



# PREDIS

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**Case Studies and Blogs:**  
**demonstrating innovations in**  
**radioactive waste management**  
**predisposal developed within the**  
**EURATOM PREDIS project**  
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<p><b>Abstract</b></p> <p>PREDIS aimed to disseminate the project outcomes in a series of less technical and thus more accessible formats of case studies and blogs targeting non-experts in the field of radioactive waste management. Case studies present a brief overview of the technology or solution together developed within PREDIS along with the main innovation aspects and ways the proposed solution addresses the industry needs. All case studies include relevant references and materials for further reading. Blogs are shorter communications of PREDIS technologies or outcomes which were published on the PREDIS LinkedIn page.</p> <p>Four case studies were produced:</p> <ul style="list-style-type: none"> <li>• Radioactive solid organic waste immobilisation in geopolymers</li> <li>• Radioactive liquid organic waste immobilisation in geopolymers</li> <li>• Metallic waste conditioning in magnesium phosphate cement</li> <li>• Network of small affordable sensors for monitoring waste packages</li> </ul> <p>Three blogs were published:</p> <ul style="list-style-type: none"> <li>• Conditioning of Molten Salt Oxidation solid waste into geopolymer matrix</li> <li>• Waste form qualification</li> <li>• Separation and determination of actinides and Zirconium-93 from radioactive waste and mineral samples</li> </ul>
<p><b>Keywords</b></p> <p>Predisposal, radioactive waste, solid organic waste, liquid organic waste, metallic waste, sensors, case study, blog</p>

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## 1 Introduction

PREDIS project aimed to disseminate the outcomes in a series of less technical and thus more accessible for non-experts formats of case studies and blogs. Case studies present a brief overview of the developed and tested technology or solution together with the main innovation aspects and the ways the proposed solution addresses the end user needs or advances the waste management field. All case studies include relevant references and point to further reading. Blogs are shorter communications of PREDIS technologies or results published on [PREDIS LinkedIn page](#).

## 2 Case studies

### 2.1 Radioactive solid organic waste immobilisation in geopolymers

Keywords: PREDIS; EURATOM; radioactive waste immobilisation; geopolymer; cementation; gasification  
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#### Challenge to solve

Pre-disposal activities including waste immobilisation prior to final disposal have traditionally been done for different waste forms using matrices such as cement and bitumen. Although cement-based immobilisation matrices are a conventional and proven method, they offer a less sustainable and effective way of waste loading than alternative binders such as geopolymers. Using alternative binders will accommodate possible future changes in binder availability. They can also support environmentally sustainable practices, such as reduction of emissions from cement production. This work was aimed at demonstrating the performance and safety of thermal waste treatment (gasification) paired with geopolymer immobilisation of reconditioned waste.

#### Approach taken

The methodology presented here focuses on immobilisation of low- and intermediate-level radioactive waste in the form of spent ion exchange resin. It also builds upon previous work on geopolymer binders done in a preceding Euratom project, THERAMIN [1, 2].

Both cement and geopolymer binders were studied to compare their performance and final waste loading rate. Additionally, direct waste immobilisation without volume reduction was compared to thermal treatment by gasification of the ion exchange resin. As a benchmark test, direct waste immobilisation was performed with resin immobilisation in cement. The aim of the benchmark test was to compare the other methodologies' performance, for example in mechanical strength with different waste loading and leachability of the immobilised waste. In the benchmark test, the samples were produced with Portland cement including the cement mortars with 66% of standardised sand aggregate, and the powdered resin mixed into the cement. In direct traditional cementation, a practical waste loading limit of 15% was achieved, as the mechanical strength of the mixture significantly decreased above this threshold. During direct immobilisation in geopolymers, the geopolymer precursor consisted of metakaolin mixed with 15% of resins (% replacement, by mass), and a similar amount of sand to the benchmark. The resins were additionally conditioned to different moisture contents to determine their influence on the wasteform performance.

The gasification was performed in a pilot-scale bubbling fluidised bed reactor, where the resin was thermally treated. Two different methods for the gasification were used: with and without iron ( $\text{Fe}_2\text{O}_3$ )

added to the resin. During the process, resins additionally impregnated with caesium, europium, and cerium (Cs, Eu, and Ce) tracers, were continuously fed into the reactor bed. The end product, solid filter dust from the plant, was immobilised into a cement-geopolymer mix in mortar sized batches.

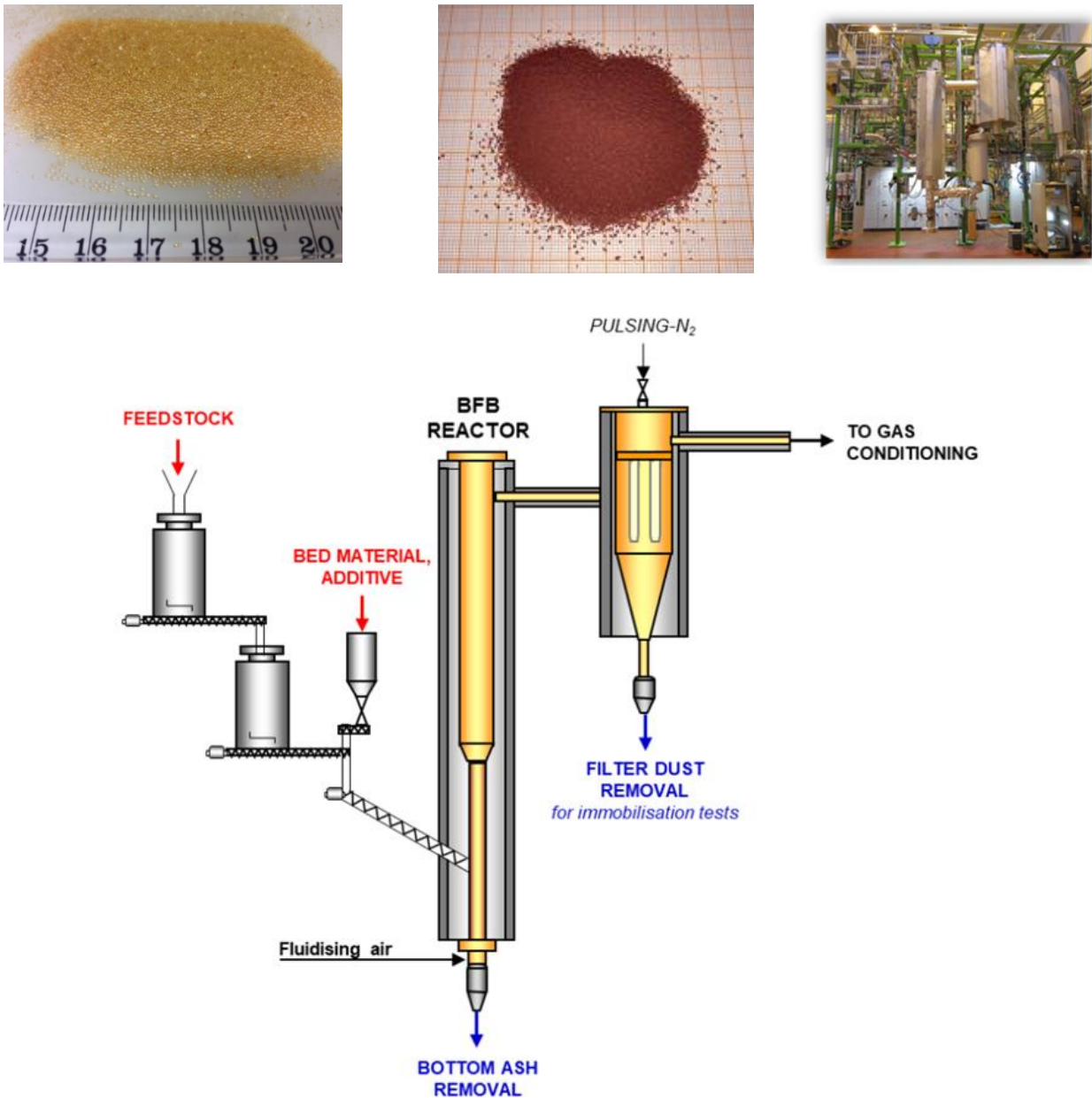


Figure 1. Ion exchange resin without iron (top left) and with iron (top middle), and the gasification reactor (top right), along with a simplified schematic with important components labelled (bottom) [3]. BFB stands for Bubbling Fluidised Bed.

### Innovation

The approach taken for the immobilisation built upon the work carried out in the THERAMIN project [1, 2]. More tracers were added to the resin before it was treated, compared with earlier work in THERAMIN. This made it more representative of real low- and intermediate-level waste (LILW) originating from a boiling water reactor type nuclear power plant. Iron ( $\text{Fe}_2\text{O}_3$ ) was also added to

better represent corrosion-related waste in resins. Furthermore, the waste loading targets for the cement and geopolymer mixtures were higher than in previous work.

