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1. Foreword

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Summary of PREDIS project

The PREDIS project, a four-year EURATOM project, targets the development and implementation of activities for predisposal treatment of radioactive waste streams other than nuclear fuel and high-level radioactive waste. The PREDIS project started in September 2020, with consortium of 47 partners from 17 countries. The project aims to bring measurable benefits to Member States and nuclear waste community including the further development and increase in Technological Readiness Level of treatment and conditioning methodologies for wastes for which no adequate or industrially mature solutions are currently available, including metallic material (WP4), liquid organic waste (WP5) and solid organic waste (WP6), and by testing and evaluating innovations in cemented waste handling and predisposal storage (WP7). These technical Work Packages align with priorities formulated within the Roadmap Theme 2 of European Joint Programme on Radioactive Waste Management (EURAD) and with those identified by the project's industrial End Users Group (EUG), which specifically targets Radioactive Waste Producers (RWP) as a separate group within the radioactive waste management process. Furthermore, PREDIS will produce tools guiding decision-making on the added value of the developed technologies and their impact on the design, safety and economics of waste management and disposal (WP2).

PREDIS will also liaise with EURAD to provide complementarity on areas including the adaptation and update of the reference founding documents of EURAD (vision, roadmap, governance and implementation mechanisms) (WP2), and the organisation of training courses and mobility training schemes to enhance sharing and transfer of knowledge and competences as part of knowledge management activities (WP3). PREDIS also encompasses the wider European Community, allowing cross-fertilisation and interaction between different national programmes. Numerous dissemination activities (WP1), including with SNETP (NUGENIA), IAEA and NEA, will be undertaken to maximize PREDIS's impact to all the identified Stakeholders in the field. The Figure 1 presents the content structure and approach of PREDIS project.

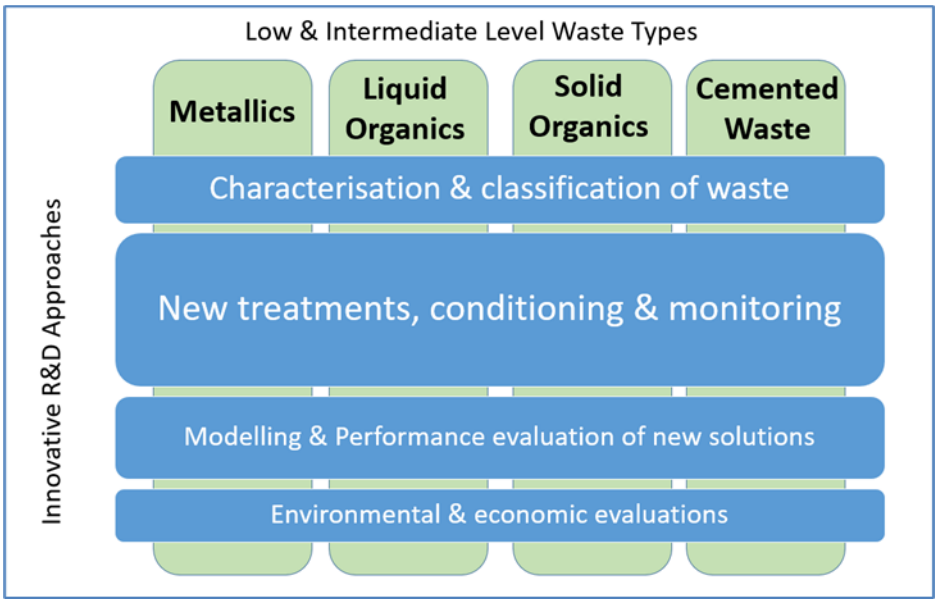

Figure 1. *Representation of project scope, addressing waste streams and approach.*

This report is the first in the series of *Deliverable 1.5 Technical proceedings of Annual workshops*.

More information of the project and its activities can be found in the PREDIS website: https://predis-h2020.eu/.

Keywords: waste, treatment, predisposal, safety, radioactive, nuclear, science and technology, monitoring, packages, material science

First Annual PREDIS Workshop

PREDIS project’s annual workshop was held May 4-6, 2021, online. During the workshop, PREDIS partners gave overall presentations on progress in the work packages (WP) and presented also first scientific activities in the technical work packages. Even though the workshop was this time only for PREDIS partners, the progress of PREDIS project will be shared by short articles based on the presentations during the workshop. The following annual workshops will be open for all interested stakeholders.

The activities and progress during the first eight months of PREDIS project have been remarkable. The cross-sectoral work package WP2 Strategic Implementation has had a very active first year in PREDIS. Strategic Implementation in the lead by Anthony Banford, NNL, UK, have established PREDIS stakeholder and end user community, consisting of European and worldwide groups, presenting e.g. waste producers, waste owners, waste management organisations, regulators, research entities and supply industry. There are already 23 external organisations, which have joined the PREDIS End User Group, to follow and support the project more closely. Analyses of Waste Acceptance Systems worldwide was on-going and the report was published in August 2021 (International approaches to establishing a waste acceptance system). Work on defining the environmental, process and economic evaluation protocol for the project based on life cycle assessment (LCA) and life cycle costing (LCC) together with establishing a consistent LCA and LCC basis for predisposal activities spanning waste generation to reuse/recycle and disposal has been started. WP2 made extensive efforts preparing the Draft Strategic Research Agenda (SRA), which is available at PREDIS website (Baseline SRA 2021). The final predisposal SRA will be published at the end of the project. Gap analysis, performed during the first eight months of the project, was finalised and the via active dialogue with the end users including six open webinars (Events - EU-project PREDIS (predis-h2020.eu)), the technology gaps that could be either included to the project plan or to the Strategic Research Agenda were identified.

The other horizontal work package WP3 Knowledge Management, as well as the technical work packages WP4 Innovations in metallic treatment and conditioning, WP5 Innovations in liquid organic waste treatment and conditioning, WP6 Innovations in solid organic waste treatment and conditioning and WP7 Innovations in cemented waste handling and predisposal storage, are presented in more detail in this Proceedings.

Acknowledgements

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2. Overview of WP3: Knowledge Management

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Abstract

The main objective of the work performed in WP3 Knowledge Management (KM) activities in the field of predisposal is to develop and transfer knowledge and competence across Member States' national programmes, but also target to preserve knowledge transfer to coming generations. To reach these goals, the work in WP3 is divided into four tasks that are all interlinked. In the first overarching task the strategy of the KM activities are developed, while the following three tasks focus on the implementation of the State-of-knowledge (SoK) production, and training and mobility actions. Activities related to the development of the PREDIS roadmap, as part of the overarching EURAD roadmap, have started and some documents to populate the roadmap are already been authored within PREDIS. Planning of the future SoK document production is in an advanced stage. In this initial period the PREDIS knowledge management activities focused on supporting the R&D workpackages with training and mobility measures based on their needs. R&D WPs training demands and suppliers of trainings within the PREDIS community have been surveyed to match the required training and existing training capacities. Furthermore, procedures and structures for mobility actions have been put in place and will make it possible for students and scientists to apply for mobility grants through the PREDIS Mobility portal.

Keywords: Knowledge Management, Glossary, Roadmap, State-of-Knowledge, Training, Mobility, Learning

1. Introduction

The identification, assessment, structuring and dissemination of past and present knowledge of predisposal R&D activities accumulated with the European Commission R&D programmes as well as international and national radioactive waste management organisations is of vital importance for early-stage programmes, advanced programs and future generations. The objective of this work is to provide access to this knowledge in a systematic and structured way to the PREDIS participants and to the European predisposal community. The KM work performed within this work package will be aligned with the KM activities existing in the European Joint Programme on Radioactive Waste Management (EURAD). The success of this work depends strongly on the integration of KM activities into the R&D WPs. Additionally, it requires strong links with EURAD, end-users, stakeholders and international organisations, such as IAEA, OECD/NEA, that have already commenced a lot of output in the predisposal field and therefore cooperation is crucial. The work-package started these interactions early at the start of the project and is obtaining useful input in the form of answers to surveys and questionnaires from the addressed organisations. The development of the KM work strategy, breakdown to sub-tasks and prioritisation of the tasks has been done, and in more detail outlined in the following text. The development of the PREDIS state-of-knowledge documentation and the training and mobility programmes is thus well underway and targeting to hit its first milestones in 2021.

1. Knowledge Management

The objective of this task focused on knowledge management is to manage and organize all WP activities and to assure that they complement the activities undertaken within EURAD, and other organizations such as IAEA, by extending them to the field of predisposal of radioactive waste.

One of the first activities coordinated within this task was the preparation of a glossary that will help to harmonize the terminology used in the whole project. It was decided to follow the terminology defined by the IAEA (International Atomic Energy Agency). IAEA published a list of more than 600 words related to nuclear safety and radiation protection (IAEA, 2019) which is the basis of the PREDIS glossary. Each WP leader was asked to select 100 words they considered relevant for predisposal activities and a preliminary glossary was elaborated with those words selected by three or more WP leaders. The final glossary will be prepared during 2021 and annually updated, to be a "living" document.

The dissemination of the information generated within PREDIS is a key aspect within the project. All the activities related with the Knowledge Management will be presented in a specific section within the PREDIS webpage (Knowledge management - EU-project PREDIS (predis-h2020.eu)). This section will be developed in the following months and it will contain information related with the glossary, training activities, mobility measures, SoK documents, etc.

2. State of Knowledge

The PREDIS project integrates well into the overall EURAD Roadmap as Predisposal has been identified as one of the seven EURAD Roadmap Themes (see Figure 1). The EURAD Roadmap is a generic framework that organises scientific and technical knowledge areas (themes) against different disposal implementation phases of a radioactive waste management programme. Each theme is programmatically further sub-divided into domains and sub-domains with their own goals and objectives. Seven themes are planned to be subdivided into ~20 sub-themes and further down to 76 domains.

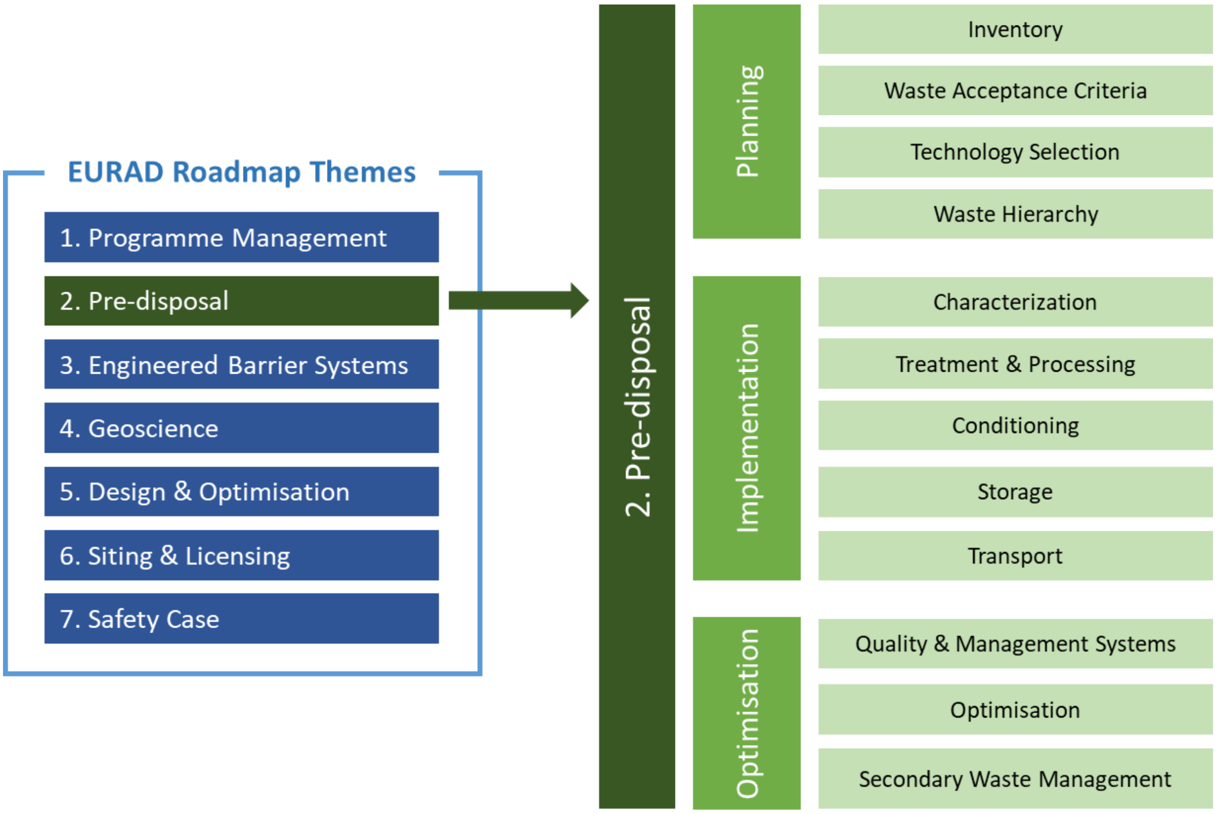

Figure 1. *Topical breakdown of the Predisposal theme in the EURAD Roadmap.*

The hierarchy of the documents (from top to the down level) is following**: Theme Overviews** (TO) will provide broad description of program goals and typical activities for each theme and how they evolve over phases of implementation. **Domain insights** (DI) are context documents that provide direct links for each knowledge domain related to safety and implementation goals. **State of knowledge documents** (SoK) represent experts' view of the most relevant knowledge with associated uncertainties in a specific topic applied in the context of a radioactive waste management programme. On the next level there are **State of the Art** (SotA) documents that include scientific and technological facts underpinning the knowledge base. Finally, the lowest documentation level is the **Scientific & Technological Basis of RWM**, which consists of technical scientific reports, journals, license applications, guidance, codified knowledge, forming a Knowledge base for the topics.

The first PREDIS Domain insights documents are planned to be launched by the end of 2021.

Moreover, PREDIS will contribute to the **EURAD Wikipedia**, a tool for compiling, preserving and providing knowledge and developed within EURAD, through our contribution to Theme 2 Predisposal. The detailed planning will be made in autumn 2021.

3. Training

The goal of this task is to develop a specific training program reflecting the interests and needs of the PREDIS community. All the activities are organized in close cooperation with other projects and organisations such as EURAD, IAEA, NUGENIA or NEA.

The training program is developed in four different steps: (i) Training needs, (ii) Preparation of training activities, (iii) Development of training activities and, (iv) Evaluation of training activities. Up to know, we are working on the first step.

A survey has been distributed to both the partners and end-user group to identify the training needs of the PREDIS community. Results of the survey were presented in the 2nd Workshop of the PREDIS project. We take advantage of this survey to ask the type of training related with predisposal that partners can offer. The main conclusion obtained from the survey is that most of the identified needs can be covered with the knowledge of PREDIS partners.

Additionally, a mapping of the courses performed during the last 5 years as well as those planned for the following year are collected to avoid duplication.

During the following months, the work will be focused on the prioritization of the identified needs and to initiate the preparation of training activities. To start with it, questions were posted during the 2nd PREDIS Workshop and answers indicate that the PREDIS community are highly interested in waste characterization, geopolymers, decontamination and waste acceptance criteria.

4. Mobility

PREDIS has special interest in setting up and implementing training and mobility programmes to allow newcomers and new generations to acquire the level of knowledge needed to develop their professional careers in the different subjects related to the predisposal of radioactive waste.

Survey within PREDIS partners clearly showed that knowledge transfer in the form of mobility measures is a priority. Most of expected mobility applicants are PhD students and post docs. The survey also showed that there exists a wide pool of potential mobility hosting within PREDIS participants.

The PREDIS Mobility Programme is intended for those who would like to improve their knowledge and skills in the field of **predisposal treatment of radioactive waste streams, other than nuclear fuel and high-level radioactive waste**.

Mobility funding will be provided for PREDIS partner organisations, based on the submission of applications through the **PREDIS mobility portal**. The portal, based on the EVALATO platform, has been developed in cooperation with EURAD WP13 and is targeted to be ready by summer 2021.

