steel and protective mechanisms, Scientific Reports 11 (2021) 197. https://doi.org/10.1038/s41598-020-79613-3.

[106]. F. Zhang, J. Qin, K. Cai, J.J. Myers, H. Ma, Anti-Corrosion Performance of Magnesium Potassium Phosphate Cement Coating on Steel Reinforcement: The Effect of Boric Acid, Materials 17 (2024). https://doi.org/10.3390/ma17215310.

[107]. M.I. Ojovan, W.E. Lee, 1 - Introduction to Immobilisation, in: M.I. Ojovan, W.E. Lee (Eds.), An Introduction to Nuclear Waste Immobilisation (Second Edition), Elsevier, Oxford, 2014: pp. 1–6. https://doi.org/10.1016/B978-0-08-099392-8.00001-2.

[108]. IAEA, Status and Trends in Spent Fuel and Radioactive Waste Management, INTERNATIONAL ATOMIC ENERGY AGENCY, Vienna, 2022. https://www.iaea.org/publications/14739/status-and-trends-in-spent-fuel-and-radioactive-waste-management.

[109]. J. Li, J. Wang, Advances in cement solidification technology for waste radioactive ion exchange resins: A review, Journal of Hazardous Materials 135 (2006) 443–448. https://doi.org/10.1016/j.jhazmat.2005.11.053.

[110]. Q. Zhou, N.B. Milestone, M. Hayes, An alternative to Portland Cement for waste encapsulation—The calcium sulfoaluminate cement system, Journal of Hazardous Materials 136 (2006) 120–129. https://doi.org/10.1016/j.jhazmat.2005.11.038.

[111]. D.S. Perera, M.G. Blackford, E.R. Vance, J.V. Hanna, K.S. Finnie, C.L. Nicholson, Geopolymers for the Immobilization of Radioactive Waste, MRS Online Proceedings Library 824 (2004) 432–437. https://doi.org/10.1557/PROC-824-CC8.35.

[112]. P. Swift, H. Kinoshita, N.C. Collier, C.A. Utton, Phosphate modified calcium aluminate cement for radioactive waste encapsulation, Advances in Applied Ceramics 112 (2013) 1–8. https://doi.org/10.1179/1743676112Y.0000000033.

[113]. I. García-Lodeiro, N. Husillos-Rodriguez, S. Chhaiba, H. Kinoshita, Á. Palomo, Encapsulation of SIERs in MKPC cements, in: Proceedings of 2nd International Conference of Innovation in Low Carbon Cements and Concrete Technology, London, UK, 2024.

[114]. S. Martínez Ramírez, Inmovilización de resinas de intercambio iónico en cementos de fosfato de magnesio, Master Final Dissertation, Universidad Carlos III (UC3M), 2024.

[115]. Q. Yang, B. Zhu, X. Wu, Characteristics and durability test of magnesium phosphate cement-based material for rapid repair of concrete, Materials and Structures 33 (2000) 229–234. https://doi.org/10.1007/BF02479332.

[116]. Y. Li, B. Chen, Factors that affect the properties of magnesium phosphate cement, Construction and Building Materials 47 (2013) 977–983. https://doi.org/10.1016/j.conbuildmat.2013.05.103.

[117]. L. Chong, J. Yang, C. Shi, Effect of curing regime on water resistance of magnesium–potassium phosphate cement, Construction and Building Materials 151 (2017) 43–51. https://doi.org/10.1016/j.conbuildmat.2017.06.056.

[118]. H. Lahalle, C. Patapy, M. Glid, G. Renaudin, M. Cyr, Microstructural evolution/durability of magnesium phosphate cement paste over time in neutral and basic environments, Cement and Concrete Research 122 (2019) 42–58. https://doi.org/10.1016/j.cemconres.2019.04.011.

[119]. L. Diaz Caselles, C. Cau Dit Coumes, P. Antonucci, A. Rousselet, A. Mesbah, V. Montouillout, Chemical degradation of magnesium potassium phosphate cement pastes during leaching by demineralized water: Experimental investigation and modeling, Cement and Concrete Research 178 (2024) 107456. https://doi.org/10.1016/j.cemconres.2024.107456.

[120]. V. Shkuropatenko, S. Sayenko, Y. Svitlycnyi, L. Diaz Caselles, C. Cau Dit Coumes, A. Rousselet PREDIS, Deliverable 4.9 Leaching behavior of magnesium phosphate cement-based materials, 2024. https://www.ejp-eurad.eu/sites/default/files/2024-12/PREDIS_D4.9-MPC-Leaching-behaviour_vFinal-28.6.2024.pdf.

[121]. S.Y. Sayenko, V.A. Shkuropatenko, Y.O. Svitlychnyi, S.O. Karsim, D.V. Kutnii, A.V. Zykova, K.V. Lobach, Behaviour of Magnesium potassium phosphate cement under leaching, Problems of Atomic Science and Technology 5 (2023) 68–76. https://doi.org/10.46813/2023-147-068.