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*“Geopolymers seem to be a highly promising technology for predisposal of radioactive waste.”*

*Henri Le Monies de Sagazan, Électricité de France (EDF), France*

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### **Impact towards practice**

The main impact of the thermal treatment and safe waste immobilisation of the secondary waste stream with geopolymers is the significant volume reaction achieved and improved disposability of the final product. With the thermal treatment, it was possible to achieve 20 % and 50 % of ash content in the cement and geopolymer mixes, respectively. The volume reduction achieved for ion exchange resin waste by thermal treatment was up to 95 % with added iron ( $\text{Fe}_2\text{O}_3$ ) and 96 % without iron. The presence of iron appears to significantly change the distribution of the sulphate phases, namely the formation of pyrite and other less soluble phases that benefit the wasteforms' durability. The total volume reduction was 98 % for geopolymer binder and 94 % for cement binder, relative to the volume of wasteforms containing directly immobilised untreated ion exchange resin. However, it should be considered that the gasification process generated secondary waste products, such as accumulated tracer elements in the reactor, and the need for separate treatment of gas fractions. These secondary waste streams decrease the total volume reduction of the entire process. Due to volume reduction, significantly fewer waste packages and thus less space in a repository is needed, allowing for longer-term optimisation of operational waste disposal with existing repository space.

When compared to the direct immobilisation in cement, the mechanical strength of the geopolymer mixture varied depending on the water content of the resins. The test showed that conditioning to 95 % relative humidity improved strength in cement samples but reduced strength for geopolymers and the opposite was true for conditioning to 50 % relative humidity (tested 7 days after sample production) [1]. The mechanical properties of the thermally treated resins immobilised in the mixture were significantly better when compared to the benchmark case. In addition, the thermal treatment improved the disposability of the waste package from the matrix reactivity perspective as it also decreased leaching.

In summary, geopolymer immobilisation offers several direct benefits such as the use of more sustainable binder alternatives, as metakaolin calcination does not produce as much emissions as cement production and it can still potentially be sourced locally. The tests demonstrated that gasification paired with geopolymer immobilisation proved to be more reliable than direct cementation and it led to 98 % final waste volume reduction, decreased leaching, improved disposability, and fewer durability concerns.

Further studies should examine the feasibility and safety of gas treatment and secondary waste generated during gasification, study the practical extent of waste volume reduction, explore alternative direct cementation methods to a greater extent, and evaluate the activity limits of waste packages. Future binder evolution including development of more green binders will further influence the properties, and research of cement replacement for waste immobilisation is also a key topic in further research. The assumption that geopolymers should be less prone to leaching damage in the very long-term is to be determined in the future experiments, which will be needed for acceptance by regulators before wide-spread deployment.



Further study of advancements made for immobilisation and gasification of spent ion exchange resins with specific emphasis on study of active material, secondary waste, and a wider scope of future binder materials can raise the Technology Readiness Level (TRL) for combined gasification-immobilisation to TRL 6-7. This will ideally prepare the necessary inputs for a detailed safety assessment for input to the repository safety case for use of these new materials and methods.

### Acknowledgements

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

We appreciate the technical contributions of PREDIS partners and commitment of end users to this work.

Further information about these results can be found from the deliverables and scientific articles as found on the PREDIS web page at <https://predis-h2020.eu/publications-and-reports/>.

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## 2.2 Radioactive liquid organic waste immobilisation in geopolymers

Keywords: PREDIS; EURATOM; geopolymer; immobilisation; liquid organic waste  
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### Challenge to solve

Cementing Low- and Intermediate-Level radioactive Waste (LILW) is a traditional method used to immobilise the waste prior to its final disposal in which to prevent radioactive material release during final geological disposal. The cement industry is a heavy producer of CO<sub>2</sub>-emissions, and therefore the trend is to supplement cement with other binders. Alkali activated binders, so called geopolymers (for systems with low calcium), are one of the options to reduce cement usage and improve sustainability often utilising industrial side streams and other lower carbon materials [1]. The CO<sub>2</sub>-emissions of geopolymers may, depending on the feedstock and transport distances, be 30-80% lower than ordinary Portland cement [2].

In addition to high CO<sub>2</sub>-emissions, cement-based binders are not very efficient in encapsulating specific wastes while maintaining performance criteria such as mechanical strength or leaching resistance. This means that the waste volumes that a unit of cement can bind are reasonably low. In the case of radioactive liquid organic wastes, such as oils, the typical addition of waste is lower than 20 vol.% of the final waste form. The lower the waste loading, the more waste packages are needed.

Even with this low level of addition of liquid waste, the resulting cementitious mixture may not hydrate properly, resulting in a low performance waste form. Because of the non-optimal aging properties, some of the waste must be re-packed during the storage period, resulting in additional costs and emissions. Certain organic wastes cannot even be mixed with cement, and non-sustainable bitumen-based binders have been used. Furthermore, Radioactive Organic Liquid Wastes (RLOW) are difficult to immobilise, and therefore they have been less studied than inorganic waste forms. Thus, it was important to understand their safe and efficient immobilisation [1].

The main challenge addressed in this Case Study focuses on understanding whether geopolymers could be used to immobilise larger volumes of RLOW in a mechanically and chemically stable form, both making disposal more efficient while reducing the CO<sub>2</sub> emissions of the process.

### Approach taken

Before studying the immobilisation capacity of a new material, it is important to understand the interactions between the waste and the binder. More properties of geopolymers can be modified in a wider range compared to that of cement, which also makes incorporating organic waste easier [3]. Liquid organic waste in geopolymers may also be an active part of the geopolymerisation process, that is when the waste is bound chemically in the geopolymer matrix. Nevertheless, unlike some inorganic waste, which may for example have pozzolanic properties, the organic waste showed none of these beneficial effects on the binder.

The immobilisation strategy depends on the composition of the waste. The main inorganic material in a geopolymer is the precursor and the choice of precursor depends on the type of waste, which needs to be immobilised. For example, blast furnace slag (BFS) or metakaolin (MK) are the suitable

precursors for waste oils [4]. Prior to immobilisation, it needs to be evaluated if the waste needs pre-treatment such as adjustment of viscosity. These treatment methods might be needed to make the waste more compatible with the immobilisation matrix. Compared to the traditional cement-based binders, the geopolymer binders are more readily adapted to different types of waste, whilst the key parameters, such as strength and workability, are maintained [5]. When the geopolymer constituents, including the water content and the type of waste have been defined, the characteristics of the resulting material can be fine-tuned by adjusting the proportions of the different constituents.

At present, there are no evaluation criteria developed specifically for geopolymers. Even though specific geopolymer criteria are currently under development at the IAEA [1], their performance is evaluated based on the acceptance criteria for traditional cementitious materials. These criteria include among others strength, resistance of the binder matrix to leaching by percolating water, setting time, segregation, and alkali-reactivity. The situation is similar in EU-countries and the UK, except for leaching tests, in which limits on radionuclide release post closure of a repository are required but no leach test or limits have been defined in the UK [6]. Most important performance factors assessed are mechanical strength and dimensional stability, which are evaluated in comparison to conventional cement systems. This occurs at the evaluation age suitable for cement-based binders, and also is based on acceptable performance limits for conventional cements which may not be applicable for geopolymer systems.

The work done in PREDIS is based on earlier work on geopolymers [7], and the waste immobilisation studies already had functional geopolymer recipes to start working with. PREDIS investigated immobilisation of two RLOW surrogates into two different MK-based geopolymer systems [8]: the first RLOW consisted of Nevastane EP 100 oil which is a Paraffin oil, representing the radioactive oil obtained after use in nuclear power plants. The second was a mixture of Tri-butyl Phosphate (TBP) and dodecane representing solvent mixtures from spent fuel reprocessing operations. Both geopolymer systems were able to immobilise the waste with loadings of up to 50 vol.% of Nevastane and up to 30 vol.% TBD/dodecane surrogates to give satisfactory processing and product characteristics in comparison to the traditional Portland cement systems. In both matrices the amount of RLOW surrogate bleeding from the mixture during the first 90 days of curing was low.

Additionally, PREDIS investigated long-term performance of RLOW immobilised in alkali-activated material [4]. The project team assessed surrogates for liquids used in the nuclear industry, such as extraction solvent and industrial oils immobilised both in a MK-geopolymer. The waste-geopolymer mixes were tested for both resulting performance characteristics and also for long-term leaching and carbonation resistance by varying a number of key influencing parameters such as water-binder (w/b) ratios and waste loading. The BFS-based geopolymers could accommodate up to 40 vol.% oil while MK-based geopolymer effectively encapsulated 15 wt.% (~40 vol.%) Tri-Butyl Phosphate, which was mainly physically encapsulated in the matrix. MK-based geopolymers exhibit excellent resistance to carbonation [9]. Factorial analysis showed that waste loading, w/b ratio, and oil type were the most significant factors influencing the properties of BFS-based waste forms. For example, with high w/b ratios the setting time was longer, and the mechanical performance decreased slightly yet still meeting the Belgian waste acceptance criteria (for cemented waste form).

Both studies concentrated on the physical binding of the waste into the binder matrix and production of materials which would fulfil generic waste acceptance criteria. The binding mechanism was not intensively investigated in the studies. However, isothermal calorimetry measurements and scanning electron microscopy analysis indicated that the organic wastes were mainly physically bound into the geopolymer matrix and/or trapped within the material's pore space.