The following forms of mobility are included into the PREDIS Mobility Programme: (i) Visit, (ii) Internship, (iii) Course/Training, and (iv) Conferences/Workshops.

Mobility funding will be reviewed by the mobility evaluation team by a thorough evaluation of application, consisting of CV, motivation letter, detailed budget, description of proposed activity and a letter of support from host institution in the case of internship.

Mobility grants will be issued using PREDIS mobility portal four times per year. Mobility budget will be reimbursed on the basis of annual financial reporting. Each grantee must file a mission report. Mobility application scheme is shown in Figure 2.

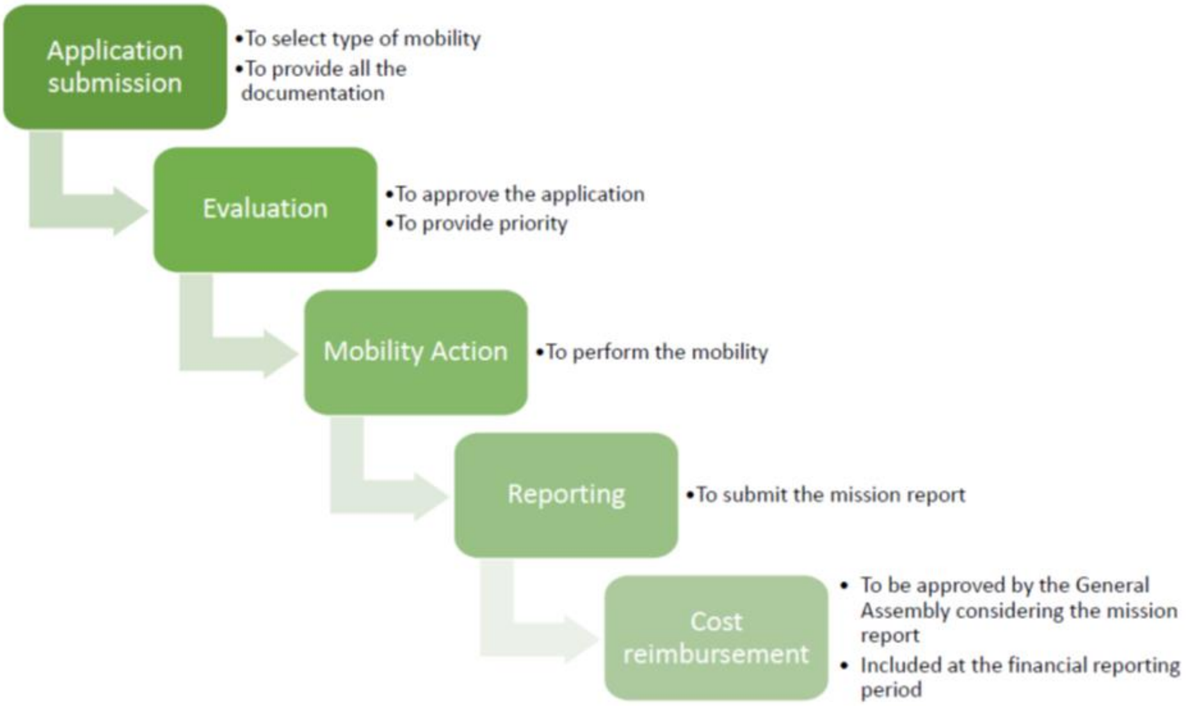

Figure 2. *PREDIS mobility application scheme.*

The basic guidelines for Mobility procedures have been stated in the Deliverable D3.6 Priority list and mobility formats, available in PREDIS website (Deliverable 3.6).

References

IAEA (2019) IAEA Safety Glossary. Terminology used in nuclear safety and radiation protection. 2018 Edition. Vienna, p. 261.

3. Assessment of Metallic, Liquid Organic and Solid Organic Waste in PREDIS Countries – WP4, WP5 and WP6 Inventories

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Abstract

To assess the needs of waste owners and end users for waste treatment, it is important to have an accurate idea of the types of waste that require treatment, and the scale of the waste arisings. To assess this need, a survey of PREDIS partners and end users has been conducted, to assess the types and amounts of metallic, liquid organic and solid organic waste arisings in countries participating in PREDIS. This survey has been conducted jointly between work packages (WPs) 4, 5, and 6. The results show that there are significant volumes of untreated waste present in the partner countries that could benefit from the treatment technologies being developed in PREDIS. The main waste types identified are steel (WP4), organic solvents, oils, organic sludges and concentrates (WP5), and resins, plastic, cellulosic waste, and bituminised waste (WP6).

Keywords: Inventory, End User Group, Metallic waste, Solid Organic Waste, Liquid Organic Waste.

1. Introduction

The PREDIS project (predisposal management of radioactive waste) is a European Commission-funded research and innovation action that targets the development and improvement of activities for the characterisation, processing, storage and acceptance of intermediate-level and low-level radioactive waste (ILW/LLW) streams. The PREDIS project targets innovation and break-through technologies for safer, more efficient, cost-effective, and environmentally friendly handling of ILW/LLW. The focus is on treatment and conditioning of metals, liquid organic wastes and solid organic wastes and the long-term storage of cemented wastes arising from nuclear plant operations and decommissioning.

Work package 4 (WP4) of the PREDIS project is concerned with the characterisation, decontamination and direct conditioning of radioactive metallic wastes, WP5 is focused on liquid organics, and WP6 is focused on solid organics. WP7 is focused on cemented waste is store, but this waste stream is being considered in a separate survey. In the first year of the project, work in WPs 4-6 has focused on understanding the needs for waste treatment, by conducting a survey of partners and end users. This survey took the form of an inventory questionnaire whereby the respondents could highlight the priority waste streams that could benefit from treatment using the technologies being tested in WPs 4-6.

This extended abstract provides a summary of the methodology employed (the questionnaire) and results to date, highlighting the priority waste streams for study. The full results from the questionnaires will be presented separately.

2. Methods

Inventory information was gathered from a questionnaire completed by PREDIS partners and end user group (EUG) members. The specific waste information requested concerned:

- Name of waste stream
- Source
- Heterogeneity
- Location (store, silo)
- Current state (raw waste, containerised, treated)
- Volume
- Physical properties
- Chemical properties
- Activity levels and main radionuclides
- Current treatment plans

To facilitate efficient responses to the PREDIS questionnaire, data for WP4, WP5 and WP6 was collected in a single questionnaire. This questionnaire was initially provided as an online form, available at the following link: https://link.webropolsurveys.com/Participation/Public/39a14620-e5d8-4b4f-a9f5-919b534b57a9?displayId=Fin2161395 (still open at time of writing). Further details of the EUG surveys are available in PREDIS deliverable D2.1 [1]. After feedback from the EUG (at the project workshops and webinars), it was decided that the questionnaire should also be made available in alternative formats to facilitate easier completion and distribution within EUG organisations. Therefore, Adobe PDF and Microsoft Word versions of the questionnaire were created and distributed to EUG and partner representatives on request. Additionally, a decision was made to allow non-standard responses from EUG partners, in whichever format suited them.

The questionnaire responses were received over a period of six months (Jan – June 2021), through the web form, PDF and Word files, and in one case as Excel tables (non-standard response). The information contained in these responses has been interrogated to draw out the key conclusions of importance to the PREDIS work programme.

3. Results

To date (June 2021) responses have been received from 11 organisations, including three responses from EUG members (Fortum, TVO, and Nagra) and eight from project partners (CEA, KIPT, NNL, CVR, SOGIN, UJV, RATEN, VTT). Of these 11, four respondents included metallic waste in their responses (for WP4), nine respondents included liquid organics in their responses (for WP5), and four respondents included solid organic waste streams (for WP6). There has been communication with a further two organisations (Studsvik and Urenco) and their responses are awaited. This section summarises the volumes of these wastes by type (WP) that have been reported in the questionnaire responses.

WP4: Metallic wastes

Figure 1 summarises the volumes of metallic waste identified by partners and EUG members, broken down by general type of metallic waste, including mixed waste that includes metals and non-metals. The dominant type of metallic waste present in Europe is steel, predominantly material arising from decommissioning and demolition of reactor buildings.

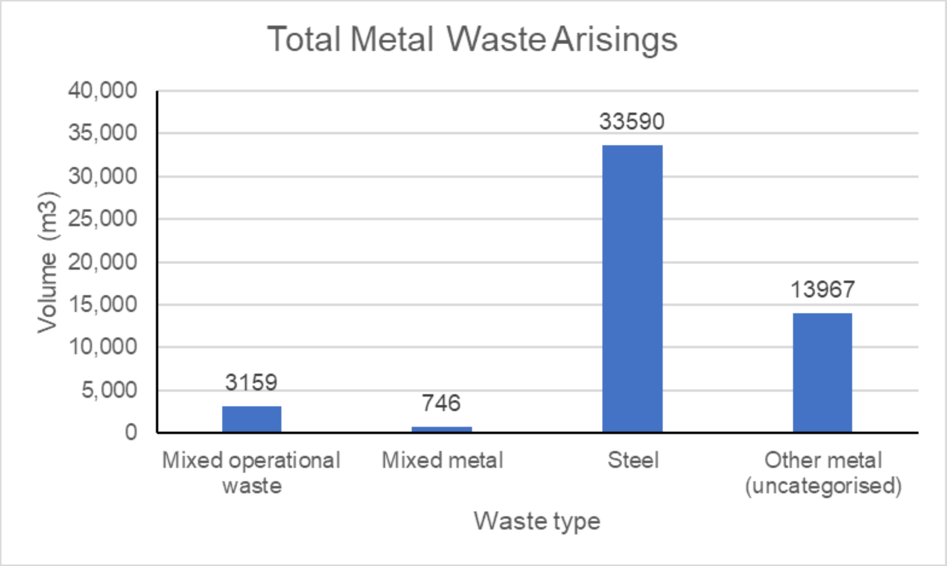

Figure 1. *Metallic waste volumes identified in the inventory responses, grouped by waste type.*

WP5: Liquid organic wastes

Figure 2 summarises the volumes of liquid organic waste identified by partners and EUG members, broken down by type of organic liquid. The dominant types of liquid organic wastes identified by the respondents were oils and organic solvents.

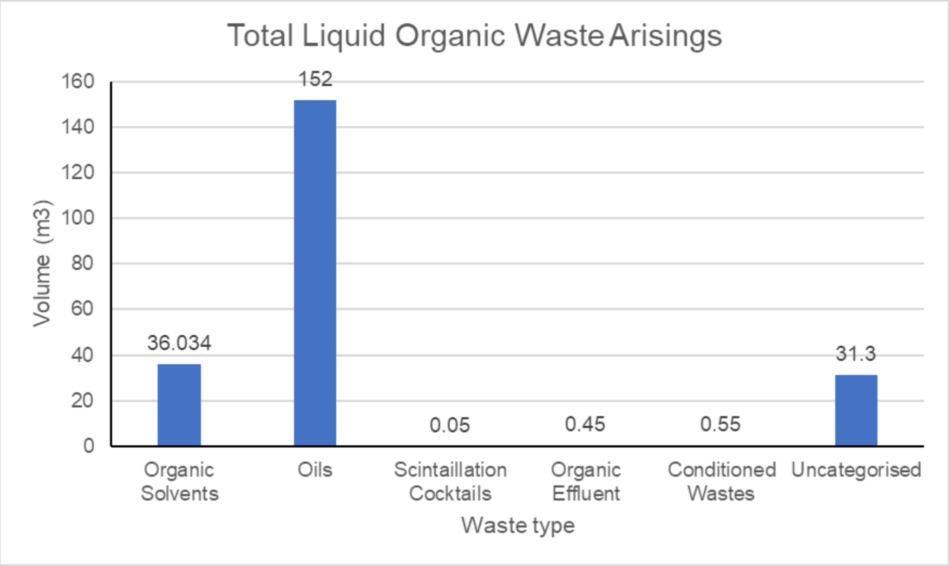

Figure 2. *Radioactive liquid organic waste volumes identified in the inventory responses, grouped by waste type.*

WP6: Solid organic wastes

Figure 3 summarises the volumes of solid organic waste identified by partners and EUG members, broken down by type of organic solid. The main solid organic waste types identified were resins and sludges. The largest volume of waste of this type was included in a non-standard return provided by CEA, where specific waste streams were not readily accessible, and much of the reported solid organic waste was part of a mixed waste streams, or reported as ’combustible waste’. Therefore, the CEA wastes were not categorised into generic waste types. The return from CEA, however, included some identifiable waste types, not reported by other respondents. These were plastic, cellulosic waste and bituminised waste. SOGIN also reported mixed cellulosic waste, but did not provide volume information.

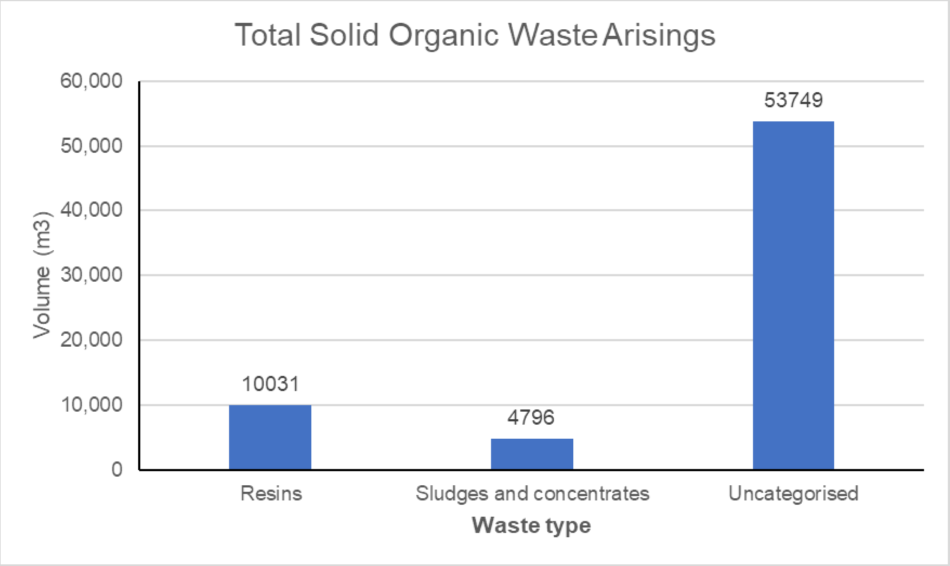

Figure 3. *Radioactive solid organic waste volumes identified in the inventory responses, grouped by waste type.*

4. Summary

An inventory questionnaire has been distributed to PREDIS partners and end users to ascertain the types and amounts of metallic, liquid organic and solid organic wastes present in Europe, that would benefit from R&D activities to support their long-term management. To date 11 responses have been received. These responses show that there are large volumes of these wastes that require predisposal management. The main types of waste that have been reported are:

- Steel
- Organic solvents
- Oils
- Resins
- Organic sludges and concentrates
- Plastic
- Cellulosic waste (wood, paper, etc.)
- Bituminised waste

Many of the identified wastes do not have any pre-defined management route, and are kept in storage, awaiting treatment/conditioning prior to disposal. The work being done in PREDIS is aiming to develop methods to treat and manage all of these waste types. Therefore, it is clear from this inventory work that there is a significant need in the European market for radioactive waste treatment, which PREDIS can help to address.

Although some additional inventory data is awaited from other end users, we do not expect this information to significantly alter the general conclusions drawn here from the information received to date.

References

E. Holt, Survey of End Users, PREDIS Deliverable 2.1, 2021. (Confidential, only for consortium members)

4. Preparation of representative samples for optimization of decontamination of Ni-alloys

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Abstract

Different types of Ni-alloys are the main structural materials in the pressurized water reactors (PWR). Under normal operating conditions of water cooled nuclear reactors most metallic surfaces oxidize and form a duplex corrosion layer of 2.5-3 µm thickness. The oxide layer erodes from the surfaces, activates in the reactor core and the radioactive corrosion product deposits on the surface. The majority of radioactive contamination are caused by radioactive corrosion products. In order to keep the contamination under safe level effective decontamination treatments are required to remove the contaminated surface oxide layer.