[122]. D. Zhong, S. Wang, L. Wang, The influence of alkaline curing systems on the strength and microstructural properties of magnesium phosphate cement, Construction and Building Materials 264 (2020) 120679. https://doi.org/10.1016/j.conbuildmat.2020.120679.

[123]. L. Diaz Caselles, C. Cau Dit Coumes, P. Antonucci, A. Rousselet, A. Mesbah, V. Montouillout, Leaching of magnesium potassium phosphate cement pastes under alkaline conditions, Applied Geochemistry 170 (2024) 106067. https://doi.org/10.1016/j.apgeochem.2024.106067.

[124]. I. Buj, J. Torras, M. Rovira, J. de Pablo, Leaching behaviour of magnesium phosphate cements containing high quantities of heavy metals, Journal of Hazardous Materials 175 (2010) 789–794. https://doi.org/10.1016/j.jhazmat.2009.10.077.

[125]. Y.-J. Du, M.-L. Wei, K.R. Reddy, F. Jin, H.-L. Wu, Z.-B. Liu, New phosphate-based binder for stabilization of soils contaminated with heavy metals: Leaching, strength and microstructure characterization, Journal of Environmental Management 146 (2014) 179–188. https://doi.org/10.1016/j.jenvman.2014.07.035.

[126]. F. Fattori, G. Magugliani, A. Santi, E. Mossini, I. Moschetti, F. Galluccio, E. Macerata, X. de la Bernardie, A. Abdelouas, D. Cori, D. Comboni, G.D. Gatta, M. Mariani, Radiation stability and durability of magnesium phosphate cement for radioactive reactive metals encapsulation, Progress in Nuclear Energy 177 (2024) 105463. https://doi.org/10.1016/j.pnucene.2024.105463.

[127]. G.L. Bykov, E.V. Abkhalimov, V.A. Ershov, B.G. Ershov, Radiolysis of Portland cement and magnesium phosphate cement: Effect of the content and state of water on the Physicochemical properties and the mechanism and kinetics of hydrogen formation, Radiation Physics and Chemistry 190 (2022) 109822. https://doi.org/10.1016/j.radphyschem.2021.109822.

[128]. I. Moschetti PREDIS, Deliverable 4.10 Effect of irradiation on the durability of magnesium phosphate cement, 2024. https://www.ejp-eurad.eu/sites/default/files/2024-12/PREDIS_D4.10-Irradiation-durability-of-MPC_vFinal-28.6.2024.pdf.

[129]. Nuclear Decommissioning Authority, Geological disposal. Guidance on the application of the Waste Package Specifications for unshielded waste packages, Harwell Oxford, 2014.

[130]. L.J. Gardner, S.A. Walling, C.L. Corkhill, S.A. Bernal, V. Lejeune, M.C. Stennett, J.L. Provis, N.C. Hyatt, Temperature transformation of blended magnesium potassium

phosphate cement binders, Cement and Concrete Research 141 (2021). https://doi.org/10.1016/j.cemconres.2020.106332.

[131]. N.E. Hipedinger, A.N. Scian, E.F. Aglietti, Magnesia–ammonium phosphate-bonded cordierite refractory castables: Phase evolution on heating and mechanical properties, Cement and Concrete Research 34 (2004) 157–164. https://doi.org/10.1016/S0008-8846(03)00256-4.

[132]. Y. Fang, P. Cui, Z. Ding, J.-X. Zhu, Properties of a magnesium phosphate cement-based fire-retardant coating containing glass fiber or glass fiber powder, Construction and Building Materials 162 (2018) 553–560. https://doi.org/10.1016/j.conbuildmat.2017.12.059.

[133]. X. Gao, A. Zhang, S. Li, B. Sun, L. Zhang, The resistance to high temperature of magnesia phosphate cement paste containing wollastonite, Materials and Structures 49 (2016) 3423–3434. https://doi.org/10.1617/s11527-015-0729-9.

[134]. X. Zhang, G. Li, M. Niu, Z. Song, Effect of calcium aluminate cement on water resistance and high-temperature resistance of magnesium-potassium phosphate cement, Construction and Building Materials 175 (2018) 768–776. https://doi.org/10.1016/j.conbuildmat.2018.04.200.

[135]. J. Yu, J. Qian, H. Chen, Y. Ji, D. Kuang, X. Jia, B. Guan, Behavior of magnesium phosphate cement with addition of sulphoaluminate cement at elevated temperatures, Construction and Building Materials 401 (2023) 132932. https://doi.org/10.1016/j.conbuildmat.2023.132932.

[136]. Y. Li, T. Shi, B. Chen, Y. Li, Performance of magnesium phosphate cement at elevated temperatures, Construction and Building Materials 91 (2015) 126–132. https://doi.org/10.1016/j.conbuildmat.2015.05.055.