In addition to the strength and ageing characteristics, one of the important aspects for acceptance of the geopolymers for real life use is the curing procedure. The procedure must remain similar to

the existing procedure, without additional heat treatments, or the material may not be usable in the waste treatment facilities. The experiments carried out showed that the curing procedure was indeed similar to cementation.

### **Innovation**

The geopolymer system for immobilising organic waste has not yet been fully optimised and there is still room for future research. In the project work done by UK partners, 50 vol.% waste loading levels were reached for Nevastane oil, which is more than double compared to cementitious systems and presents great potential for geopolymer use. The mixtures with Tri-Butyl Phosphate, which is a radioactive organic solvent, reached a 30 vol.% waste loading, which is a significant increase compared to the current systems. No unexpected new problems were observed, but some of the already known problems remain to be solved. For example, it remains challenging to keep the oil in the binder matrix after its incorporation. In the test materials, a surface sheen remained after 90 days of curing. The surface liquor was insufficient to be analysed but it was most likely oil released by the matrix.

The outcomes of PREDIS activities led by the Belgian group similarly observed oily leachate in their leaching tests. Thermogravimetric analysis was used to study the temperatures at which different organic materials segregate from the geopolymer matrix. The tests demonstrated that the BFS-systems successfully incorporated 40 vol.% of oil. The next step includes upscaling the test from the very small-scale laboratory tests to life-size test systems. One of the aims for current and future larger scale tests is to study the thermal development during hydration and adiabatic calorimetry tests in different barrel sizes. To achieve this, bio-resistance measurements are ongoing where positive preliminary results have been achieved in heating the material up to 800 °C. Segregation is not the only possible issue rising from elevated temperatures. Delayed ettringite formation (that is the delayed deleterious expansion of a binder, which has been exposed to elevated temperatures during the hydration) is well known to present problems for the cement-based binders, if they are exposed to elevated temperatures during hydration. However, this has been found not to be an issue with geopolymers. Geopolymers are much more likely to suffer from thermal cracking than the traditional cement-based binders, and this is an issue that needs to be understood and addressed before full-scale implementation and regulatory approval.

RLOW immobilisation in geopolymer shows that geopolymerisation can potentially reach higher waste loadings than conventional cementitious methods. The performance of geopolymers regarding mechanical and chemical strength is also promising. If applied in the nuclear industry, geopolymers could both decrease the number of disposed waste packages, as one waste package could incorporate a higher waste-loading, but also decrease the carbon intensity of the overall process. However, the long-term performance of geopolymers needs further investigation.

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*“PREDIS has increased interest in geopolymers in Hungary and thanks to that, there is a thorough investigation program planned. At the same time, to achieve the wider use of geopolymer, the compliance of the material to the WAC must be demonstrated to the regulator.”*

*Peter Ormai, Public Limited Company for Radioactive Waste Management (PURAM), Hungary*

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Despite geopolymers being a promising waste immobilisation matrix for RLOW, not many countries with active nuclear sectors have yet to accept their usage. Impact of PREDIS research on the geopolymers for the industry is fully dependent on the acceptance of geopolymers for use in parallel

with conventional cementitious systems. Results, such as the ones summarised in this Case Study and in the PREDIS Case Study 'Solid organic waste immobilisation using geopolymers' showing good performance of geopolymers are vital in incentivising the regulators to consider their approval. Work for acceptance is ongoing at least in Belgium, Czech Republic, Slovak Republic, and the UK among others.

In addition to fulfilling other acceptance criteria, the compatibility of geopolymers with engineering barriers must be ensured, for them to be accepted in the industry. The change in material properties is noticeable yet acceptable compared to traditional cementitious systems, and the waste loading has been noted to increase, which should incentivise the acceptance of geopolymers. For instance, end users such as Sellafield Ltd in the UK have already shown interest in the potential use of geopolymers for ion exchange resin immobilisation. PREDIS work has been an important step in bringing geopolymers closer to real implementation by producing experimental data, which can be used as the basis of decisions for acceptance in the future.

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We appreciate the technical contributions of PREDIS partners and commitment of end users to this work.

Further information about these results can be found from the deliverables and scientific articles as found on the PREDIS web page at <https://predis-h2020.eu/publications-and-reports/>.

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## 2.3 Metallic waste conditioning in magnesium phosphate cement

Keywords:	PREDIS; EURATOM; metallic waste; magnesium phosphate cement; waste conditioning
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### Challenge to solve

Prior to final disposal, radioactive metallic waste typically needs to be conditioned so that it meets the Waste Acceptance Criteria (WAC) of the repository which is specific to each country. Such waste is usually conditioned by encapsulating into Portland Cement (PC) inside of steel drums. The cementitious matrix, in which the waste has been encapsulated, is a porous network that can affect the corrosion environment of the metal. The PC creates an alkaline environment, and in such an environment steel is generally considered passive, that is corrosion is not likely to occur. However, when conditioning aluminium (Al) and beryllium (Be) into PC the situation is quite opposite and alkaline conditions can lead to increased corrosion of both Al- and Be-metals by water, and subsequent hydrogen production (Figure 1), which makes PC unsuitable for Al and Be conditioning [1]. The main consequences of the metal corrosion are the increase of the pressure inside the waste the package, and the formation of cracks if the corrosion products can have a higher density than the metal, and the modification of the mechanical properties. The confinement of the radioactivity could no longer be ensured. Historically, conditioning these wastes has not been possible leading the waste to be stored indefinitely waiting for a solution.

Recently, Magnesium Phosphate Cements (MPC), which have a significantly lower pH than PC, have been proposed as a solution for conditioning Al and Be. MPCs are produced by mixing magnesium oxide MgO, a phosphate salt like monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ) with water. The main reaction product responsible for the binding properties is K-struvite ( $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ ) in the case of magnesium phosphate salt. The resulting binder sets and hardens very rapidly, and therefore a retarder is also needed to ensure the workability. This way binders with reasonably high compressive strength, which most interestingly are within the Al and Be passivation range, can be produced.

Due to the lower pH conditions - between pH 5 and 9 - of the resulting MPC, corrosion rates of Al and Be are decreased, also decreasing the rate of hydrogen production. However, the waste is typically conditioned into steel drums, and thus effect of the lower pH environment on steel corrosion needs to be considered as well. Within PREDIS, multiple groups have been investigating usage of MPC for Al and Be conditioning with the focus on mechanical, chemical, economical, and long-term performance [2–5].

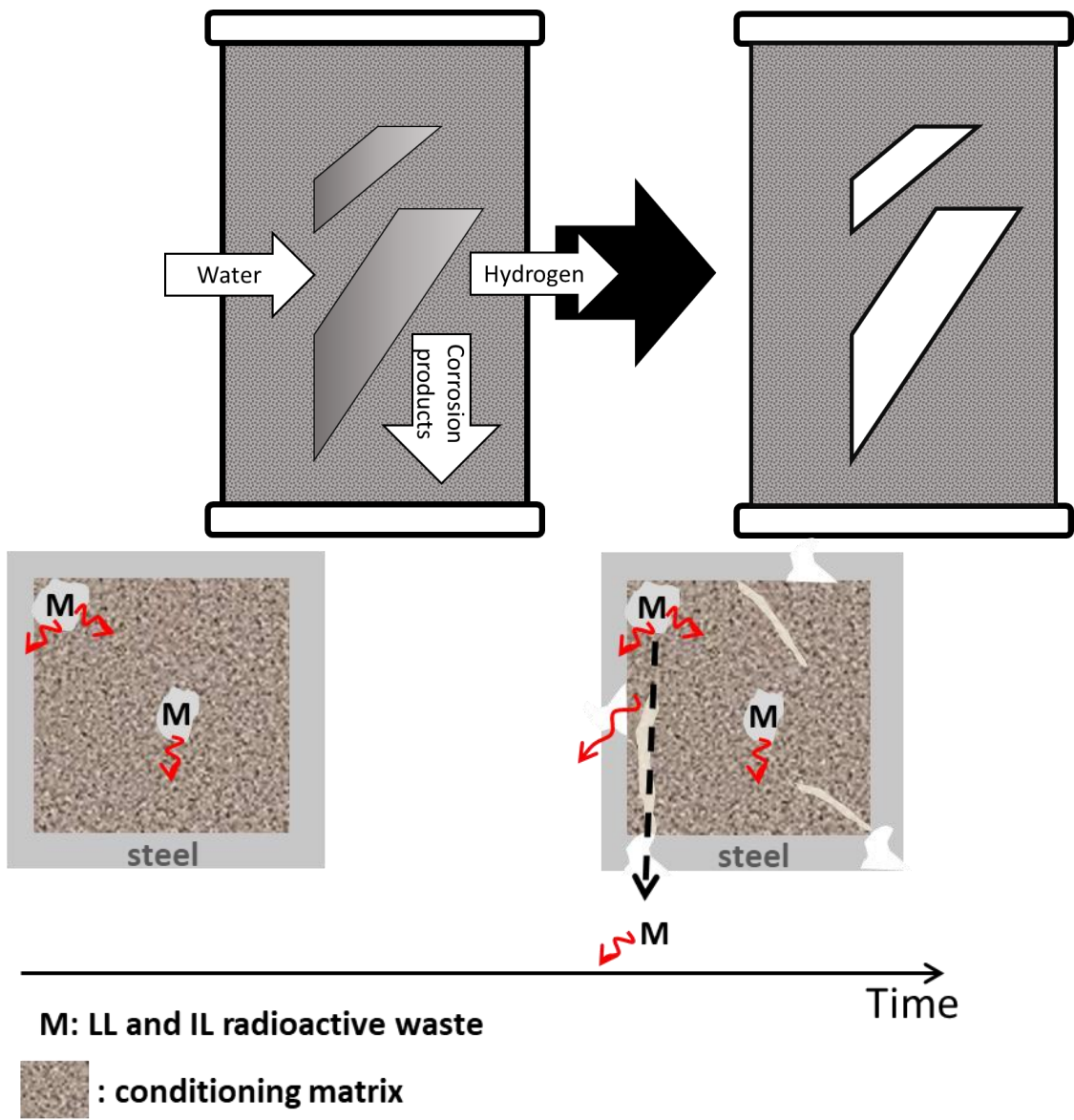


Figure 1. Schematic of metallic corrosion within a cementitious matrix. M represents the low-level (LL) and intermediate level (IL) radioactive metallic waste.