Laboratory techniques were developed to prepare non-radioactive metal samples with oxide-layer for the optimization of decontamination technology. Normal operating conditions of nuclear reactor (Method A) and high-temperature, water vapour (Method B) conditions were used to form oxide layer on stainless steel surfaces. The structure of the formed layer in Method A was similar to the layers formed under reactor operation conditions, however the investigation time was long and uniform surface was hard to achieve. Method B was better suited for the requirements to optimize decontamination technology. The investigation time was shorter and uniform oxide coatings were prepared. The next step must be to form oxide-layer on Inconel alloys in cooperation with Institut Mines-Télécom Atlantique / Laboratory SUBATECH.

Keywords: Ni-alloys, oxide layer, corrosion, decontamination

1. Introduction

Different types of Ni-alloys are the main structural materials in the pressurized water reactors (PWR). Austenitic stainless steel type 314/316 are widely used in the structure of the reactor pressure vessel and the pressurized boundary piping [1]. In the steam generator tubing Inconel alloy 600/690 are typically used [2].

Under normal conditions of nuclear reactor most metallic surface oxidize and form a duplex corrosion layer of 2.5-3 µm thickness [3]. The upper oxide layer on austenitic stainless steel (17-9% Cr, 9-11% Ni, 1-2% Mn as well as some Ti, Si, P and S) is normally magnetite and the main part consists of mixed oxides with the composition $Cr_xNi_yFe_{3-x-y}O_4$ where $0 \leq x+y \leq 3$ [3]. The distinctive oxide structures on Inconel alloys (617) consists of surface layer, sub-layer, and internal oxides. Cr_2O_3 are formed as the sub-layer and the internal oxide is identified as Al_2O_3 [4]. The formed layer erodes from the surface and it is transported to the high neutron flux reactor core, where the oxides activates. The activation products circulate throughout the system and deposit on the surface. The contaminants tend to settle on rough surface and at the discontinuity points of the fluid flow. The radioactive corrosion products are the majority of radioactive contamination (when there is no fuel cladding failure). The most important corrosion product radionuclides are ^{60}Co, ^{58}Co, ^{51}Cr, ^{54}Mn, ^{59}Fe. [5].

Safe, effective, cost-effectiveness, easy feasible and low-waste decontamination technologies are fundamental importance from environmental and radiation protection aspects [6]. Technological data of ten steam generator in VVER-type pressurized water reactors were analysed for a continuous period of seven years and the results showed, that the decontamination factors (DF) are rather low (DF<20) [7]. Other findings claim that the chemical methods, which provide excellent DFs, produce large waste volumes and the low-waste chemical decontamination technology operates without the desired DFs [8].

In the PREDIS WP4 Sub-Task T4.3.1 laboratory techniques were developed to prepare non-radioactive metal samples with oxide-layer for the optimization of decontamination technology.

2. Materials

Oxide coatings on 316 grade of stainless steels were prepared. The composition of the metal sample is summarized in Table 1. All chemicals were analytical grade.

Table 1. *Composition of 316 grade of stainless steel (%).*

	C	Mn	Si	P	S	Cr	Mo	Ni	N
min.	-	-	-	-	-	16.0	2.00	10.0	-
max.	0.08	2.0	0.75	0.04	0.03	18.0	3.00	14.0	0.10

3. Methods

Two different types of methods were developed to form an oxide layer on the surface of stainless steel. *Method A* uses normal operating conditions of nuclear reactor and the metal samples were prepared in water vapour according to *Method B*. Before each oxidation experiment the surface of the metal samples was cleaned by polishing, washing with water and acetone. Blast-cleaning machine was used for surface polishing. To evaulate the formed oxide layer Scanning Electron Microscope (SEM) was used.

3.1 Method A

The schematic flow diagram and the picture of the equipment can be seen in Figure 1. The laboratory equipment consists of a tank, a pump, a furnace, a cooler, sensors, which measures the conductivity and the dissolved oxygen concentration of the circulated water.

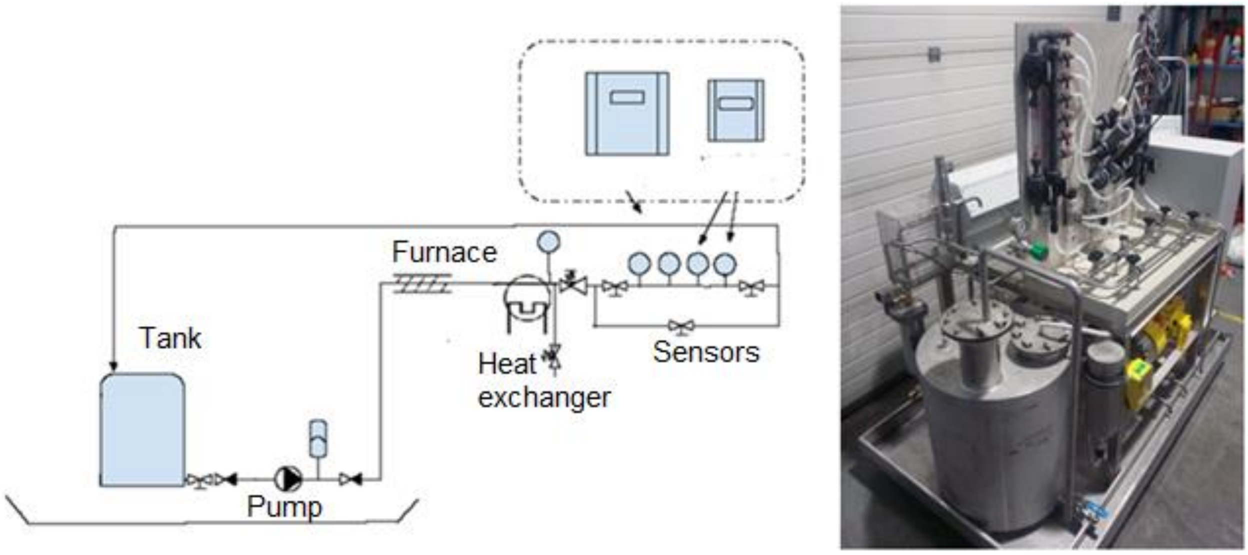


Figure 1. *The schematic flow diagram and the picture of the used equipment (Method A).*

The stainless steel metal samples are placed in the furnace and treated at 300 °C, 85 bar for 1080 h. The boric acid concentration of the circulated water was 15 g/dm^3.

3.2 Method B

The principle of Method B is that the stainless steel metal samples are heated up to 800 °C for 8 hours and water vapour is used to form oxide-layer. Figure 2 shows the schematic flow diagram and the picture of the laboratory equipment.

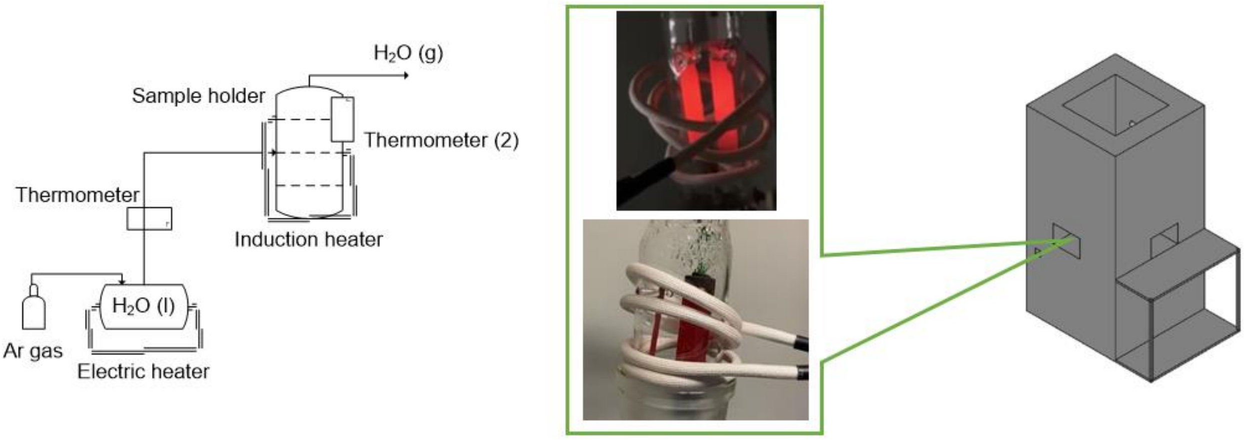
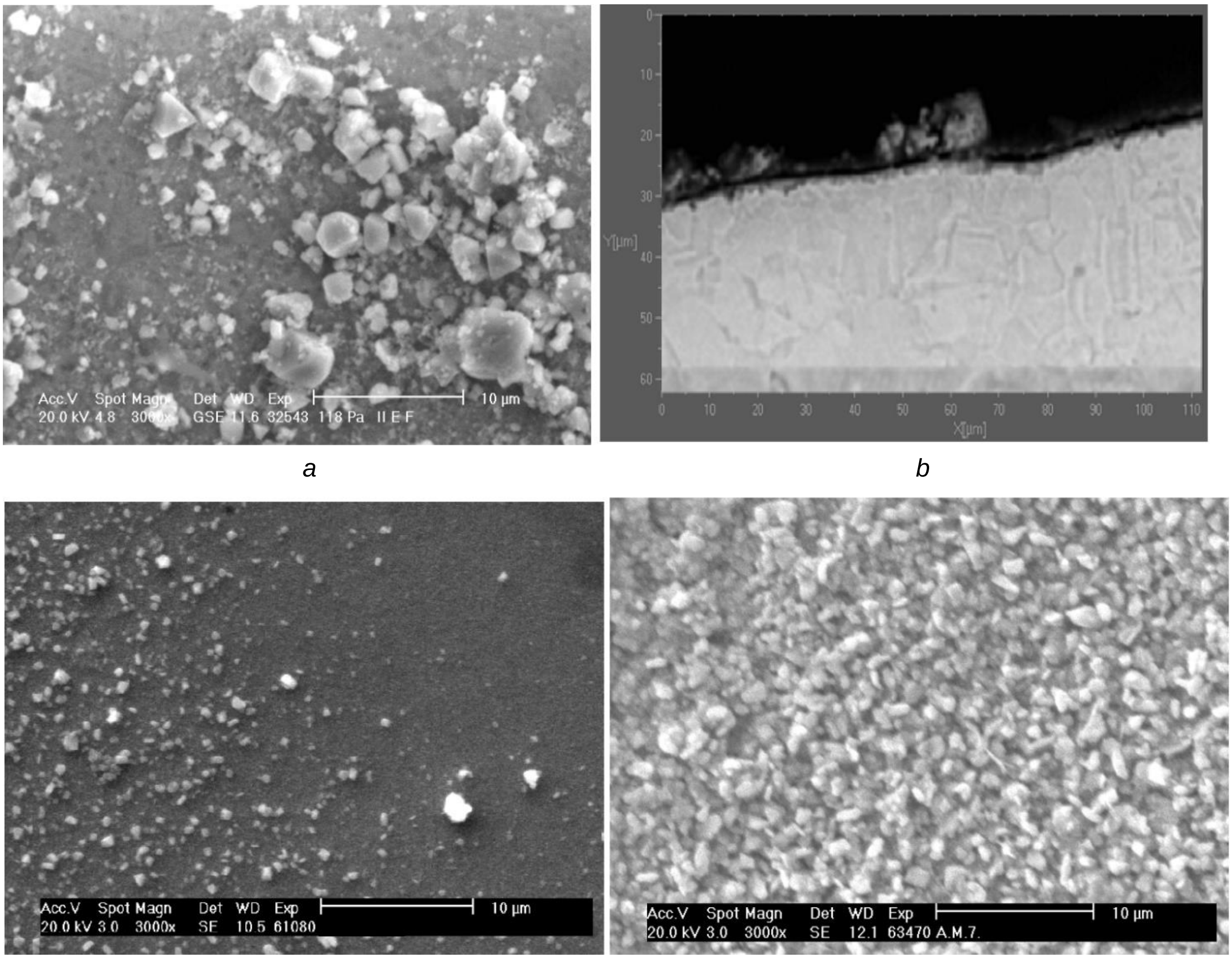


Figure 2. *The schematic flow diagram and the picture of the used equipment (Method B).*

During the measurement, the temperature are controlled on the heating points and Ar gas is used to control the water vapour flow.

4. Results

Cross-sectional and surface SEM images of stainless steel pipe from steam generator in nuclear power plant of Hungary are illustrated in Figure 3 [9]. Furthermore, on the Figure 3 the surface SEM images of the formed oxide-layers on laboratory metal samples are presented.



a *b*

c *d*

Figure 3. *Surface (a), cross sectional (b) SEM images of stainless steel pipe from steam generator in nuclear power plant of Hungary [9]. The formed oxide layer by Method A (c) and Method B (d) are also illustrated.*

On Figure 3, it can be seen that the oxide-layer on the surface of an industrial sample (operated in a the nuclear reactor) was more similar to the prepared coatings in Method A then Method B. On the other hand uniform oxide-layer was achieved in Method B, which could be beneficial for optimization and comparison of different decontamination technology. Furthermore, the investigation time of Method A was long and the repetition of the test conditions was hard due to the complexity of the system. Figure 4 shows the prepared stainless steel metal samples according to Method B. The thickness of the layer was 5 µm.

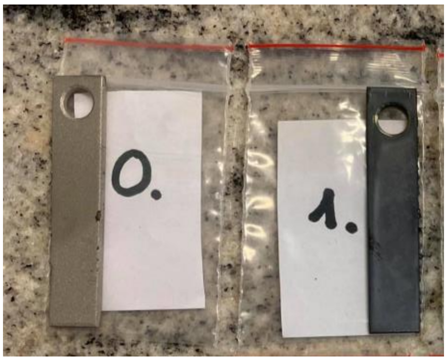


Figure 4. *316 grade of stainless steel with oxide coatings (Method B).*

5. Conclusions

In the PREDIS WP4 Sub-Task T4.3.1 laboratory techniques were developed to prepare non-radioactive Ni-alloy samples with oxide-layer for the optimization of decontamination technology. Normal operating conditions of nuclear reactor (Method A) and high-temperature, water vapour (Method B) conditions were used to form oxide layer on stainless steel surfaces. The structure of the formed layer in Method A was similar to the industrial samples, however the investigation time was long and uniform surface was hard to achieve. Method B was better suited for the requirements to optimize decontamination technology. The next step will be to prepare oxide-layer on Inconel alloys in cooperation with Institut Mines-Télécom Atlantique / Laboratory SUBATECH.

References

[1] Féron, D.; Herms, E.; Tanguy, B. Behavior of stainless steels in pressurized water reactor primary circuits *Journal of Nuclear Materials 427,* 364–377, 2012.

[2] Airey, G.; Vaia, A.; Aspden, R. A Stress Corrosion Cracking Evaluation Of Inconel 690 For Steam Generator Tubing Applications. *Nuclear Technology 55*, 436-448, 1981.

[3] Homonnay, Z.; Vértes, A.; Kuzmann, E.; Varga, K.; Baradlai, P.; Hirschberg, G.; Schunk, J.; Tilky, P. *Journal of Radioanalytical and Nuclear Chemistry 246*, 131-136, 2000.

[4] Kim, D.; Kim, D.; Lee, H.; Jang, C.; Yoon, D. Corrosion characteristics of Ni-base superalloys in high temperature steam with and without hydrogen *Journal of Nuclear Materials 441,* 612–622, 2013

[5] Varga, K.; Hirschberg, G.; Németh, Z.; Myburg, G.; Schunk, J.; Tilky, P. Accumulation Of Radioactive Corrosion Products On Steel Surfaces Of VVER-Type Nuclear Reactors. II. 60Co. *Journal of Nuclear Materials 298*, 231-238, 2001.