[137]. L. Chong, J. Yang, Z.Z. Xu, X. Xu, Freezing and thawing resistance of MKPC paste under different corrosion solutions, Construction and Building Materials 212 (2019) 663–674. https://doi.org/10.1016/j.conbuildmat.2019.03.269.

[138]. https://nochar.com/n-series-nuclear-products/

[139]. D. Kelley, WM 2017 Conference 2017, March 5-9, 2017, Phoenix, Arizona, USA "Proven Technologies for the Solidification of Complex Liquid Radioactive Waste (LRW): Global Case Studies of Applications and Disposal Options"

[140]. H. Cassidy and D. Kelley, "Oil Immobilization Program at Sellafield: An Innovative Approach", WM 2007 Conference, Tucson, Arizona (2007)

[141]. C.E. Vaudey, S. Renou, J. Porco, D. Kelley, C. Cochaud and R. Serrano, "NOCHAR Polymers: An Aqueous and Organic Liquid Solidification Process for Cadarache LOR (Liquides Organiques Radioactifs), WM2013 Conference, Phoenix, Arizona (2013)

[142]. G. Teodorov, L. Toro, A. Sandru, A. Musat, D. Kelley, and D. Dumitrescu, "Solidification Technology for Organic Liquid Waste Combined with Solid Materials from Cernavoda NPP, Romania", WM2016 Conference, Phoenix, Arizona (2016)

[143]. G. Teodorov, L. Toro, A. Sandru, D. Kelley, and D. Dumitrescu - Presentation on theme: "Pre-Treatment of Organic Liquid Waste Stream at Cernavoda NPP", 14th International Conference on environmental remediation and radioactive waste management. France 2011

[144]. Y. Pokhitonov, V. Babain, S. Strelkov, D. Kuznetsov, and D. Kelley, "Radiation and Thermal Stability of Solid Radwaste after Immobilization in Polymer Matrix", WM2013, Phoenix, Arizona 2013

[145]. Y. Pokhitonov, V. Babain, and D. Kelley, "Russia: Results and Prospects of Liquid Solidification Experiments at ROSATOM Sites", Canada Nuclear Society-Waste Management, Toronto, Canada 2011

[146]. D. Campbell and D. Kelley, "Proven Technologies for the Treatment of Complex Radioactive Liquid Waste Streams; U.S. Department of Energy and International Case Studies", 10th International Conference on Environmental and Radioactive Waste Management, Glasgow, Scotland, 2005

[147]. F. Pancotti, R. Oliva, G. Pugliese, E. Grossi, P. Geraldini, F. Troiani, "Multiphase (oil/water/sludge) radioactive liquid waste solidification with polymer and cement – Sogin Experience" - Nuwcem 2022 International Symposium on Cement-Based Materials for Nuclear Wastes, Avignon, France 2022

[148]. E. Mossini et al., "Pre-impregnation approach to encapsulate radioactive liquid organic waste in geopolymer", Journal of Nuclear Materials 585 (2023) 154608

[149]. B. Liangjin, L. Meiqiong and D. Kelley, "China's Scientific Investigation for Liquid Waste Treatment Solutions", Alternative Materials for Radioactive Waste Stabilization Conference, Barga, Italy, 2007

[150]. D. Kelley, A. Guelis, A. Ivanov, I. Yakovlev, A. Galkin, A. Klepikov, "Kazakhstan: Treatment and Safe Disposal of Liquid Radioactive Waste from the BN-350 Reactor Unit at the LRW Processing Facility- 14016", WM214 Conference, Phoenix, Arizona 2015

[151]. A. Galkin, I. Yakovlev, N. Bachilova, A. Klepikov, A. Blynskiy, T. Tolebayev, A. Abdulgalieva, A. Ivanov, A. Glis and D. Kelley, "Dual Solidification Process of BN-350 Liquid Radioactive Waste Using High Technology Polymers and Newly Designed Encapsulation Techniques", WM2015 Conference, Phoenix, Arizona 2015

[152]. M. Kostanjevec, S. Sučić, "The Solidification of Liquid Radioactive Waste – New Technique and Knowledge Applied in Institutional Waste Management in Slovenia" NENE 2014, 23rd International Conference Nuclear Energy for New Europe, Slovenia, 2014

[153]. B. Andris, "Development of cement based matrix for immobilization of ILW sludge with organics residues", poster at Nuwcem 2018 International Symposium on Cement-Based Materials for Nuclear Wastes, Avignon, France 2018

[154]. Altmaier M., Ricard D., Vandenborre J., Garcia D., Henocq P., Macé N., Missana T. (2024): CORI - Final Report integrating the R&D performed in CORI, including application to the Safety Case. Final version as of 15.07.2024 of Deliverable D3.5 of the HORIZON 2020 project EURAD. EC Grant agreement no: 847593