### **Approach taken**

As with any conditioning material, the MPC needs to meet the WAC of a specific country, thus rigorous performance testing needed to be done. First, the formulation for the MPC had to be optimised. Key parameters in the optimisation included the mix design, that is the ratio of the reactants (MgO,  $\text{KH}_2\text{PO}_4$ , and water) to one another, any additives used and the curing conditions of the binder products. Small changes in the ratios changed the characteristics of the MPC greatly. To find an optimal formula the binder performance (mechanical strength and setting time) was rigorously measured, and the solid phases formed were characterised.

### **Formulation tests**

The different mix designs were tested for their mechanical strength. While higher ratios of MgO/ $\text{KH}_2\text{PO}_4$  lead to higher mechanical strength, values with lower ratios were also above the French WAC of 7–9 MPa in uniaxial compressive strength tests [2]. Adding filler materials increased the amount of inert solid, which can improve the workability and the mechanical strength. Moreover, fillers are less expensive than MgO and  $\text{KH}_2\text{PO}_4$ . Their use can decrease the global cost of the material. Volcanic ash shows good characteristics to be incorporated into MPC. However, its distribution and its homogeneity are not guaranteed. The formulation should include the minimum amount of water (water/solid mass ratio 0.25) to generate K-struvite as the main product. Absence of retarder leads to a rapid exothermic reaction, fast setting, and efflorescence. It is thus recommended to add a retarder. The type of retarder influences the fluidity of MPC.

Studies were also performed to decrease the price of the MPC preparation. Reactive magnesium oxide can be used instead of dead burned magnesia if the retarder is based on thiosulphate alone or in addition to boric acid. Blast furnace slags, which are currently more available than fly ash, can be used as filler to decrease the price of MPC.

### **Leaching behaviour**

The leaching behaviour of the binders was tested by immersing samples in both distilled water and in alkaline water for 90 days [3]. The cumulative concentration of elements was then analysed from the leachate. The effective diffusion coefficient and leachability index were calculated to be used for evaluating the performance and suitability for waste conditioning. The mineralogy and microstructure of the samples was also studied before and after testing. Signs of both diffusion and dissolution-recrystallisation were observed. The alkaline solution appeared to be more aggressive towards the MPC binder than distilled water. In general, the leaching behaviour of the MPC was not considered sufficient, and more work to better understand the leaching of MPC is needed.

### **Irradiation properties**

The main objective of irradiation experiments was to determine the behaviour and thus long-term performance of MPC [4]. In the PREDIS project, gamma radiation was used to determine the matrix durability because of its penetrating ability and the radiation levels expected from radioactive metallic waste (RMW). The MPC samples were irradiated during the period of 6 days to 2 months to achieve total doses of 200 kGy. The main phase in non-irradiated MCP sample was struvite-K ( $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ ) with traces of unreacted periclase (MgO), crystalline quartz ( $\text{SiO}_2$ ) and mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) from fly ash. X-Ray Diffraction (XRD) output patterns produced similar results considering the curing time and the total radiation dose compared to the non-irradiated sample. The XRD results are as expected based on the composition, that is including phases from the sand grains and fly ash, which were used as an addition in the MPC binder. The phase composition was also corroborated by the EDS analysis. These results were supported by previous research, and the irradiation does not generate measurable mineralogical changes. Thus, the matrix is stable for RMW application in the field [4]. During the analyses samples were irradiated at a constant rate of 2.5 kGy/h with three resulting absorbed doses of 200, 500 and 1000 kGy. A preliminary visual inspection

indicated no structural degradation, swelling or shrinkage. Mineralogical phases were also observed to be stable.

Compression tests were conducted within PREDIS by compressing the samples after a 90-day immersion in osmotic water to simulate the flooding at the repository. The irradiated samples demonstrated high mechanical resistance and similar compression strengths to non-irradiated mortars. After 90 days of leaching test, 70% of the samples' original strength was maintained, which was higher than WAC requirements.

### **Metallic corrosion**

The reactivity of aluminium, beryllium and steel were studied in different types of binder matrices, including blended cements and MPCs made with different quality of MgO, different magnesium-phosphate ratios, different moisture content while curing, and different retarder types [4, 5]. The results were compared to the ones obtained in PC. The studies were conducted in mortars, but also in simulated pore solution by electrochemistry, chromatography and surface characterisation (XRD and scanning electron microscopy (SEM)).

Al was found to corrode less in MPC and produce less hydrogen (H<sub>2</sub>), compared to the PC based binder environments. Phosphate was found to contribute to the passive layer protecting the metals. Al is less corroded in low-cost MPC prepared with reactive MgO and thiosulphate: lower H<sub>2</sub> release was measured. Similar corrosion behaviour was observed for the tested Be qualities. From pH 12.5 up, the corrosion rate increased exponentially. Pitting corrosion, which was found to originate from surface defects, and a layer of corrosion products was found on the surface of the metal. Close to neutral pH, the pure beryllium corroded slower, and at pH 7.7 boric acid decreased the corrosion rate. In cementitious binder the corrosion rates were lower than in solution, and even lower if the metals were embedded in MPC binder. The main result obtained for steel is that its reactivity depends on the type of retarder: boric acid was found to perform better than thiocyanate but using both types together created synergies.

### **Innovation**

As the Al and Be wastes have previously been problematic with no real disposal route, most research conducted here has increased the knowledge of a promising conditioning material. Different MPC formulations were tested and optimised for mechanical, corrosion, irradiation, and leaching properties. With the formulas all but leaching properties showed good performance and especially the Al and Be corruptions was decreased. Unfortunately, the leaching performance was poor and more research on the topic is needed after adjustments of the material parameters.

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*“At the moment, using chemical decontamination requires caution due to the new secondary wastes. However, PREDIS has been successful in demonstrating the advances of metallic waste treatment. We see future benefit in decontaminating large volumes of metallic waste and developing low-cost formulations for waste conditioning.”*

*Jose Luis Leganés Nieto, Empresa Nacional de Residuos Radiactivos, Spain*

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### **Impact towards practice**

While the research is still on a low technological level, the impact of the findings for the industry could be significant. If the leaching resistance of the MPCs can be increased, the technology could be used to dispose waste that has previously been without a disposal route. The results on the other

parameters are very promising and thus major work should go into finding formulas with better resistance. In addition, pilot-scale tests could help bringing the technology closer to implementation.

As with other new conditioning materials, rigorous work needs to be conducted to show to the industry and regulators that the material can be safe and efficient for disposal. Thus, promising results as the ones summarised here can make the waste management organisations and regulators aware of a possible solution and eventually lead to implementation of the new technology.

### Acknowledgements

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

We appreciate the technical contributions of PREDIS partners and commitment of end users to this work.

Further information about these results can be found from the deliverables and scientific articles as found on the PREDIS web page at <https://predis-h2020.eu/publications-and-reports/>.

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## 2.4 Network of small affordable sensors for monitoring waste packages

Keywords:	PREDIS; EURATOM; waste package monitoring; integrity testing; small sensors; durability
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Version date:	12.9.2024
Review person:	Maria Oksa & Erika Holt (WP1, Coordinators)

### Challenge to solve

The case study focuses on the development and testing of a network of small affordable sensors for monitoring radioactive waste packages, which are composed of waste cast into a cementitious binder sealed inside a steel barrel. The need for developing the novel monitoring approaches stemmed from the industrial end users' desire to know what happens inside the waste packages and how the conditions and waste characteristics change over time. It was essential to develop a technical solution that would ensure the waste packages remain completely unaffected. This solution must not involve opening or disturbing the waste packages in any way, and it must eliminate the need for cabling or other elements that could potentially create vulnerabilities, such as those that might lead to corrosion or other alterations of the waste packages. One of the main aims was also to demonstrate the reliability and soundness of this technology to the end users.