[6] Han, S.; Hong, S.; Nam, S.; Kim, W.; Um, W. Decontamination Of Concrete Waste From Nuclear Power Plant Decommissioning In South Korea. *Annals of Nuclear Energy 149*, 107795, 2020.

[7] Varga, K.; Németh, Z.; Somlai, J.; Varga, I.; Szánthó, R.; Borszéki, J.; Halmos, P.; Schunk, J.; Tilky, P. *Journal of Radioanalytical and Nuclear Chemistry 254*, 589-596, 2002.

[8] Murray, A. A Chemical Decontamination Process For Decontaminating And Decommissioning Nuclear Reactors. *Nuclear Technology 74*, 324-332, 1986.

[9] Baja, B.; Varga, K.; Szabó, N.; Németh, Z.; Kádár, P.; Oravetz, D.; Homonnay, Z.; Kuzmann, E.; Schunk, J.; Patek, G. Long-Term Trends In The Corrosion State And Surface Properties Of The Stainless Steel Tubes Of Steam Generators Decontaminated Chemically In VVER-Type Nuclear Reactors. *Corrosion Science 51*, 2831-2839, 2009.

5. Optimization of Chemical Decontamination Methods of Radioactive Metallic Wastes

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Abstract

Nuclear energy as a power source is currently our best option in the fight against climate change. But the radioactive waste generated from nuclear power plants and their related facilities is a cause of concern. Though the high-level and intermediate-level activity wastes are contained in small volumes (≤ 10%), significant volumes of lower activity wastes are generated. Metallic wastes are a major component of these radioactive wastes with 72000m^3 of such wastes expected by 2040[1]. The majority of these metals are made of Stainless steel 316 alloy or Inconel 600. These make up the majority of the primary circuit of a PWR plant. Under the primary circuit water and irradiation effect, these components corrode and the corrosion products may be activated when close to the fuel and be transported throughout the circuit. These products can be deposited on the surface of other metal components, causing contamination of the latter. The contamination can be adsorbed on the surface but can also diffuse in the oxide layers and sub-surface. The oxide layer is composed of an inner layer of Cr oxide under a layer of Ni and Fe oxide. Chemical decontamination is the preferred form of treatment due to the possibility of decontamination of difficult geometries and tube bends. To decontaminate these materials, it is important to dissolve the oxide layers chemically and a few microns of base metal where it could have diffused. Some existing chemical methods used to treat these materials are selected. These methods include Chemical Oxidation Reduction Decontamination (CORD) and Metal Decontamination by Oxidation using Cerium (MEDOC). These methods are studied and a few parameters to be optimized are identified to dissolve the oxide layer and also the diffused activity by subsurface dissolution. The dissolution will first be carried out on powders followed by surrogate steel and Inconel samples provided by SORC will be tested initially to optimize the processes before moving on to the real active samples. The experiments will be carried out in the batch method with some optimizations before moving on to a loop system. The optimization steps will target reducing the volumes or treatment strategies for the effluent wastes while keeping in mind the Waste Acceptance Criteria (WAC) for nuclear waste.

Keywords: metallic, decontamination, Waste Acceptance Criteria (WAC), Radioactive, Inconel

1. Introduction

Nuclear power is a safe and clean way of generating energy. But the radioactive waste it generates is a matter of concern for the industry and others. Though the majority of the activity is contained in small volumes of high-level wastes, significant volumes of low and intermediate-level wastes are produced. Metallic wastes are a significant contribution to these volumes. The primary circuit of a PWR power plant constitutes a major proportion of this waste including the steam generator and the associated systems. Under the primary circuit water and irradiation effect, these components corrode and the corrosion products may be activated when close to the fuel and be transported throughout the circuit. These products can be deposited on the surface of other metal components, causing contamination of the latter. The contamination can be adsorbed on the surface but can also diffuse in the oxide layers and sub-surface. These wastes can be classified as Intermediate Level Wastes (ILW). Left untreated, these wastes will quickly fill up the current waste disposal repositories for hundreds of years. Treatment of these wastes can lead to significant savings in space at the waste disposal repositories by leading to a change in classification of the waste to either Low-Level Wastes (LLW) or Very Low-Level Wastes (VLLW). Different types of techniques available to decontaminate metallic wastes, namely, chemical, physical, biological, and electrochemical decontamination. Chemical decontamination is the method of choice mainly due to the complex geometries found in steam generator tubes, which make the applicability of the other methods difficult. This work will focus mainly on Nickel Alloy and Stainless-steel systems. The objectives of the present work include optimization of the decontamination processes. This includes either reducing the number of secondary waste streams or wastes that can be treated further. There is also an aspect of accounting for the cost of this treatment, whether it is feasible for the industry to carry out this treatment and to what extent, i.e., the decontamination has to be carried out only for the upper layer of oxides or even the base metal. The environmental impact of such a process would also need to be accounted for. A Life Cycle Analysis (LCA) study is planned along with our colleagues from the University of Manchester (UK).

A wide variety of existing chemical decontamination techniques were studied and compared. Two processes were selected for initial testing namely

- Chemical Oxidation Reduction Decontamination (CORD)
- Metal Decontamination by Oxidation with Cerium (MEDOC)

These processes were selected based on interaction with experts from the end-user group. The processes are explained in detail in section 2.1**.**

2. Literature Survey

Before studying the decontamination processes, it is important to characterize the oxide layer which is to be dissolved. For Stainless steel and Ni-alloys, it was found that under the conditions of PWR primary circuit operation, multilayer corrosion was observed. [2]–[4] Panter et al. exposed Ni-alloy 600 sample at 330°C for 300h at simulated primary circuit water conditions and found, using SEM large crystals on the outer layer whereas the inner oxide layer was compact with smaller crystals as seen in the SEM image in Figure 1. [2]

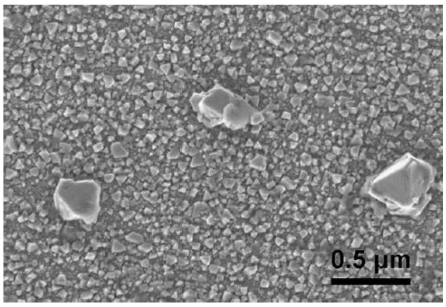

Figure 1. *SEM image of oxidized Ni-Alloy 600 by Panter et al. [2].*

When he studied the TEM cross-section of this oxide layer showed a thin fuzzy layer of about 10 nm beneath the outer oxide layer, as shown by the arrow in Figure 2. The layer looks compact and continuous. The external oxide crystallites seem to be embedded in this layer. TEM EDX profile on this sample revealed an outer oxide enriched in Ni and Fe whereas the layer under this has an increase in Cr concentration. [2]

In the work of McGrady, a sample of alloy 600 was exposed to PWR conditions of 320°C for 1730 hours showing similar multi-layered corrosion as seen in the TEM analysis shown below in Figure 2 [5]

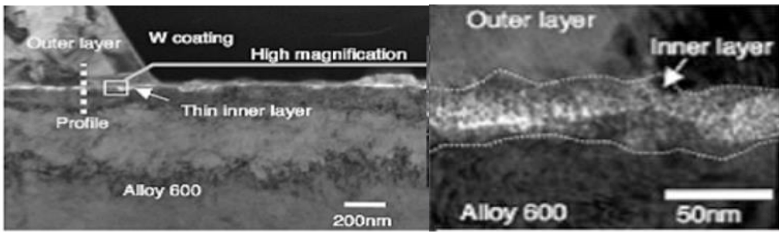

Figure 2. *TEM image of Ni-alloy 600 exposed to PWR conditions by John McGrady [5].*

The inner layer of chromium oxide with a thickness of roughly 50 nm, acts as a barrier layer protecting the base metal from further corrosion. Above this layer, a layer of Ni-Fe Oxide with a thickness of roughly 100nm is observed, as seen in the EDS analysis below in Figure 3.

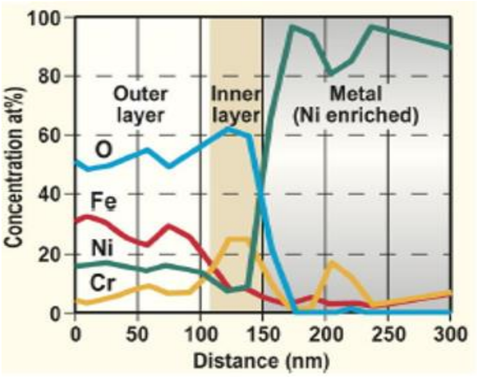

Figure 3. *EDS chemical profiles for an oxide film formed on Ni-alloy 600 [5].*

Similar results were observed by Panter et al. [2], confirming the composition of the oxide layer. When J. Panter carried out the TEM EDX profile for a Ni-alloy sample exposed to primary circuit water conditions. It is seen that the outer oxide is enriched in Ni and Fe whereas the layer under this has an increase in Cr concentration.

Marchetti-Sillans [6] summarized the findings through an illustration (Figure 4) showing an internal barrier layer of mainly Cr oxides under an external oxide layer enriched in Ni and Fe.

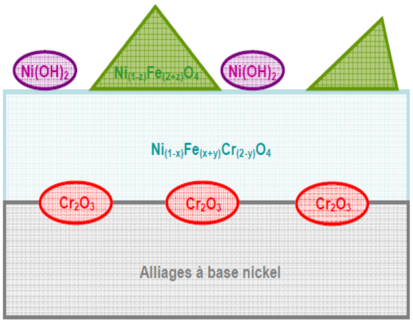

Figure 4. *Oxide film composition with precipitates as drawn by Marchett-Sillians [6].*

As previously stated, the radioactive nuclides are deposited in these oxide layers. Pick summarised the activity of these radionuclides found in a typical PWR steam generator, as shown in Table 1.

Table 1. *Summary of radionuclides found in PWR Steam Generators [7].*

Radionuclide	Activity (kBq/cm^2)
^{60}Co	250-1000
^{54}Mn	4-30
^{58}Co	150-500
^{65}Zn	2-6
^{57}Co	0-2
^{137}Cs, ^{144}Ce, ^{152}Eu, etc	<1

These activities can be converted into a Co-60 equivalent. In Europe, the free release criteria for Co-60 is 0.1 Bq/g. Ideally, through the cycles of chemical treatment, this is a target but to achieve this there are other barriers such as volume of secondary waste generated, the cost, etc.

2.1 Decontamination techniques

2.1.1 Chemical Oxidation Reduction Decontamination (CORD)

CORD is a 2-step process with the first step involving attacking the Chromium Oxide layer using a permanganate ion (MnO_4^-) (Figure 5). This ion comes from permanganic acid in the case of HP CORD, or potassium permanganate in the case of NP CORD (Nitric acid medium) or AP CORD (Alkaline permanganate-KOH medium). The lower pH of the acid medium was found to be more effective therefore HP and NP CORD are selected for testing [8]. A simple summary of HP CORD is shown below [9]. The permanganate ion attacks the chromium oxide layer to release chromate ions. The ion exchange resins are not used at this stage. Stoichiometric amounts of oxalic acid are then added in the reduction stage to convert the permanganate ion to give aqueous Mn^{2+} ions. Additional oxalic acid is added for the decontamination step and the ion exchange resins are now used. The oxalic acid attacks the Ni-Fe oxide leading to metal ions in solution. These ions are then captured by the ion exchange resins. This constitutes 1 cycle of the process.

To begin the second cycle, the ion exchange resins are disconnected and permanganate is added to the solution to go back into the oxidation stage. Ion exchange resins are removed due to incompatibility with the permanganate. The process is then repeated. For the final clean-up step, chemical decomposition is possible but the use of UV is preferred. UV, in presence of hydrogen peroxide, is used to destroy the remaining oxalic acid leading to only water and CO_2 in solution, which can be captured. Due to this, HP CORD doesn't require any anion exchange resins which leads to lower volumes of final waste.

A variation of CORD, known as CORD D UV, where D stands for decommissioning, makes use of the UV in the decontamination stage, which leads to a change in redox potential from +100mV to -275mV (versus Ag/AgCl). This increases the efficiency of the decontamination step. This system will be tested in the lab with a loop system.

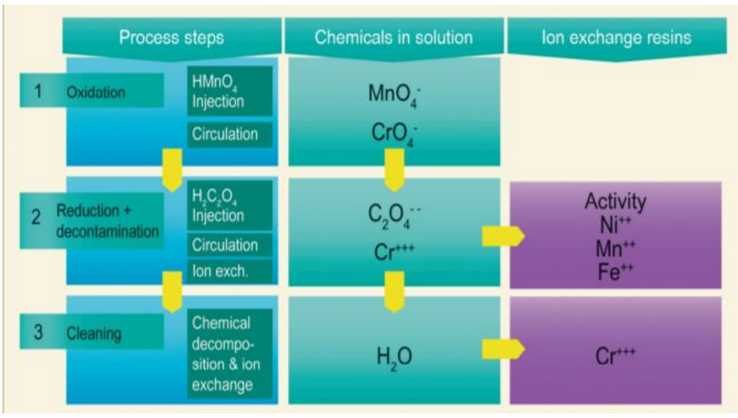

Figure 5. *Redrawn and modified from original AREVA work by A.N.T International [8].*

2.1.2 Metal Decontamination by Oxidation with Cerium (MEDOC)

MEDOC is a single-step regenerative process that uses the strong oxidation properties of Ce^{4+} (Figure 6). It can be used in either Nitric acid or sulphuric acid medium. This process has no particular affinity to any metals and attacks them equally according to the reaction.

$$nCe^{4+} + M \rightarrow nCe^{3+} + M^{n+}$$

This leads to an attack of the base metal as well which can lead to the higher efficiency of the process. The Ce^{4+} is converted into Ce^{3+} thereby reducing the efficiency of the reaction. This process includes a regeneration step, wherein Ce^{4+} is regenerated from Ce^{3+} by using Ozone gas (O_3). This Ce^{4+} can therefore be reused for further attack on the metal surfaces. The metal ions in the solution are removed by passing the solution through ion exchange resins. The regenerative process can be placed in line with the system loop with the use of a static mixer to mix in the ozone gas. The final solution can then be treated as waste.

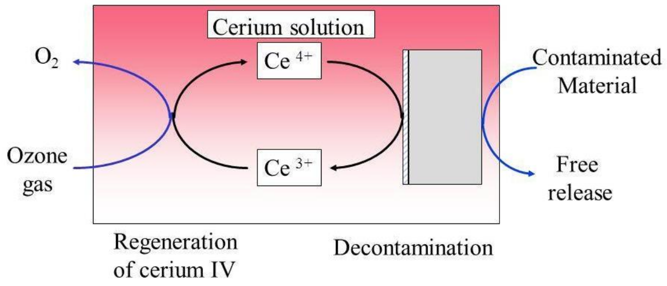

Figure 6. *MEDOC treatment process taken from the work done by Ren and Zhang [9].*

2.2 Parameters for Optimization:

Some parameters for these processes are identified which could be modified to check for better optimization of these treatment methods.

1*) Flow rate of chemicals*: By changing the flow rate through the pump, the kinetics of the system can be changed. The flow can be increased or decreased via the pump which will allow for a change in the flow patterns for the chemical solutions, this could lead to an increase or decrease in turbulence in the system which might affect the decontamination efficiency.

2) *Temperature of the solution:* The temperature of the solutions can be increased or decreased alongside changing other parameters, which can make the process easier to manage and can also lead to change in operating costs.

3) *Concentrations:* The concentration of the solutions can be increased or decreased based on the efficiencies while keeping in mind the compatibility of the system and the final resins. This parameter can be tweaked alongside the temperature for easier application.

4) *Contact times:* The time of contact of the chemical solution can be changed. It might be possible to decrease the concentration/temperature and increase the time of contact for easier application.

5) *Chemical compositions*: The composition of the chemicals could also be changed, such as using the sulphuric acid medium for MEDOC, Trying to dilute Aqua Regia, etc. These changes would account for the Waste Acceptance Criteria (WAC).

6) *Liquid to oxide layer ratio*: This parameter would allow for changing the amount of solution in the system to try and reduce total volumes used. This means, ideally optimize the volume of the solution to utilize the right amount needed to reach the decontamination targets in terms of dose rates. This will allow for a reduction in total volume used and therefore the volume of waste generated.

The treatment processes will first be applied to pure powders where some factors could be optimized such as temperature, concentration. These processes would then be applied to surrogate stainless steel and Ni-alloy samples, the oxidation of which is being carried out by SORC at the University of Pannonia, as a part of the PREDIS project. Here some more parameters can be tweaked such as contact times, liquid to the oxide layer, etc. These tests will first be carried out in the batch system but later a loop could be implemented to represent the industrial system.

3. Materials and Methods

Oxidized surrogate samples of carbon steel and stainless steel 316 samples were obtained from SORC, a partner in this project. The oxidation process will be detailed in the report from SORC. Inconel alloy samples will be obtained from EDF, which is an end-user group and these samples will be prepared and sent to SORC for oxidization. Pure powders of Ni-Fe oxide and Chromium oxides are being used initially to test the decontamination efficiency. These can be used individually or mixed. The chemicals required for the two selected decontamination techniques include HNO_3(Laboratory-grade ACS reagent, 70%), $KMnO_4$(Sigma Aldrich,≥99% purity), Oxalic Acid(Sigma Aldrich, anhydrous, ≥99% purity), and H_2O_2(Sigma Aldrich, 50 wt.% in H_2O, stabilized) for the CORD process, and HNO_3 (Laboratory-grade ACS reagent, 70%) and $Ce(NO_3)_3$(Sigma Aldrich, ≥99% purity) for MEDOC. A UV source for CORD and an Ozone generator for MEDOC are yet to be obtained. The oxide layers are being characterized before and after treatment using tools such as XRD(D8 Advance, Bruker), Optical Microscope and will also be characterized by SEM, and Raman Spectroscopy. ICP-MS will be used to check the efficiency of the dissolution. An environmental test chamber (Thermotron) is being used to maintain the temperatures required for dissolution and to provide stirring.

4. Results

The oxidized samples received from SORC are being characterized by an optical microscope. The samples are seen below in Figure 7. Each sample is roughly 6 cm in length, roughly 1cm wide, and 2mm thick. A sample of stainless steel 316 was observed under an optical microscope. It was found that the oxide layer was fairly homogenous and contained some large particles with an average size of 1.52 ± 0.59 mm as seen in Figure 8.

Figure 7. *Oxidized metallic samples and one unoxidized sample (right) received from SORC.*

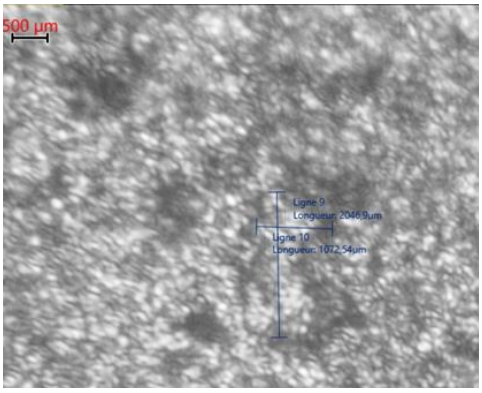

Figure 8. *Zoomed-in image of the 50x magnification of oxidized stainless steel sample.*

These samples are currently being prepared for observation under XRD. The Ni-Fe Oxide powder was characterized using XRD. This was done to help identify the oxides which could be found in the oxidized sample.

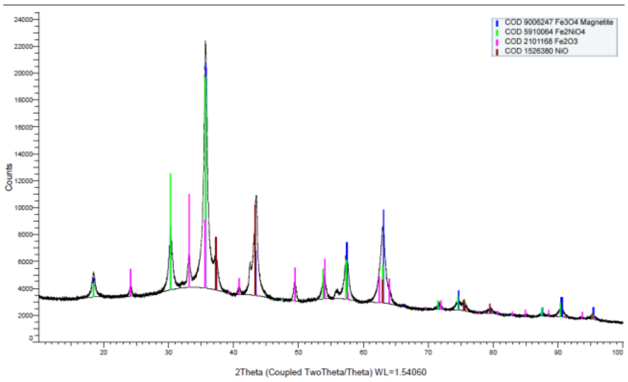

Figure 9. *XRD pattern of Ni-Fe Oxide Powder.*

Fe_2NiO_4 could be identified, but the presence of Fe_3O_4, Fe_2O_3, and NiO could not be ruled out as seen from Figure 9. These are the kinds of oxides that could be found in the actual samples.

The dissolution of Ni-Fe oxide powder is being carried out in oxalic acid under the protocols of the CORD process (Figure 10). This test was carried out using 18mM oxalic acid, with a pH of 1.48 in contact with 2.5 g/L of oxide powder. 3 hours of contact time was used at 80°C with stirring. The efficiency of this dissolution will be tested with ICP-MS by measuring Ni, Fe, Cr.

Figure 10. *Dissolution test of Ni-Fe Oxide powder.*

Similar tests will be carried out by varying the concentration of oxalic acid and the concentration of the oxide powder according to Table 2.

Table 2. *Planned variations in oxalic acid dissolution.*

Oxalic Acid Concentration (mM)	**Oxide powder concentration (g/L)**
18	1.25
18	3.75
12	1.25
12	2.5
12	3.75
24	1.25
24	2.5
24	3.75

5. Conclusions and Way forward

A thorough literature survey of the oxide film was carried out. To summarize this, a multi-layered oxide film was found with a base layer of Cr-Oxide. This layer acts as a barrier layer protecting the base metal. The upper layer is made up of Ni and Fe oxides. It is in these oxide layers, where the radionuclides can be deposited. To dissolve these oxide layers, a literature survey of the existing decontamination methods currently in practice across the globe was carried out. Two processes were selected after consulting with the end-user group and some parameters were identified which could help optimize the processes. The waste generated by these processes is an important factor and some compounds which are usually not easily accepted by the waste disposal authorities will be avoided. The treatment of any waste generated is going to be studied further by another PhD. thesis to start in Autumn 2021 in the WP4 - metallic structure.

Characterization of the oxidized samples received from SORC is currently being carried out. The samples need to be cut into smaller pieces to fit into the sample holders. The samples will be characterized initially using an optical microscope followed by XRD. Following this, the samples are being prepared for characterization using SEM. The dissolution tests with powders are in progress with the plan for dissolution at different concentrations to check for a change in the efficiency. Following these dissolutions, a temperature change is foreseen.

References

[1] ANDRA, “Inventaire national des matières et déchets radioactifs.” 2018. [Online]. Available: https://inventaire.andra.fr/

[2] J. Panter, B. Viguier, J.-M. Cloué, M. Foucault, P. Combrade, and E. Andrieu, “Influence of oxide films on primary water stress corrosion cracking initiation of alloy 600,” *J. Nucl. Mater.*, vol. 348, no. 1–2, pp. 213–221, Jan. 2006, doi: 10.1016/j.jnucmat.2005.10.002.

[3] F. Delabrouille, “Caractérisation par MET de fissures de corrosion sous contrainte d’alliages à base de nickel : influence de la teneur en chrome et de la chimie du milieu,” p. 68.

[4] C. G. Panait *et al.*, “Microstructural investigations of a steam generator tube oxide after zinc injection,” p. 12, 2018.

[5] J. McGrady, “The Effect of Water Chemistry on Corrosion Product Build-Up under PWR Primary Coolant Conditions,” University of Manchester, 2017.

[6] L. Marchetti-Sillans, “Corrosion généralisée des alliages à base nickel en milieu aqueux à haute température: Apport à la compréhension des mécanismes,” e l’Ecole Nationale Supérieure des Mines de Saint-Etienne, 2007.

[7] “New methods and techniques for decontamination in maintenance or decommissioning operations.” IAEA, Jun. 1998.

[8] “Decontamination Handbook,” EPRI, Palo Alto, CA:, TR 112352, Jul. 1999.

[9] R. Riess, S. Odar, and J. Kysela, “Decontamination and Steam Generator Chemical Cleaning,” p. 39, 2009.

6. Decontamination of metallic small and complex geometry items using inorganic self-drying gels

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Abstract

Inorganic self-drying gels have been developed in the nuclear clean-up applications. These gels are spread on the contaminated surface and corrode the substrate down to few microns. This releases the radio-contaminants from the substrate, which are then traped into the gel by sorption. The gel finally dries and fractures into a non-powdery solid, containing the contamination, which can be removed by brushing or vacuum cleaning. Their application by spraying is particularly adapted to large and plane surfaces (walls, floor…) but not for small items having a complex geometry (pipes as an example). In this work, we study a new implementation mode for these gels to treat small and complex geometry metallic objects. Gels are used as a bath and the items are dipped into it to be coated by a layer of gel. This new process requires the development of gel formulations having specific physicochemical properties.

Keywords: Decontamination, gel, stainless steel, pipe, sheet

1. Introduction

For nuclear industry, the decontamination of metallic waste is of high interest to reduce the volume of nuclear waste but also to decrease the cost related to their handling and storage. For that aim, different decontamination technologies have been developed over the years. The two crucial criteria to satisfy are that the decontamination be efficient and the amount of secondary waste produced limited. Inorganic self-drying gels is a decontamination technology developed at the CEA, France [1]. Such gels are composed of mineral colloidal particles (typically silica or alumina) dispersed in a decontaminating solution. Due to their viscoelastic properties, the gel adheres to surfaces and forms a thin layer, which induces a prolonged contact between the surface and the corrosive decontaminating solution. This solution is specifically chosen to attack the substrate down to few microns and then release incrusted contaminants. Finally, the gel dries and fractures into a non-powdery solid trapping the contamination that is readily removable by brushing or vacuuming. The main advantage of this process is that only an inorganic solid is produced as secondary waste. Such gels are particularly well adapted for the treatment of large and plane surfaces because they can be largely spread using existing and commercial spraying devices. However, spraying is clearly not an option for objects with complex geometries (spring-like structures, or those with holes or internal surfaces, etc.). For such items, a solution using thermos-responsive gels in form of bath rather than by spraying has been proposed by Castellani et al. [2]. The contaminated material is immersed in a cold bath of liquid gel, which ensures a perfect coating even if the object's geometry is complex. If the object is cold, the gel remains liquid and flows over the surfaces. If the piece is heated prior to immersion however, the gel's viscosity increases upon contact and remains attached to the surface (see Figure 1). However, such formulations includes thermos-responsive organic compounds, which are not well suited for nuclear applications due to their weak resistance to irradiation.

Figure 1. *Decontamination process of a small items in a bath gel [2]*

In this work, we aim to develop a new process for the decontamination of small and complex geometry items using bath of gels without adding any specific polymer compounds in the gel formulation. For that, we will study in details the relationship between gel formulations, their physicochemical and rheological properties, surface covering and decontamination efficiency. This proceeding presents the first development performed in the frame of the PREDIS project.

2. Materials and Methods

Experiments were performed on model inorganic gels. A first gel was composed of alumina Aeroxide Alu C (Evonik Industries), as a viscosing agent, dispersed in deionized water with a weight ratio of 20 wt % (Gel 1). To formulate a second gel (Gel 2), around 1 wt % of a surfactant, a three tri-block copolymer poly(ethylene oxide)$_{14}$-poly(propylene oxide)$_{31}$-poly(ethylene oxide)$_{14}$ with commercial name Pluronic PE6200 (BASF), was added to the previous formulation.

The dipping experiments were performed using an Ossila Dip-Coater device. Stainless steel coupons were dipped for 1 second in a bath of gel and removed with different speeds from 1 to 10 mm.s^{-1}. The deposited gel mass was evaluated by weighting the coupons before and after the dip.

The wettability of surfactant-water solutions on stainless steel was analysed by measuring the contact angle of a drop of a solution on a stainless steel plate using a Tracker Automatic Drop Tensiometer from Teclis Scientific.

3. Results

The Figures 2a and 2b are photographs of stainless steel coupons after a dip in bathes of Gel 1 and 2 respectively. For Gel 1 (without surfactant), the gel does not adhere on stainless steel and slips on the coupon when it is removed from the bath. However, the Gel 2 (containing a surfactant) leaves a thin layer on the coupon. This phenomenon could be explained by the better wettability of the liquid solution in presence of a surfactant, as demonstrated on Figure 2c. Indeed the contact angle of a surfactant solution drop increases with the surfactant concentration. The surfactant thus improves the wettability of the gel on the stainless steel and consequently allows a better adhesion of the gel on the surface. Moreover, thanks to the gel viscoelastic properties, a gel layer remains attached to the coupon. Comparing these results, the presence of the surfactant in the gel formulation seems to be necessary to have a significant gel coating on a stainless steel surface.

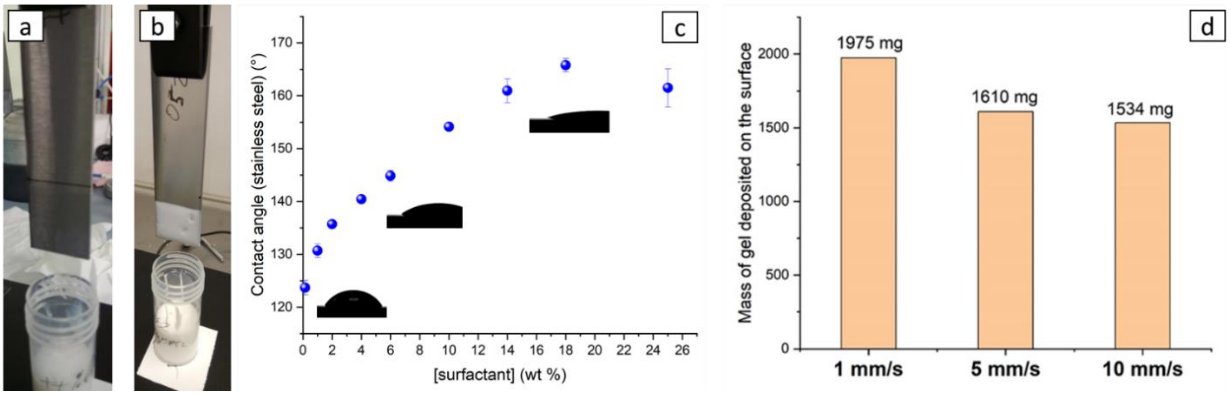

Figure 2. *(a-b) Stainless steel surface after a dip into a bath of model gels without (a) and with (b) surfactant; (c) Evolution of the contact angle of a solution of surfacant in water on stainless steel as a function of the surfactant concentration; (d) Evolution of the masse of gel deposited on a coupon as a function of the withdrawal speed.*

The influence of the withdrawal speed has also been studied using a bath of Gel 2. As reported on Figure 2d, a higher speed of withdrawal leads to a lower mass of gel deposited on the coupon. As the surface dipped into the bath is maintained constant, and if we assume a homogeneous coating, these results are consistent with a decrease of the gel thickness when the withdrawal speed increases. The gel thickness (e) values were estimated using the equation $e = \frac{m}{d.S}$ with *m* the mass of gel, *S* the coated surface and *d* the gel density (calculated at 1.11 g.cm^{-3}) and are summarized in Table 1.

Table 1. *Evolution of the evaluated gel thickness deposited on a suface after dipping in a bath of Gel 2 with different withdrawal speeds.*

Withdrawal speed	1 mm/s	5 mm/s	10 mm/s
Evaluated thickness	≈ 1.2 mm	≈ 1 mm	≈ 0.9 mm

The deposited gel thickness varies from ≈ 1.2 mm for a withdrawal speed of 1 mm.s^{-1} to ≈ 0.9 mm for a withdrawal speed of 10 mm.s^{-1}. The influence remains thus relatively low. Moreover, the gel thicknesses are well adapted for a decontamination operation using inorganics gels. Indeed, for a too thin thickness, the gel will not crack and the secondary solid waste containing the contamination will be difficult to detach and recover [3]. On the other side, if the thickness is too important, the gel will flow down. A thickness around 1 mm is considered as perfect for an efficient decontamination operation [1]

4. Conclusions and Way forward

These first results have demonstrated the deposition of a layer of gel on a metallic coupon after dipping it in a bath of gel. Experiments have been performed on model gels and the presence of a surfactant has proved to be essential to have a thick and homogeneous coating. Moreover, the withdrawal speed also influences the gel layer thickness, which is thinner for higher speed. However, the layer remains thick enough to answer to the process specification.