### Approach taken

To address the challenge of waste package integrity while surveying the conditions inside the package, small sensors which can send data at fixed intervals were developed to be placed inside the waste package in contact with the waste and the cementitious binder. Sensors measure parameters that were identified by end users and experts as important for running the prediction or simulation models on material and package performance. These parameters include temperature, relative humidity, pressure, and electrical voltage, which is essential for determining possible corrosion rates. The multipurpose devices can communicate through both the cementitious matrix and metal (cemented waste in steel barrels), and they ensure the integrity of the waste package and its outer shell. The sensors can be installed inside the waste package to transmit the recorded values either temporarily or permanently. Currently, the technology has been tested for one month in an experimental setup to follow the evolution of new types of waste over time. However, special mock-ups for testing the technical aspects can stay in storage for decades. The sensors were tested in realistic conditions in a waste storage facility in the Czech Republic. The investigated waste package was equipped with seven sensors [1].

Several challenges needed to be overcome to succeed in non-destructive monitoring of the ageing of the conditioned waste. The main challenge was to ensure the communication of data from sensors to the receivers outside of the steel barrels. A part of this obstacle was powering the sensors, since batteries inside the waste packages were not an option due to the potential additional hazard. To overcome this issue, the radio frequency identification (RFID) technique was applied. RFID uses electromagnetic waves from the outside to charge a device inside the waste package. To send the data back using the electromagnetic waves, different radio frequency ranges compared to industry standards were used, which allowed charging and data communication at the same time. Although this setup was only tested for one month during the project end phase, the instrumentation can potentially withstand significantly longer times as demonstrated by more than a decade-long monitoring of other civil concrete structures, e.g., bridges.

Another challenge was to make sensors and cables robust enough so that they can withstand years of service in a fairly aggressive (alkaline) cementitious environment. The sensors needed to be very

small, so it was possible to install a network of sensors with the minimal amount of cabling within the package. The sensors must also have no influence on the behaviour of the cementitious matrix or the incorporated waste. The PREDIS project partner Studiecentrum voor Kernenergie/Centre d'Etude de l'Energie Nucléaire (SCK CEN) assisted by providing the cement, in which the small sensors were embedded. Cementitious binders develop heat during hydration, with the amount of depending on the cement type. The high heat of hydration associated with certain binders commonly used in waste conditioning posed additional challenges for the sensors. While these sensors can only withstand temperatures up to 60 °C, the heat of hydration can often reach 80 °C or higher, which could compromise the sensors' integrity. Another consideration included the different concrete mixtures having different microstructure, specifically pore structure, which affect the distribution of relative humidity. In more porous binders the distribution is more uniform, whereas in high density binders the humidity distribution and measurement data from a single sensor can be very localised. Another issue related to humidity was flooding of sensors with internal water, which could prevent the measurement of the gaseous phase within the pore structure. This was overcome by placing a membrane between the concrete and the sensor to keep the sensors “dry” and capable of producing reliable measurements. Considering all these important aspects allowed for designing better performing and more robust sensor networks, data from which was used for numerical simulation models on material performance developed and applied in PREDIS. Using a network of sensors instead of single sensors also ensured the redundancy of the system in case of malfunction of an individual sensor [1].

The sensors have been calibrated at Bundesanstalt für Materialforschung und -prüfung (BAM) facilities and they have been tested and verified to perform successfully in a nuclear facility (but not with radioactive waste; Figure 1). Similar sensor and network performance is expected when used with wastes having higher radioactivity. However, even though different binder types were tested successfully, the behaviour of the sensors in geopolymers as an alternative binder to cement-matrices still remains to be tested. The main concerns arose from the aggressive environment in some waste-binder matrices such as elevated temperatures, salinity and pH that can interfere with the sensors. The main considerations for successful sensor performance included very alkaline pH and temperature extremes [1].

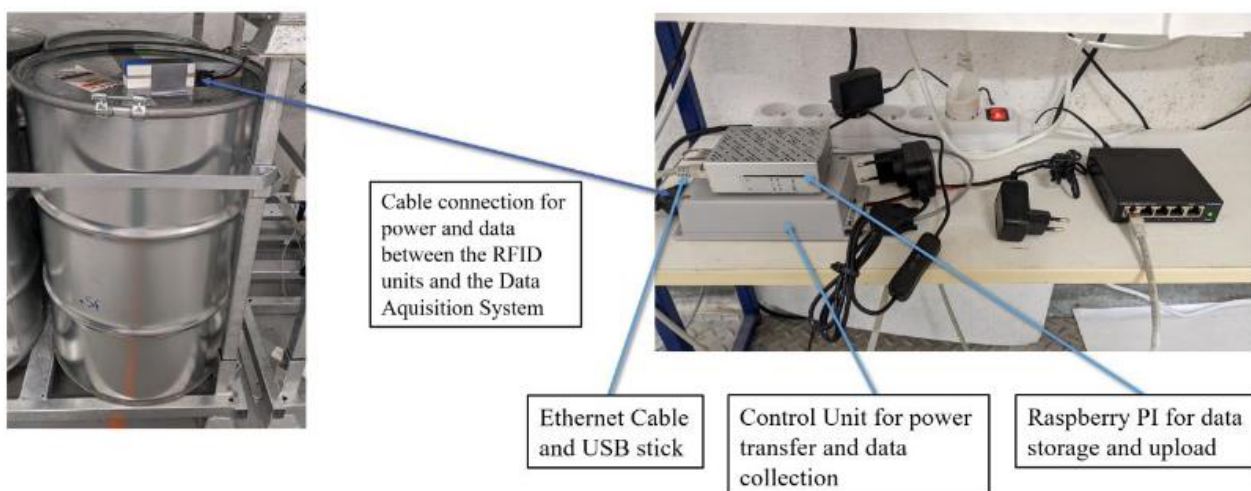


Figure 1. Demonstration setup [1].

### Innovation

The innovativeness of the approach lies in being the first non-invasive/non-destructive measurement set put for radioactive waste packages that the project team was aware of. This is achieved by implanting a network of miniature sensors inside the waste package that do not influence the

package behaviour, providing data without disturbing the waste package and providing reliable information about the current integrity state of the package, which will also help in predicting the future performance of the package. Prior to this project work and technology development, most of this data (temperature, relative humidity, electrical voltage) has been impossible to obtain without disturbing the package. With additional sensors, even more parameters could be measured, the most interest being in measurement of chemical presence and chemical composition.

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*“Our expectations are to find new, safer and more cost-effective ways to handle and treat different kinds of radioactive waste.”*

*Annikka Laitonen, Teollisuuden Voima Oyj (TVO), Finland*

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### **Impact towards practice**

This technology in combination with the simulations and prediction models offers substantial benefits such as optimising the interim storage of waste packages and making the process of confirming the package integrity from interim storage to final disposal smoother and more reliable. The immediate improvement is provided to the workers in the interim storage facility who can thus spend considerably less time inspecting the waste packages leading to improved health and safety and reduction of associated costs. There are expected savings in the interface between interim and final storage. The sensor technology itself is reasonably affordable, and the cost should be easily mitigated with the improvement of efficiency. Uncertain risks on the evolution of waste packages are greatly reduced, so earlier mitigation measures can be taken if needed in the case of deterioration. Regulator authorities should also be interested in having such verification of package stability associated with licensing of facilities and safe transport of packages.

The aim of demonstrating the soundness of the approach to the end users stemmed from the concerns about the degradation of electronics and their subsequent effect on the behaviour of the packages. This was demonstrated with mock-ups packages during PREDIS. More robust sensors with ceramics replacing the organic materials could in the future further optimise the soundness of the approach.

### **Acknowledgements**

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

We appreciate the technical contributions of PREDIS partners and commitment of end users to this work.

Further information about these results can be found from the deliverables and scientific articles as found on the PREDIS web page at <https://predis-h2020.eu/publications-and-reports/>.

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## 3 Blogs

### 3.1 Conditioning of Molten Salt Oxidation solid waste into geopolymer matrix

Keywords: PREDIS; EURATOM; solid waste; geopolymers; immobilisation; conditioning; molten salt oxidation

Company/institute: Research Centre Řež (CVRez, Czech Republic)

Authors of the blog: Vojtech Galek, Anna Sears, Martin Vacek, Petr Pražák

Version date: 11.4.2024

Link to page: <https://www.linkedin.com/pulse/conditioning-molten-salt-oxidation-solid-waste-geopolymer-wtPMC/?trackingId=qvCGFPCUd4etJ6pWJu3Zvg%3D%3D>

#### Introduction to Molten Salt Oxidation (MSO)

Finding new innovative approaches to sustainably process organic-containing radioactive waste is a demanding task. Molten Salt Oxidation (MSO) offers a new possibility to process these wastes, which however introduces additional challenges to solve.

Solid waste from MSO is generated through the flameless oxidation of organic waste in molten salts with oxidising agents. During the process, the molten salts (mainly alkaline carbonates) neutralise the acidic compounds within the organic waste. The salt is saturated with neutralisation products, such as ashes and other inorganic compounds, and it should be disposed of. One of the aims of PREDIS project was to study the immobilisation of the MSO waste generated with this process.