The next studies will be oriented on the modification of the gel formulations to integrate decontaminating solution. The relationship between the gel rheological properties, the surface wetting and the adhesion of the gel, and the thickness of gel deposited on substrates will be investigated as a function of the gel composition. Then, the corrosion of surrogate coupons will be evaluated after gel drying to highlight the gel decontamination ability.

References

[1] S. Faure, P. Fuentes, Y. Lallot, Vacuumable gels for decontaminating surfaces and use thereof. Patent WO 2007/039598.

[2] R. Castellani, A. Poulesquen, F. Goettmann, P. Marchal, L. Choplin, A topping gel for the treatment of nuclear contaminated small items. Nuclear Engineering and Design, 278, p. 481–490, 2014.

[3] A. Gossard, C. Lepeytre, An innovative green process for the depollution of Cr(VI)-contaminated surfaces using TiO2-based photocatalytic gels. Journal of Environmental Chemical Engineering, 5, p. 5573-5580, 2017.

7. Classification of the metallic radioactive waste streams of the different types of reactors in PREDIS

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Abstract

Waste classification include the quantification of specified radionuclides in the waste materials dedicated for the specific disposal site. The aim of classification of the metallic radioactive waste (MRW) streams is changing together with MRW activity: the higher activity RW (HLW, ILW) needs classification related to radioprotection and best packaging concept, LLW and VLLW needs decontamination and declassification afterwards to meet the WAC of the disposal site. The largest volumes of waste from the dismantling of nuclear installations is mainly be VLLW and LLW [1]. The main aim of the 4.5.1 subtask of PREDIS is to provide a scheme for classification of the reactor materials regarding the level of activation: highly activated, intermediate, low activation metal constructions and non-activated materials in order to facilitate the procedure of decontamination and clearance or declassification. The methodology for characterization of the metallic waste is similar to all reactors and is based on nuclide vector (NV) determination. An essential part of the metallic waste characterization is the separation of neutron activation and surface contamination activity parts to identify the best way of management.

Keywords: metallic waste, nuclide vector, scaling factors

1. Introduction

Waste classification is the major issue of radioactive waste management and disposal strategy and is important for each member state having operating nuclear power plants (NPP) or NPP under decommissioning. Metallic radioactive waste (MRW) in different reactors usually has a wide list of radionuclides of different concentrations. The majority of the NPP waste resulting from decommissioning and dismantling is radiologically unrestricted material i.e. exempt waste. The remaining one-third is the radioactive waste with different activity levels [2]. The MRW has to be collected, segregated, characterized, treated, stored and finally disposed of in special disposal facilities.

2. Description of work and main finding

Following the aim of the 4.5.1 subtask of PREDIS to provide a scheme for classification of the reactor materials regarding the level of activation: highly activated, intermediate, low activation metallic constructions and non-activated materials, the main steps that are carried out to facilitate the procedure of decontamination and clearance or declassification are:

1. Pre-dismantling: classification of MRW using (MCNP6/SCALE6.2) modelling obtaining neutron activation map in the 3D of reactor core and peripheral hardware (experience in RBMK, PWR reactors).
2. Detailed characterization of MRW during dismantling via experimental measurements applying non-destructive and destructive measurement techniques (analysis of samples of surface contamination and activation).
3. Optimized characterization: determination of Nuclide Vectors (NV) for MRW stream. Together modelling and experimental measurements allows separating waste streams to homogeneously activated MRW, mixed (activated and surface contaminated) MRW and surface contaminated metallic waste.

3. Materials

Metal structures are made from various grades of steel and metal alloys during the construction of nuclear reactor. The most commonly used are stainless steel, steel and various metal alloys such as zirconium for fuel rods and assemblies as resistant material to high temperatures and neutron activation. The materials used in the construction of the reactor become radioactive during neutron activation, and can be contaminated with activation products due to corrosion of activated materials and fusion products due to radiation leakage during the normal reactor operation or incident events. All these materials have impurities, the amount of which is regulated during production, and their permissible values are usually indicated in their passports. However, maximum permissible concentrations are often indicated only for main composing chemical elements. All this information is needed for neutron activation calculation in the reactor using deterministic or Monte Carlo codes.

Usually, the assessment of the neutron activation of metallic structures of the reactors is made with the assumptions of the maximum concentrations of impurities according to metal production standards and scientific literature data. The comparison of the calculation with experiment is needed for model validation and allows to reduce conservatism of the waste disposal.

4. Methods

Simulation models can give the neutron flux distribution in a 3D reactor core and evaluation of neutron activation in the reactor materials. With appropriate model, the neutron activation in the nuclear reactor metallic construction materials (reactor pressure vessel, pipelines, fuel channels, reactor internal constructions, and control rods, equipment of low or medium activation) can be determined for different reactors. After validation of the models it becomes possible to classify the reactor materials regarding the level of activation. Furthermore, the nuclide composition in the HLW and ILW is preliminary determined before representative measurement campaign, because usually measurement access is limited due to high dose rates and cost of analysis. For pre-dismantling classification of metallic waste the modeling codes MCNP /SCALE6.2 are used.

The application of scaling factor methodology based on measurement of easy-to-measure key radionuclides (for example, ^{137}Cs, ^{60}Co) and usage of scaling factors determined after sampling and quantitative analysis, allows determination of activity of the difficult-to-measure (DTM) radionuclides. Briefly, the scaling factor method is based on the empirical dependence between specific activities of nuclides in the investigated sample when the main contamination source is the same. Firstly, it is necessary to determine whether such a correlation exists, i.e. whether the scaling factor method is applicable. The activities of DTM nuclides in waste packages are then estimated by measuring the gamma emitting nuclides and applying the scaling factors for the list of required nuclides for disposal site.

5. Results

Radionuclide production and distribution in MRW generated at nuclear reactors (differences for types: PWR, BWR, RBMK, VVER) depends on: composition of different nuclear reactors metallic components (PWR only the reactor building, BWR - also the turbines and the generator, RBMK – fuel/control channels, reactor metal plates etc.), neutron flux, irradiation history and time after reactor shutdown. Due to the structural design of the different facilities (PWR, BWR, RBMK), the radiation control area for MRW is different. Composition of activated radionuclide influences directly the selection of dismantling and other management technologies, which allows the minimization of the volumes of radioactive waste and the cost of management [4]. Besides the activation products inside the construction materials, the concentration of activation products in the surface contamination of the reactor components is due to the corrosion of the reactor materials and the solubility of the radionuclides in the coolant liquid, resulting in transportation inside the primary circuit and deposition on the components. Furthermore, fission products are transported inside the primary circuit and detected in the surface contamination. For that reason, sampling and specific measurements are needed after dismantling of the components to distinguish activation products inside nuclear reactor construction materials and to evaluate the level of contamination.

The activation calculation results is effectively used for the scaling factor determination to couple the easy to measure and difficult to measure nuclides present in MRW. In reality, both the neutron activation and the surface contamination terms are present and contribute to waste activity [4]. Their input to waste composition and corresponding results of activity measurement may vary depending on the reactor operational history. Experimental measurements data of the MRW of different types of reactors are used for analysis and classification of the metallic waste streams.

6. Conclusions

Optimized NV is obtained by analysing and systemizing the information about radioactive metallic waste streams, identifying the optimal list of relevant radionuclides (e.g., selection of Co-60 and Nb-94 for zirconium-niobium alloys), describing inter-correlations between key nuclides and difficult to measure nuclides (Ni-59, Ni-63, actinides) including analysis of the already measured data at the sites and numerical analysis of activation and contamination parts for the waste streams.

Acknowledgements

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We would like to thank the participants in subtask 4.5.1 for the fruitful discussion.

References

[1] L.A. Nieves, S.Y. Chen, E.J. Kohout, B. Nabelssi, R.W. Tilbrook, & S.E. Wilson,: Analysis of disposition alternatives for radioactive contaminated scrap metal. Journal of the Franklin Institute 335 (6), 1089–1103, 1998.

[2] J. Samseth, A. Banford, B. Metcalf, M. Cantone, P. Lietava, H. Peimani, A. Szilagyi, Closing and Decommissioning Nuclear Power Reactors: Another Look Following the Fukushima Accident", UNEP Year Book 2012: Emerging Issues in our Global Environment, pp. 35-49, 2012.

[3] IAEA NUCLEAR ENERGY SERIES No. NW-T-1.18, DETERMINATION AND USE OF SCALING FACTORS FOR WASTE CHARACTERIZATION IN NUCLEAR POWER PLANTS, IAEA, VIENNA, 2009.

[4] V. Remeikis, R. Plukienė, A. Plukis, V. Barkauskas, A. Gudelis, R. Druteikienė, R. Gvozdaitė, L. Juodis, G. Duškesas, E. Lagzdina, D. Germanas, D. Ridikas and S. Krutovcov Characterisation of RBMK-1500 graphite: a method to identify the neutron activation and surface contamination terms, Nuc. Eng. and Design, Vol. 361, p. 1–10, 2020.

8. Characterization and sorting of metallic waste in different management routes

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Abstract

After dismantling of nuclear facilities, radiological characterization of metallic waste, to decide if decontamination is needed (clearance criteria haven't been met and can be met after decontamination) as well as to select the most efficient decontamination process should be carried out. Besides the metallic waste that are classified as ILW, the others should be effectively classified into: LLW to be managed as radioactive waste; VLLW to be decontaminated; EW for release. Characterization is carried out by sampling for scaling factors determination and non-destructive measurements. The objective of this work is the optimization of the non-destructive measurements to reduce crucially the bias. A new non-destructive γ-spectrometry layout is proposed for accurate and fast characterization of metallic waste regarding the activation as well as the surface contamination of the materials. The actual source geometries are studied and compared with simplified geometries. Furthermore, a sensitivity analysis is performed in regard to the characteristics of the metallic waste. For description of the source-detector geometry, Monte Carlo simulations are carried out by using the MCNPX code. The models are validated by volume sources of nominal activity or by the ISOCS software.

Keywords: Radiological characterization, non-destructive gamma spectrometry, bias, Monte Carlo simulations

1. Introduction

After dismantling, in-situ characterization is carried out to classify and package of the generated waste [1] . This is usually achieved by using portable devices to measure dose rate or total counts. Then, the packages that are usually of 1-2 m^3 are monitored by non-destructive gamma spectrometry or plastic scintilators for assessment of the activity and determination of the management route. The measurement uncertainties in this case is high, some times higher than 90%. The uncertainty is mainly due to the density inhomogeneity as well as the geometry (that encompasses the geometry of the measurement package and the positioning of the sources). For localization of the sources and better estimation of radioactivity in waste packages, technique based on gamma camera [2] or system of plastic scintillation detectors [3] are examined. The objective of the present work is to propose a new measurement layout for the non-destructive gamma spectrometry as well as the parameters of the measurement to determine with higher accurancy the activity of the metallic waste for more effective sorting.

2. Description of work

For the proposed non-destructive gamma spectrometry layout, we estimate the efficiency of the measurement for several source geometries (i.e straight & convex pipes, sheet metals and slightly convex surfaces, screws and bolts, flanges and filters, etc) and the results are compared with the results of simplified geometries (e. g., pipes of specific diameter and thickness, homogeneous density distribution etc). Sensitivity analysis against the parameters that influence the measurement efficiency are carried out (e.g. diameter of pipes, thickness of metallic slabs etc). Furthermore, the bias for each source geometry (real or simplified) is determined [4]. The aim of this work is the determination of the optimum parameters of the measurement to achieve significant reduction of the uncertainty while the sensitivity for key radionuclides (Co-60, Cs-137 and in some cases Am-241 but could be also others) is sufficient for acceptable measuring time.

3. Methodology

For determination of the efficiencies, a semi-empirical method based on combination of MCNPX Monte Carlo simulations and gamma spectrometry measurements of nominal volume sources is used. Also, the software ISOCS will be used alternativelly for validation of MCNPX models.

In Table 1 the causes of uncertainty in non-destructive gamma spectrometry measuments for metallic waste characterization as well as the way to cope with them are shown.

Table 1: *The causes of uncertainty in non-destructive gamma spectrometry measurements and the way to cope with them.*

causes of uncertainty	way
a. Density in-homogeneity	Segregation based on the geometries of the metallic segments
b. Activity in-homogeneity (1): different measurement efficiencies for different distances of the source from the detector -	Reduction of the range of the distances/ removal of the detector away from the source
c. Activity in-homogeneity (2): different measurement efficiencies for different angles of the source to the detector -	Reduction of the solid angle of detection/ removal of the detector away from the source
d. Activity in-homogeneity (3): different attenuation of radiation -	Reduction of the source thickness
e. Statistic of the measurement	Sufficient measurement efficiency and acceptable measuring time to achieve MDA ≤ 10 times lower than the clearance criterion

The steps of this work is the following:

1. Selection of the measurement layout and preliminary parameters of the mesurement: segregation of the metallic segments based on their geometries; small amount of metallic waste/ thin source; sufficient amount of metallic waste to be measured/ about 100 kg; removal of the detector away from the source while ensuring that the MDA ≤ 10 times lower than the clearance criterion for acceptable measuring time;
2. Estimation of the efficiencies for several geometries of the metallic segments (i.e. pipes, metallic slab, convex surfaces, screws and bolts, flanges etc). The efficiencies should allow sufficient statistic for 1-2 min measuring time;
3. Determination of bias for several geometries of the segments;
4. Study of the simplified geometries and carry out sensitivity analysis against the parameters that influence the efficiency of the measurement;
5. Drawing of the layout for the non-destructive gamma spectrometry measurement and determination of the parameters of the measurement.

At each step, the simulation models are validated by volume sources of nominal activities or by the ISOCS.

4. Materials and Methods

4.1 Measurement layout

There are two option for source-detector configuration (see Figure 1):

1. The segments are put on a square shallow box 1.2mX1.2m. The measurement is performed by one detector above the box, at the middle.
2. The segments are put on a square shallow box 1.2mX1.2m. The box is divided in four squares and four detectors are above each square at the middle.

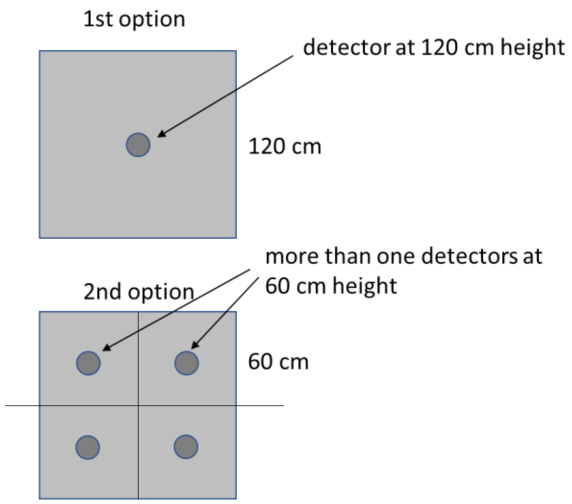


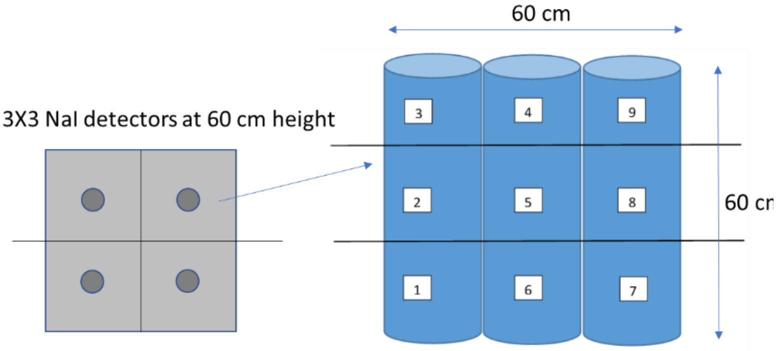
Figure 1. *The two options for source-detector configuration.*

4.2 Preparation of volume sources

Standard source representing metallic segments (e.g. a pipe, or a metallic slab, etc.) with Cs-137 contamination are prepared. A filter paper is subdivided into squares of 9 cm^2 each. In the center of each square, 0.05 ml (uncertainty in volume determination 10%) of Cs-137 acid solution (2 M HNO_3,) of (240 ± 24) Bq/ml is dispensed, using a 0.5 ml pipette. The mean surface activity of the contaminated paper, eventually equalling the surface contamination of the volume source, is 1.30 ± 0.13 Bq/cm^2. The paper is positioned between two plastic sheets and cover the surface of a metallic segment.

5. Results

One representative example of the runs is presented in Figure 2. Four 3X3 NaI detectors are put at 60 cm above the bottom of the shallow box. On each square of 0.6mX0.6m, 3 pipes of 20cm diameter and 0.3cm thickness are put. Each pipe is divided into 3 segments. The efficiency for each square and the corresponding detector is 5.74*10^{-4}. The bias for each segments is shown in the table at the right.



Part	MCNPX efficiency for 662 keV (10^{-4}) Relative Error< 6‰	BIAS (%)
1	5.26	-8
3	5.28	-8
7	5.28	-8
9	5.23	-9
2	5.98	+4
4	5.89	+3
6	5.93	+3
8	5.95	+4
5	6.85	+19

Figure 2. *The geometry of the measurement on the left. The efficiency and the bias for each pipe segment is shown in the table at the right.*

6. Summary and Way forward

The first results showed that by the proposed source-detector/ detectors layout, crucial reduction of the measurement uncertainty can be achieved in acceptable measuring time. The activities of the metallic waste will be determined with higher accurancy and sufficient sensitivity and thus a more effective classification and sorting of metallic waste will be achieved.

The next step of this work will focus on the investigation of simplified geometries as well as on the sensitivity analysis. The aim is to make the implementation of the process for characterization and sorting of metallic waste easier.

Acknowledgements

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We would like to thank all the participants in subtask 4.5.2 for the fruitful discussion.

References

[1] Nuclear Energy Agency. *Radiological Characterization from a Waste and Materials End-State Perspective.* Radioactive Waste Management, NEA No.7373 (2017). M. Duerr, K. Krycki, B. Hansmann, T. Hansmann,

[2] Havenith A., M. Fritzsche, D. Pasler, T. Hartmann, Advanced sectorial gamma scanning for the radiological characterization of radioactive waste packages, Waste Management, Atw. Internat. Zeitsch. fuer Kernen. 6 (3) 160-166 (2019).

[3] Pastena M. et al., A novel approach to the localization and the estimate of radioactivity incontaminated waste packages via imaging techniques, submitted to Elsevier, November 23, (2020).

[4] Savidou A., I.E. Stamatelatos, Non Destructive Technique to Verify Clearance of Pipes. Journal of Nuclear Technology Radiation Protection, Vol. 25, No. 2, pp. 133-137 (2010).

9. Development of new methods for the difficult to measure radionuclides (DTM)

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Abstract

Zirconium 93 is a long-lived fission product and activation product with a half-life of 1.61 × 10^6 years. It is a pure beta emitter that contributes significantly to the total waste inventory over long timescales and then it is considered as a difficult to measure radionuclide (DTM) with a maximum beta energy of 59.5 keV (73%). This radionuclide will be the first DTM to be studied in this work whose objective is to develop new methods of detection, measurement, analysis, and chemical treatments to separate and isolate DTMs in order to accurately determine their activities. The precise quantification of these DTMs will allow reinforcing the results obtained by the scaling factor method. The first results present the optimizations performed for the determination of stable Zr-90 used as a tracer in the chemical separation step on chromatographic resin of Zr-93 from other metal elements (e.g. Ni, Cr, Fe) and tetravalent elements. The tests are performed in solutions containing only Zr and in solution with Zr, Ni, Cr and Fe. Considering the elution media during the separation, HNO_3 5% / HCl 1 mol·L^{-1} medium will be used for the ICP-MS analyses in collision chamber mode. The next step will be to optimize the separation protocols where two types of resins will be tested: UTEVA and TK400. These resins will have the interest to enable the separation of tetravalent oxides and the metallic and interfering elements in particular Fe, Mo and Nb.

Keywords: DTM, zirconium-93, pure beta emitter, low energy, chemical separation, chromatographic resin

1. Introduction

Analyses of disposal site safety are based on criteria that include the activity, half-life and mobility of radionuclides in the environment. These analyses could be refined by characterizing and measuring radionuclides that are difficult to measure (DTM) and for which few methods exist to quantify them. These DTMs occur by surface contamination or neutron activation in materials. In this study, we focus on metallic structures. Table 1**.** shows the major DTMs present in metalic structures. Metallic wastes may be historical or predisposed wastes, or in materials present at the plant sites awaiting treatment. The particularity of these DTMs is due to the total absence of X-ray or gamma photon emissions, or the emission of low-energy and/or low-intensity photons, or the very low activity of these radionuclides in the waste package [1]. Finally, some DTMs are pure beta emitters or alpha emitters making their detection difficult, especially when they are located in the core of the waste package. To access these measurements, the method generally used is the scaling factor or correlation functions which multiplies the activity of a key or reference radionuclide by a factor obtained beforehand [1]. These key radionuclides are generally cobalt-60 and cesium-137 [2]. In addition, there are non-destructive methods such as gamma and X-ray spectrometry which have the advantage of mapping and performing in situ measurements, especially for simple and homogeneous surfaces and geometries. The complexity of these measurements arises when the geometries become complex (e.g. pumps, valves) and the nature and composition of the materials heterogeneous (electrical cable with a plastic sheath and metal wires). It is then necessary to characterize these wastes in order to establish an accurate radiological inventory. In order to obtain more precise measurements of the activity of these DTM, the objective of this work is to develop a radiochemical method to determine their radiological activity present in metallic structures.

Table 1. *Examples of radionuclides difficult to measure in metallic materials [2]*

Be10	**Zr93**	Cl36	**Se79**	I129	Tc99
C14	Nb94	Ca41	Fe55	Ag108m	**Pd107**
Ni63	Sn126	Sr90	Mo93	**Ni59**	Cs135
Sn121m	Sm151	Fe55	Sr90		

2. Description of work

In this study, we will work on the measurement of Zr-93 formed by neutron activation of Zr-92 in the zircaloy cladding (a few ppm) and resulting from the fission reaction of U-235 (20% of the inventory of zirconium fission products) [3-5]. Zr-93 is a high yield fission product (6.35% thermal yield) which is also produced via neutron irradiation of stable Zr-92 (natural abundance 17.15%, σ_{therm} 0.2 barns) used in zircalloy fuel cladding in certain reactor designs [4]. The quantity of Zr-93 produced is of the order of 1200 g $MTHM^{-1}$ for a burn-up of 60 MWd $MTHM^{-1}$ in a pressurized water reactor [3]. It can also be found by contamination on the metal surfaces of structures following the corrosion of the fuel cladding of the primary circuit. Zr-93 is a very long-lived radionuclide ($T_{1/2}$ 1.61 × 10^6 years). It is a pure beta emitter with a maximum energy of 59.5 keV (73%) and decays on the Nb-93m (73%) and Nb-93 (27%) levels [6]. In the storage site, Zr-93 contributes significantly to the activity of long-term nuclear waste repositories and it represents the second largest contributor to the activity of fission products after 1000 years [3,5]. It is therefore important to develop measurement and quantification methods to refine the quantity of Zr-93 and thus its activity in the waste packages. Among the metal structures, steam generators have a large surface area of contamination, especially on the internal surfaces of the tube bundles.

3. Methodology

The measurement of DTM will be performed by means of radiochemical procedures, involving chemical treatment of metallic samples in order to dissolve the contaminated layer formed at the metal surface or diffused within the first few micrometers beneath the surface. Focusing on the detection and measurement of Zr-93, the Figure 1 presents the main steps of the methodolgy.

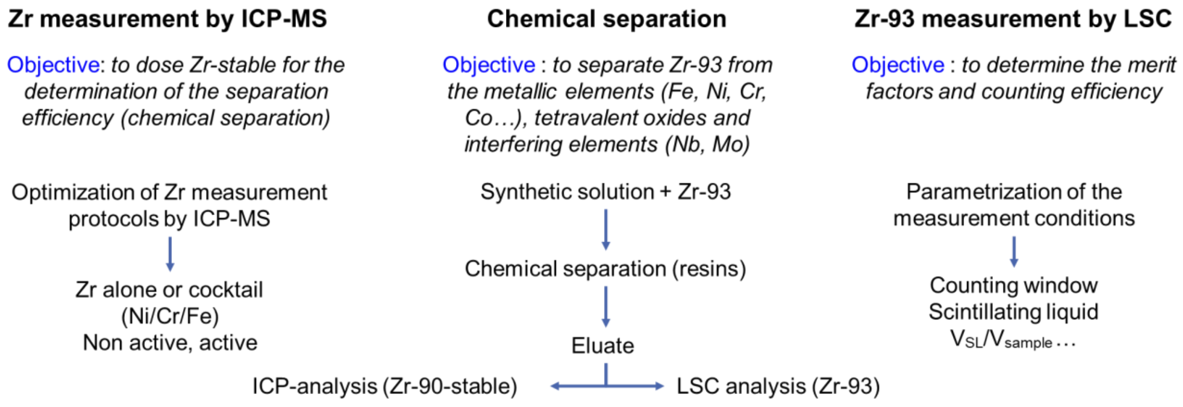

Figure 1. *Methodology employed for the detection, the measurement and the quantification of Zr-93 in metallic structure.*

The first step concerns the optimisation on the measurement of stable Zr by inductively coupled plasma mass spectrometry (ICP-MS). To achieve the objectives, a simple solution fo Zr is prepared in acidic media, which will simulate the solution composition obtained in the second steps after a chemical separation. Two types of solution are prepared: (i) a solution of Zr alone in acidic media, and (ii) a solution mixing Zr and metallic elements contained in metallic structures such as inconel or stainless steel. This step is performed with non-active solution. This optmisation is required notably for the determination of separation yield efficiency during the second step.

The next step is dedicated to the chemical separation of Zr from other metallic elements in aqueous media. A series of chromatographic resins will be used to separate Zr from Ni, Cr and Fe which concentrations are dominant compared to Zr-concentration. The chromatographic resins will be tested first with Zr alone, then in presence of Ni, Cr and Fe. The experiments will be performed with stable isotopes, and with radioactive tracer. The eluats will be measured by ICP-MS to dose the Zr after chemical separation and to determine the extraction efficiency, and by LSC to quantify the activity of Zr-93.

The third step will concern the optimisation of the measurement of Zr-93 by LSC. This step needs to be performed in parallel to the two other steps. A series of samples will be prepared to optimize the measurement conditions: counting window, volumic ratio between sample and scintillation cocktail, duration of measurements, etc. These optmisations will allow to determine the measurement efficiency by performing chemical quenching curve.

The methodology proposed in this work will be complementary and an alternative solution to the analytical method developped by Russel and al. who used an ICP-QQQ to measure the Zr-93 without chemical separation for environemental samples [5,7].

4. Materials and Methods

4.1 Preparation of solutions

Stable zirconium (Zr-90) solutions are prepared from standard solution (SCP Science) in the concentration range 0.02 ppb - 0.7 ppb. The solutions are prepared in various media to evaluate the influence of the acid composition during the detection by ICP-MS. Two series of acidic media are prepared: the concentration range of HCl varied from 5×10^{-3} mol·L^{-1} to 1.5 mol·L^{-1} for two concentrations of HNO_3 fixed at 0.3 mol·L^{-1} (2%) and 0.8 mol·L^{-1} (5%).

To evaluate the effect of metallic elements during the detection and measurement of Zr in solution by ICP-MS, a synthetic solution of Ni, Cr and Fe is prepared. The composition of Inconel 600 is chosen containing 73%-75%wt of Ni, 14%-17%wt of Cr and 6%-10% of Fe. For the experiments, the following concentrations are prepared: [Ni] 0.5 mol·L^{-1}, [Cr] 0.1 mol·L^{-1} and [Fe] 0.07 mol·L^{-1}.

4.2 Solution analysis

The measurements of Zr, Ni, Cr and Fe are performed by ICP-MS (Quadrupole ICP-MS Xseries 2, THERMOELECTRON) in collision chamber mode. All the solutions are prepared in distilled HNO_3 and HCl acidic solutions of high purity. An internal standard solution of Indium-115 is mixed with the solutions for analyses. The quantification limit of Zr is 5.5×10^{-8} mol·L^{-1} with relative uncertainties at 5-10%.

5. Results

5.1 Optimisation of Zr detection and measurement in acidic media

The Figure 2 shows the results of the concentration ratios of Zr recovered in various concentrions of HNO_3 and HCl compared to a reference, corresponding to a commonly used dilution media of HNO_3 2% / HCl 5×10^{-3} mol·L^{-1} in laboratory. In HNO_3 2%, the results show a decrease of the ratio (76% → 68%) when the concentration of HCl increases from 5×10^{-2} mol·L^{-1} to 1.5 mol·L^{-1}. In HNO_3 5%, the ratio is in mean 77.5% with almost no influence of the concentration of HCl.

The dosing of stable Zr-90 by ICP-MS will be performed after a chemical treatment on chromatographic resins of an acidic solution containing metallic elements, tetravalent elements and interferents. This separation will be performed in acidic media, mainly in HNO_3 and HCl solutions. The stable Zr-90 will be used as a tracer to dose the separation efficiency. Therefore, considering the concentrations expected in the eluates after chemical separation (about HCl 1-4 mol·L^{-1} [8,9]) and the minimization of dilution factors to reduce the analytical uncertainties, the measurements of Zr by ICP-MS will be performed in HNO_3 5% / HCl 1 mol·L^{-1}. In this aim, an optimisation of detection and measurment of ^{90}Zr by ICP-MS is a pre-requiste taking into account the concentrations of acids in the eluate and the maximal limits of analytical conditions of the device.

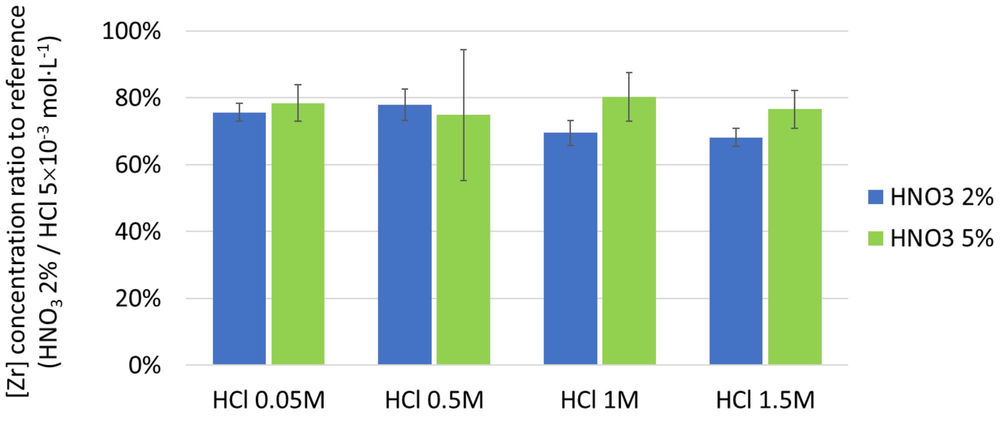

Figure 2. *Distribution of Zr-concentration ratios prepared in HNO_3 5% and HNO_3 2% for a HCl concentration range between 0.05 to 1.5 mol·L^{-1} compared to the reference (HNO_3 2% / HCl 5×10^{-3} mol·L^{-1}).*

5.2 Optimisation of Zr detection and measurement in presence of metallic elements in acidic media

A second pre-requist consists in verifying and optimizing the detection of Zr in presence of metallic elements such as Ni, Cr and Fe, present in non-neglectible concentration in the solution of dissolution of the metal structure. A synthetic solution composed of Ni, Cr and Fe contained in the Inconel 600 matrix was prepared and mixed with a solution of zirconium at 0.02 $\mu\cdot L^{-1}$, 0.20 $\mu\cdot L^{-1}$ and 0.78 $\mu\cdot L^{-1}$.