*Figure 1. MSO salt discharge.*

The immobilisation of this type of waste has proven to be a challenge. With the composition of  $\text{Na}_2\text{CO}_3$  and its hydrates, the waste is very hygroscopic and tends to swell, even when mixed in the solid matrix. Different techniques for immobilisation were tested, but the focus of the project team was on the geopolymer matrices. Geopolymers, as a substitute for cement, are inorganic polymers created by the reaction of an aluminosilicate precursor with an alkaline activator, even at room temperature. Various precursors can be used, including fly ash, blast furnace slag, volcanic tuff or metakaolin.

As the waste arising from this process is not common and its nature suggests difficulties in immobilisation, the waste samples were sent to the PREDIS partners in dedicated tasks to try

different mixtures. The results have been published in several journals and conference proceedings [1-4].

### Work, Experiments and Experience

In the Research Centre Řež laboratories, experiments were conducted with metakaolin Mefisto L05, as well as with dried and crushed MSO waste. The series was made with different waste loadings, ranging from 5 to 25 wt.%. Higher waste loading was not possible due to the poor workability of the mixture. The metakaolin and waste were mixed with an alkaline activator and left to cure under three conditions: dry cured, high moisture environment, and under water curing. The cured samples were analysed for compressive strength, and by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses.

With the higher composition of waste within the matrix, difficulties arose with decreasing workability, lower viscosity, and slower setting times. Furthermore, the blooming effect occurred with 15 wt.% and higher waste load, which led to a lower compressive strength and caused swelling and cracking in the samples exposed to a high moisture environment. However, with dry curing, the compressive strength of samples with 5 wt.% waste load was, on average, 90 MPa. With increasing waste load, the compressive strength values decreased, and the average compressive strength of samples with 25 wt.% waste load was 31 MPa. The Czech Republic Waste Acceptance Criteria (WAC) for immobilised waste is 10 MPa. Therefore, the obtained results are above WAC and with certain curing techniques this matrix can be used for immobilisation.



*Figure 3. Blooming effect on prepared metakaolin sample (left) and blooming effect on the cracked sample with 25 wt.% in high moisture environment (right).*

To improve the workability of the mixture and the overall mechanical strength of the resulting samples, we performed experiments with different variations of formulation from the basic recipe. The upgrade was managed by adding 10 wt.% metakaolin, sand or volcanic tuff to the recipe. The best results were obtained with added metakaolin, which enhanced mechanical strength but decreased workability. The same results were obtained with sand addition. Volcanic tuff addition decreased overall performance.



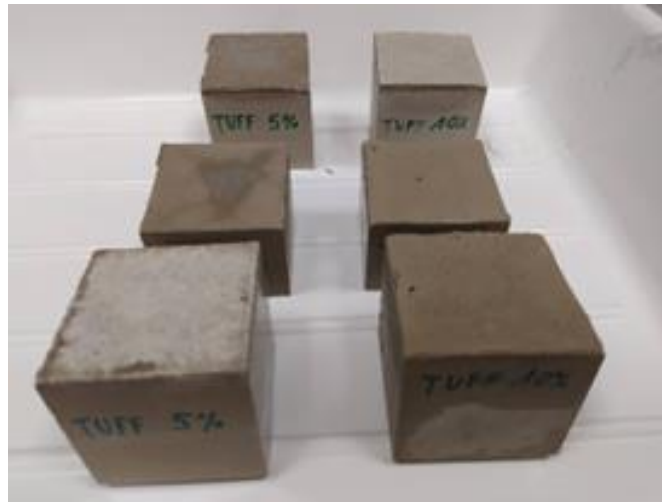


Figure 4. Prepared samples with tuff addition to improve their properties.

The MSO waste had deteriorating effects on the geopolymer matrix, so one of the possible methods is to chemically enhance the waste by a chemical reaction with a lime solution. The method is simple, and it involves preparing the MSO waste solution and slowly adding the lime solution. The precipitation of calcium carbonate occurs, which can be separated by filtration. The MSO waste solution can be reprocessed, and precipitated solid waste can be immobilised in the geopolymer matrix.

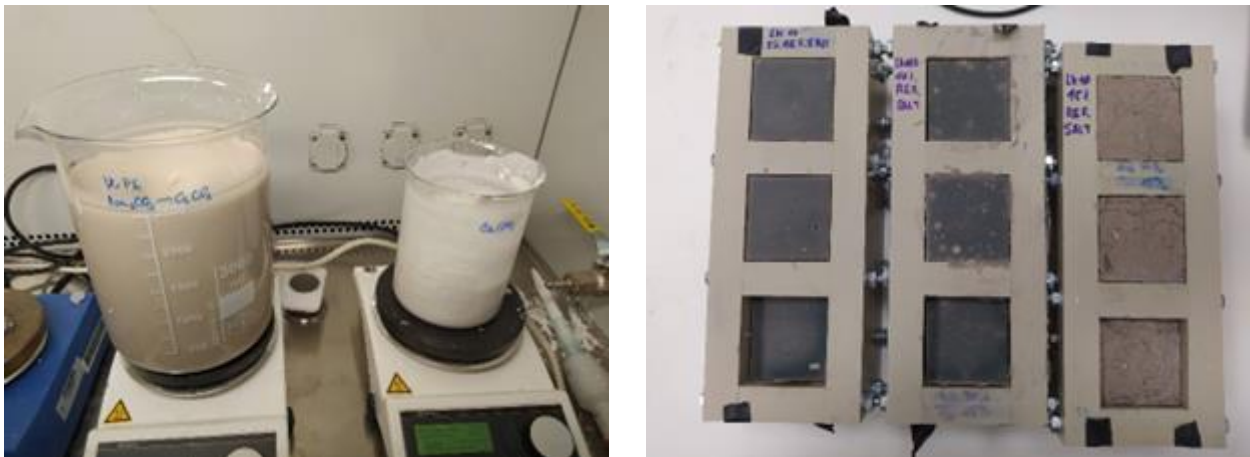


Figure 5. Preparing the enhanced salt (left) and prepared samples with enhanced salt (right).

### Outcomes

Overall, the MSO process can be used to process radioactive solid organic waste, and it offers an alternative route compared to conventional methods. However, the next step, solidification of MSO waste, proved to be a challenging task, with numerous mechanical testing experiments performed in Research Centre Řež facilities. Nevertheless, geopolymer matrix research has provided a positive outcome, and with the possibility of chemically enhancing the final waste, this type of waste can be immobilised. The next steps aimed at advancing the method include the upscaled experiments up to 100 L volume, long-term exposure experiments, and leaching experiments.

The innovative in-one-building processing facility can be achieved by connecting MSO waste processing technology, salt reprocessing, and subsequent metakaolin immobilisation. The used MSO technology is a scale-up version with a dosing rate from 1 to 2.5 kg of ion exchange resin, and up-scaling it even further would not be a challenging task. Metakaolin is already used in several

recipes for ion exchange resin immobilisation, and its overall safety is reported to be similar to the cementation techniques. This waste treatment methodology aims at all radioactive organic waste processing facilities to decrease their impact on the flue gas cleaning system or lower the amount of CO<sub>2</sub>.

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## 3.2 Waste form qualification

Keywords: PREDIS; EURATOM; radioactive waste management; waste acceptance  
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Version date: 24.4.2024  
Link to page: <https://www.linkedin.com/pulse/waste-form-qualification-predis-h2020-txxff/?trackingId=4k2rlxeIFGNOFK6OkKwoOw%3D%3D>

### Introduction

The radioactive waste acceptance system consists of two basic elements: (i) the waste form qualification (WFQ) process which is understood as a proof that a selected waste form is compatible with the designated disposal system, and (ii) waste acceptance criteria (WAC) which is a set of parameters selected to check whether the generated waste form complies with the requirements established for the safe operation of a disposal facility. Generally, waste form qualification should be performed in the context of a specific set of qualification requirements, usually based on nuclear safety, technical safety and radiation protection directives. These conditions are set for a specific facility and a particular waste form(s).

Waste form qualification is based on the comprehensive assessment of its performance in conditions describing the environment of a disposal facility. Its results are twofold: they provide requirements for formulating waste acceptance criteria and serve also for determining how radioactive waste shall be processed so that it complies with operational and post closure repository safety.

### Work, Experiments and Experience

The research consists of the identification of parameters to be used for waste form characterisation, developing techniques suitable for testing the waste form, and application of modelling tools convenient for the interpretation of measured results (performance assessment). Approaches employed include the selection of parameters suitable for testing a particular waste form (i) based on its characteristics described during waste processing, (ii) found in published references, and (iii) inspired by tests already performed on other types of waste forms. The modelling results are confronted with the safety case of a disposal facility and consequently become its part.

Waste form qualification shall be performed for any new type of a waste and/or waste conditioning system (processing procedure and binding materials) and linked to a disposal facility which shall accept the resulting waste form.

For each waste stream converted to a waste form, there is a defined set of tests and assessments, that shall provide the evidence of the waste form compatibility with the disposal system. This is summarised in the Figure 1 below. While the spectrum of testing methods is generally known, their selection to be applied on a particular waste form shall respect specifics of the waste form as well as of the disposal system where this waste shall be buried. This process may require further studies targeting namely long-term performance of the disposal system (incl. new types of waste forms) and interpreting their results to the formulation of acceptance criteria adequately ensuring the required quality of considered final waste forms.

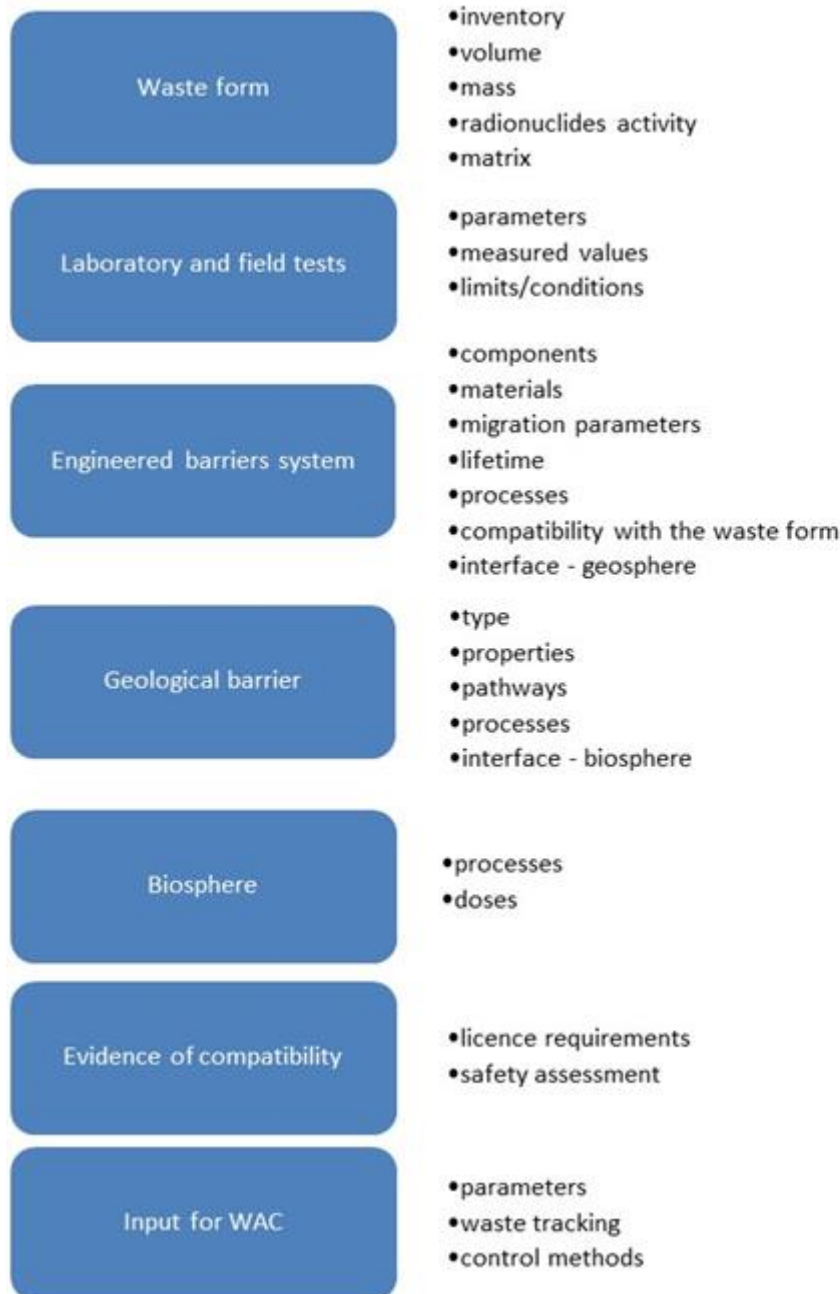


Figure1. WAC development process [1].

### Outcomes

The approach (described in [1]) provides direct guidance and practical advice for Member States regarding the WFQ in practice. It can be applied to waste forms resulting from conditioning specific types of waste (e.g., geopolymers). For example, in the initial stages of the development of new waste forms, their WFQ process (based on waste form characterization) can be simplified by testing simulated waste form – so called "simulates". "Simulates" are materials designed to represent specific types of chemical or physical behaviour of actual radioactive wastes. Simulated waste form can be developed to exhibit only a limited set of important properties for a specific application or may be tailored to exhibit a broader range of chemical, physical, and rheological properties for a wide range of tests. Simulates testing is then used to reduce the costs and demands of the WFQ process itself, as well as to reduce the costs and hazards of developing treatment/conditioning processes designs, demonstrating that the proposed waste conditioning flowsheet is suitable and processable. However, final testing of waste forms produced from actual radioactive waste is essential to definitely

demonstrate that the proposed treatment/conditioning processes and product control strategies are robust enough to produce waste forms that meet all applicable waste acceptance requirements.

The research/work also describes the practical recommendations for small inventory programmes – e.g., it advises how the WFQ system can be simplified or minimized using experience from more advanced programmes, using established and verified technologies for processing similar types of waste, etc. In order to minimize the number of WF samples required for tests/determination of selected WFQ parameters, careful selection of a limited number of samples using a uncertainty analysis approach is recommended.

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### 3.3 Separation and determination of actinides and Zirconium-93 from radioactive waste and mineral samples

Keywords:	PREDIS; EURATOM; molten salt oxidation; solid waste; liquid waste; actinides; measurement techniques; separation methods; DTM radionuclides
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Link to page:	<a href="https://www.linkedin.com/pulse/separation-determination-actinides-zirconium-93-from-radioactive-unshf/?trackingId=9rdB9%2FsudGkmMvvrwIPmRw%3D%3D">https://www.linkedin.com/pulse/separation-determination-actinides-zirconium-93-from-radioactive-unshf/?trackingId=9rdB9%2FsudGkmMvvrwIPmRw%3D%3D</a>

#### Introduction

Radioactive waste characterisation is based on the physical, chemical and radiological properties of the waste. The amount and type of radioisotopes in a waste package is one of the most important characteristics. Radioisotopes in waste packages may occur in solid and liquid as well as gaseous forms, and their physical, chemical and biological properties may largely differ from each other. Radioactive waste storage requires measures that prevent the release of radioisotopes into the environment, and regular monitoring of waste deposition sites to detect any possible radioactive leakage.

From the perspective of measuring techniques, radioisotopes can be described as “easy-to-measure” (ETM) or “difficult to measure” (DTM). “Easy-to-measure” radioisotopes emit isotope-specific gamma radiation of high energy and intensity which can be detected outside the waste package eliminating the need for opening it.

In contrast, “difficult-to-measure” radioisotopes do not have such easily measurable gamma radiation. Long-lived isotopes may have low gamma-radiation intensity that merges into the background spectrum. The energy of some radioisotopes’ gamma- or X-ray emission is so low that it cannot penetrate the walls of the waste package. Other radioisotopes are pure alpha- or pure beta emitters, and therefore do not emit highly penetrative gamma rays at all. Alpha and beta radiation is easily absorbed in solid materials, so they cannot be detected from outside the waste container. Due to such properties of the DTM radioisotopes, their precise determination requires pre-treatment, including dissolution of the sample and the separation of the element of interest.

Zirconium-93 is a long-lived radioactive isotope which is produced in nuclear reactors during nuclear fission, and via the neutron capture of the natural, stable Zr-92 nuclei. Natural zirconium is used for the cladding of nuclear fuel rods, but Zr is also a trace component of concrete as well as it is used in metal alloys. Its half-life is 1.6 million years, and it decays to Nb-93m while emitting a beta particle of 60 keV. Due to its long half-life and low-energy beta decay, it is a DTM nuclide, which can be measured only by destructive analytical methods. The long half-life makes Zr-93 also a concern for long-term storage of radioactive waste (liquid waste, concrete, rubble, spent fuel cladding, etc.). Although Zr is considered to be quite immobile in the environment, it is able to form water-soluble complexes with organic acids and other organic compounds and might enter the biosphere.

The chemotoxicity and radiotoxicity of actinides has a long research history as well. Uranium, neptunium and plutonium have multiple valence states in natural environment and can be mobilized. For this reason, their monitoring around radioactive waste deposits is important. In addition to Zr-93, several nuclides of actinides are DTM. Their determination by alpha spectrometry (AS) or liquid

scintillation counting (LSC) requires chemical separation prior to analysis. Some DTM nuclides can be determined by state-of-the-art combined methods, which do not require separation of radioisotopes before the analysis, since the separation is done during the measurement. Such methods are:

- inductively coupled plasma tandem mass spectrometry with collision/reaction cell (ICP-MS-CRC-MS)
- online liquid chromatography with inductively coupled plasma mass spectrometry (LC-ICP-MS) techniques.

However, many facilities have access only to more conventional routine analytical methods such as ICP-quadrupole mass spectrometry (ICP-Q-MS) and ICP sector field mass spectrometry (ICP-SF-MS), and less-selective radioanalytical methods (alpha spectrometry, gas ionization counting, gas proportional counting, liquid scintillation counting), which also require chemical separation before analysis.

As a contribution to the PREDIS project, an improved rapid and robust extraction chromatographic (EC) method was developed for the determination of Zr-93 and actinides (Th, U, Np, Pu, Am, Cm) from low and intermediate level radioactive waste samples (evaporation concentrates of liquid radioactive wastes, mineral samples).

### **Work, Experiments and Experience**

In extraction chromatography, the dissolved sample is loaded onto a column of polymer resin containing one or more compounds (i.e., extractants) that specifically bind certain elements, or groups of elements. Then these elements are sequentially washed off from the column with different solvents, one by one. This step of the process is called elution. If some elements are chemically very similar, they elute together, and further separation steps are required to separate them from each other, often on another EC column.

Separation of actinides and Zr were made on DGA-N and TEVA resins. The extractant of DGA-N resin (tetra-octyl-N,N,N',N'-diglycolamide) is highly selective for all actinides of interest, as well as for Zr, due to the chemical similarities of Zr and actinide. The extractant of the TEVA resin is a tetraalkyl-ammonium compound, which selectively retains the TETraVAleNT metal ions (Th(IV), U(IV), Pu(IV), Np(IV) and Zr(IV), hence its trade name.

The DGA resin has a high selectivity for actinides and a high tolerance for the sample components not of interest (the so-called matrix components). This allows us to load liquid waste sample solutions onto the column without pre-concentration of actinides. Uranium, Pu and Am-Cm are stripped separately, while Np, Th and Zr are eluted together from the DGA column, then separated from each other on a TEVA column. Alpha sources prepared from the individual strip solutions are analysed by alpha spectrometry, Np-237 and Zr-93 are determined by ICP-MS. The flowchart of the separation process applied for liquid radioactive waste is given in Figure 1.

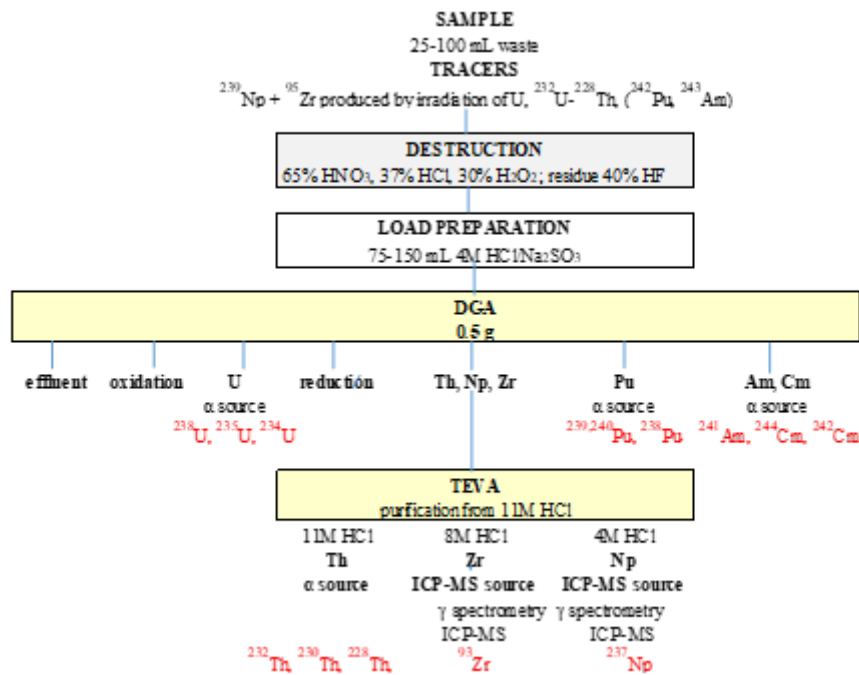


Figure 1. The flowchart of the separation process applied for liquid radioactive waste.

This EC separation scheme was adapted also for solid mineral samples (e.g., concrete, cement, other building materials). Solid samples must be completely dissolved, since actinides often incorporate in chemically resistant minerals, such as zircon and other silicates. These minerals can be dissolved by acid mixtures which contain hydrofluoric acid, or can be fused with alkali. We used alkali fusion, during which the solid sample is mixed with radioactive tracers and sodium hydroxide and heated up to 400°C. As the NaOH melts, it destroys the crystalline structure of minerals and converts them into a fuse of sodium silicates, aluminates, zirconates etc. The silicates and aluminates, along with other major components (Ca, Na, K, Mg, halogenides) readily dissolve in water, while iron and manganese will precipitate as hydroxides. Actinides and Zr will adsorb on the surface of hydroxides, or incorporate into them, thus concentrating in the small volume of the precipitate. Further dissolution and precipitation steps are required to completely remove the matrix and concentrate An's and Zr. The separation scheme for solid samples is shown in Figure 2.



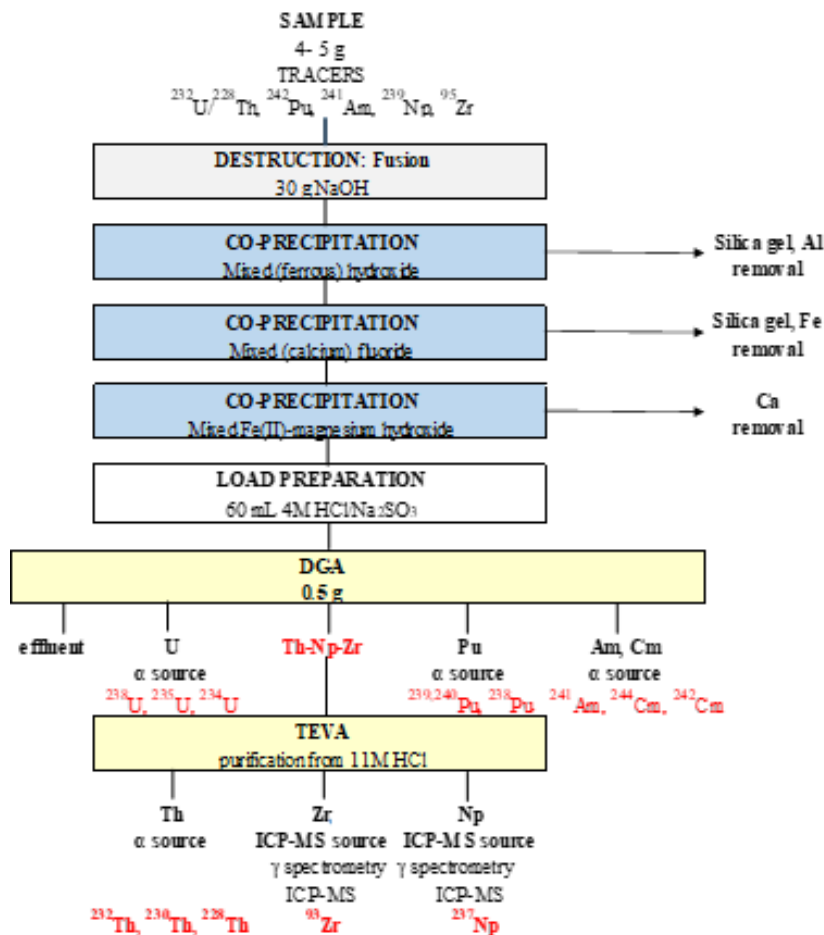


Figure 2. The flowchart of the separation process applied for mineral sample.

## Outcomes

Numerous actinide separation methods exist and are being applied in the nuclear industry and in radioactive waste management facilities. Many of them are optimized for the separation of one or two actinides, or apply different procedures for different actinides.

The novelty of the improved rapid and robust extraction chromatographic method is the separation of all the actinides from Th to Cm in one single process, also including Zr. The procedure might be extended further to include molybdenum, which also has difficult-to-measure radionuclides, like Mo-93.

Considering the high price of chromatographic materials, this method may be cost-saving, since two small EC columns (cca 2 mL each) are used to separate multiple elements. Less resin is used, therefore less waste is produced. The procedure may be adopted for high-performance chromatography and suitable for automatization as well.

The procedures were tested with certified reference materials (CRM's) with good results: recoveries were above 90% for all actinides and Zr. The reliably high recoveries provide low detection limits and low measurement uncertainty.

The procedures were presented at 3rd International Conference on Radioanalytical and Nuclear Chemistry, RANC2023 [1], and the detailed description of methods is published in Journal of Radioanalytical and Nuclear Chemistry [2].

### References

- [1] Papp, I. & Vajda, N. (2023). Determination of actinides and  $^{93}\text{Zr}$  in radioactive waste and mineral samples. Proceedings of the 3rd International Conference on Radioanalytical and Nuclear Chemistry. 7-12 May 2023 Budapest, Hungary.  
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- [2] Papp, I., Vajda, N., Bokori, E. & Molnár, Z. (2024). Determination of  $^{93}\text{Zr}$ ,  $^{237}\text{Np}$  and Th radionuclides in radioactive waste and mineral samples: extension of the method for determination of actinides. Journal of Radioanalytical and Nuclear Chemistry, 1-15.  
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## 4 Conclusion

PREDIS project has produced four case studies and three blogs to highlight and disseminate the project's achievements and impact on the activities of industrial end users.