The Figure 3 presents the nominal concentration of Zr versus the measured concentration in presence of [Ni] 0.5 $mol\cdot L^{-1}$, [Cr] 0.1 $mol\cdot L^{-1}$ and [Fe] 0.07 $mol\cdot L^{-1}$. The results show that there is almost no influence of Ni, Cr and Fe during analysis with a good agreement between nominal and measured values of Zr-concentration. Under these experimental conditions, the limit of quantification is 0.01 ppb. Complementary experiments will be performed by adding other metallic compounds such as Co, Zn, Sb, Cs, etc.

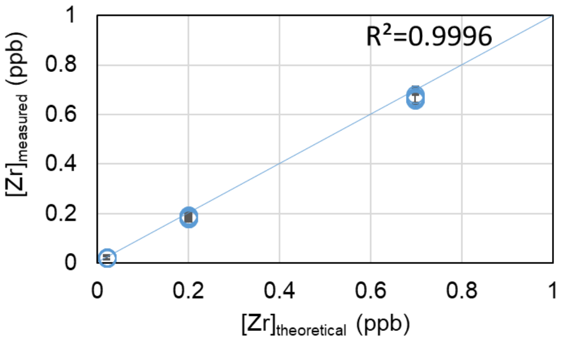

***Figure** 3. Comparison of the Zr-concentration measured by ICP-MS versus the nominal value in a complex acidic media in presence of [Ni] 0.5 $mol\cdot L^{-1}$, [Cr] 0.1 $mol\cdot L^{-1}$ and [Fe] 0.07 $mol\cdot L^{-1}$.*

6. Summary and Way forward

The preliminary studies determined the analytical conditions for the measurement of stable Zr by ICP-MS in presence of metal elements (Ni, Cr, Fe) in the aim to determine the separation efficiency during the chemical separation by resins.

The next step of this study will be the optimisation of chemical separation of Zr with chromatographic resins in aqueous acidic solutions containing interfering metallic elements. In collaboration with TrisKem, two types of chromatographic resins will be tested (UTEVA and TK400 manufactured by TrisKem International) in presence of Zr alone then in presence of metal compounds. The general scheme is presented in Figure 4. UTEVA resin is used mainly to remove tetravalent metallic elements while TK400 will be used to separate Zr from Nb, Mo and Fe [10].

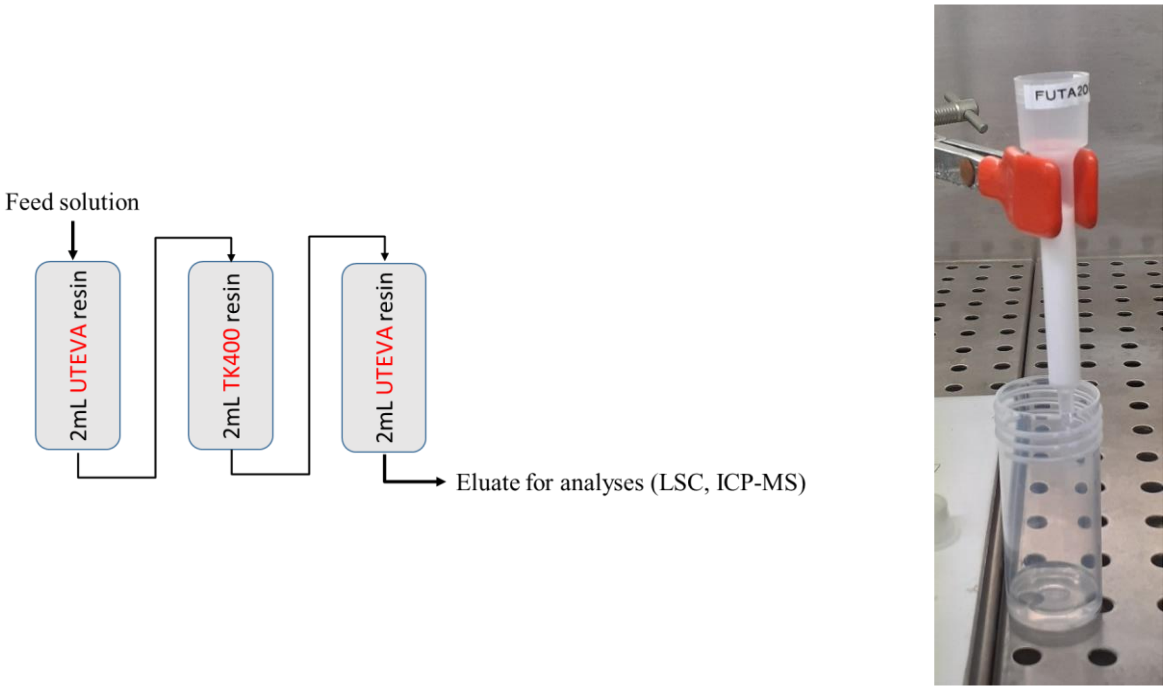

***Figure 4.** Chromatographic resins used for the chemical separation technique intended to apply for the separation of Zr from tetravalent oxides, Mo, Nb and Fe.*

Acknowledgements

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We would like to thank TrisKem company for the collaboration on this project and for providing their expertise and known-how.

References

[1] IAEA. *Determination and Use of Scaling Factors for Waste Characterization in Nuclear Power Plants*. (INTERNATIONAL ATOMIC ENERGY AGENCY, 2009).

[2] Taddei, M. H. T., Macacini, J. F., Vicente, R., Marumo, J. T. & Terremoto, L. A. A. Determination of scaling factors to estimate the radionuclide inventory of wastes from the IEA-R1 research reactor. *J. Radioanal. Nucl. Chem.* **303**, 2467–2481 (2015).

[3] Cassette, P. *et al.* Determination of 93Zr decay scheme and half-life. *Appl. Radiat. Isot.* **68**, 122–130 (2010).

[4] Petrov, P., Russell, B., Douglas, D. N. & Goenaga-Infante, H. Interference-free determination of sub ng kg−1 levels of long-lived 93Zr in the presence of high concentrations (µg kg−1) of 93Mo and 93Nb using ICP-MS/MS. *Anal. Bioanal. Chem.* **410**, 1029–1037 (2018).

[5] Bombard, A. Dosage de radionucléides à vie longue, 93Zr, 93Mo et 94Nb, dans des échantillons issus de l'industrie nucléaire. (Unversity of Nantes, 2005).

[6] LNHB. *Zirconium 93*. *Données Nucléaires* (2013).

[7] Thompkins, H., Russel, B. & Goddard, S. Direct analysis of zirconium-93 in nuclear site decommissioning samples by ICP-QQQ. *Agil. Technol. Appl. Note. P/N5994-1532EN* 1–5 (2020).

[8] Marinov, G. M. *et al.* Determination of distribution coefficients (Kd) of various radionuclides on UTEVA resin. *Radiochim. Acta* **104**, (2016).

[9] Osváth, S., Vajda, N., Molnár, Z., Széles, É. & Stefánka, Z. Determination of 237Np, 93Zr and other long-lived radionuclides in medium and low level radioactive waste samples. *J. Radioanal. Nucl. Chem.* **286**, 675–680 (2010).

[10] Dirks, C., Happel, S. & Jungclas, H. Développement de méthodes pour la séparation sélective du Scandium et du Zirconium pour l'application en radiopharmacie. in *Réunion d'utilisateurs France* (2014).

10. Encapsulation of reactive metals in magnesium phosphate cement-based matrices

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Abstract

Magnesium phosphate cements (MPC) have been proposed to encapsulate aluminum and beryllium nuclear waste in a C-steel drum. Work has been dedicated to the MPC formulation by considering both the mechanical properties and the economical aspect. Indeed, the MPC cost is too high to envisage this type of cement for conditioning the radioactive waste at an industrial scale. First results have shown the impact of the MgO source and the nature of the filler. The behavior of MPC under leaching and irradiation has also been considered to determine their behavior in the storage conditions. During this period, attention has been paid on the methodology and the device for the leaching and irradiation experiments. Aluminum, beryllium and C-steel corrosion are studied in MPC (with a formulation already studied by the CEA) and in solutions mimicking the interstitial solutions of the cements. The results are compared to the ones obtained in commonly used cements in the storage, the ordinary Portland cement or the El-Cabril cement. The set-ups for the electrochemical and chromatographic measurements have been developed. Preliminary results have shown that Al and Al-Mg alloy are only in the passivity zone for the solution containing phosphate ions or for a mortar composed of MPC. This work has also put in evidence the inhibition effect of the boric acid, used as a retarder for the MPC, against the steel corrosion in neutral media (solutions or MPC).

Keywords: magnesium phosphate cement, conditioning matrix, Aluminium, Beryllium, Steel

1. Introduction

The operation and decommissioning of the nuclear facilities generate a large volume of radioactive metallic waste. Concrete encapsulation is one strategy to manage the low- and intermediate-level wastes (LLW and ILW) by isolation them from the environment. The major risk of this type of confinement is the aqueous corrosion, resulting in hydrogen release. The eligible H_2 amounts in the storage site, fixed by the radioactive waste managers, correspond to the concentration of the explosive limit or to the pression increase, which can lead to the damage of the package and so the loss of the radioactivity confinement. The chemical diversity of nuclear metal waste requires an adaptation of the conditioning matrix nature. The reactivity of the metal has to be as low as possible to limit the production of H_2. In specific pH range, a protective layer can be formed at the metal surface and can limit its corrosion. As there is a large diversity of metallic waste, a wide variety of chemical behaviour is expected. It is then primordial to be able to propose new conditioning matrix.

The high basicity of matrices based on Portland cement is an obstacle for conditioning aluminium. According to thermodynamics, Al is oxidized into $Al(OH)_4^-$ or AlO_2^- in basic media. [1] Alternative cementing systems which have pore solution pH close to the neutrality may be beneficial for Al waste storage. This is attributed to the protective oxide layer which is stable in the pH range 4 – 9. It has already been demonstrated that the use of Magnesium Phosphate Cements (MPC) can significantly decrease the Al corrosion rate. [2-4]

There is also a need for beryllium waste management, as this metal forms the heart of the Belgian Reactor 2 and the main plasma facing for the first wall of the tokamak and the neutron multiplier in the breeding blanket of the fusion facilities under study. The literature on the behaviour of beryllium in cementitious media is really scarce. [5] According to the thermodynamic data, Be would be protected against the corrosion from neutral to basic media. [1, 6]

Task 6 is then focused on the management of LLW and ILW waste by proposing MPC as alternative systems to the conventional Portland cements. The aims are: (1) the optimization of the MPC formulation by considering the physical properties and the economical aspect, (2) their behaviour under storage conditions, in particular the impact of leaching and irradiation, (3) the reactivity of Al, Be and the steel drum in contact with MPC.

2. Description of work and results

2.1 MPC formulation

The process to prepare MPC is based on a reaction between burnt MgO, potassium dihydrogen phosphate (KH_2PO_4) and water leading to the precipitation of the main reaction product, which is magnesium potassium phosphate hexahydrate (k-struvite: $MgKPO_4.6H_2O$). Various composites (fly ash, blast furnace slag, wollastonite) are also added to improve the mechanical strength and chemical resistance. Although MPC have been studied previously, there has been no systematic investigation to identify the raw materials (MgO, phosphates, filler) and to define the formulation for producing suitable matrices for nuclear waste conditioning.

A formulation has been proposed as a reference one to begin all the studies undertaken in the task 6 (Table 1). This formulation was optimized by the CEA for the Al encapsulation. In this formulation, the cement is composed of an equimolar of MgO and KH_2PO_4 mixture, and the mass ratio MgO/KH_2PO_4 is equal to 0.3. The used magnesium oxide is a hard burnt MgO, with a high purity (98.3%). To prepare the MPC mortar, sand and fly ash are added in an amount equivalent to the mass of cement (MgO + KH_2PO_4). Boric acid (2 wt.% cement) is added as a retarder, and the ratio water/cement is equal to 51 wt.%. With this high quality of MgO source, the fluidity and workability of the paste were good and the setting occurred after 24 h.

***Table 1**. MPC formulation defined as a reference for all the studies (mass of components are expressed to obtain 1 L of cement mortar).*

Reference starting reagents	Mass (g)	Mass ratio reagent/($MgO+KH_2PO_4$)
MgO (MAGCHEM 10CR, hard burnt 98.3 wt.%)	131.39	-
KH_2PO_4 (KristaTM, 98 wt.%)	443.58	-
Sand MI 0.1/1.2 (Sibelco, 99,3 wt.% SiO_2)	574.97	1
Fly ash (class F, low CaO content)	574.97	1
H_3BO_3 (VWR)	11.50	0.02
H_2O (distilled wáter)	293.24	0.51

Three other MgO sources have been tested (Table 2): dead burnt MgO (83%, Impalmag), calcined MgO (87%, MCB100) and semi-calcined MgO (60%, PC8) (all of them supplied by Magnesitas Navarras SA). For dead burnt MgO (Impalmag), the workability was poor for a water/cement ratio of 0.3 and good for a ratio of 0.4. For a MgO/KH_2PO_4 mass ratio of 0.3, no setting was observed after 24h. The paste prepared with burned MgO (MCB100) was discarded because the mixture was too reactive, the reaction was highly exothermic, the setting was too fast and the workability poor. A good workability was found for paste prepared with semi-calcined MgO (PC8). However, no setting was observed after 24h.

***Table 2**. Studied MPC formulations (pastes) by changing the MgO source and with a MgO/KH_2PO_4 mass ratio of 0.3.*

	Magchem	Impalmag	MCB100	PC8
Mass of MgO (g)	24	20	20	20
Mass of KH_2PO_4 (g)	81.02	67.52	67.52	67.52
Mass of fly ash (FA) (g)	105.02	87.52	87.52	87.52
Mass of H_2O (g)	42.01	35	35	35
Mass of H_3BO_3 (g)	1.44	1.75	1.75	1.75
$H_2O/(Mg+KH_2PO_4)$ wt.%	0.4	0.4	0.4	0.4

FA/($MgO+KH_2PO_4$) wt.%	1	1	1	1
MgO/KH_2PO_4 wt.%	0.296	0.296	0.296	0.296
H_3BO_3/($MgO+KH_2PO_4$) wt.%	0.02	0.02	0.02	0.02

Additional tests were also performed with a MgO/KH_2PO_4 ratio of 0.5 (Table 3) by changing the MgO source and the amount of water, fly ash and boric acid. [7]

Table 3*. Studied MPC formulations (pastes) with a MgO/KH_2PO_4 mass ratio of 0.5.*

	Impal.	**Impal.**	**PC8**	**PC8**	**Impal.**	**Impal.**	**PC8**	**PC8**	**MAG.**
MgO (g)	24	24	33.3	33.33	24	24	33.3	33.3	24
KH_2PO_4 (g)	48	48	66.66	66.66	48	48	66.66	66.66	48.8
FA (g)	-	51.84	-	71.99	-	-	-	-	72.8
H_2O (g)	28.8	28.8	40	39.99	14.4	14.4	20	20	29.12
H_3BO_3 (g)	1.44	1.44	2	2	-	0.72	-	0.99	1.45
H_2O/($Mg+KH_2PO_4$)	0.4	0.4	0.4	0.4	0.2	0.2	0.2	0.2	0.4
FA/($MgO+KH_2PO_4$)	-	0.72	-	0.72	-	-	-	-	0.72
MgO/KH_2PO_4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.49
H_3BO_3/($MgO+KH_2PO_4$)	0.02	0.02	0.02	0.02	-	0.01	-	0.01	0.02

The pastes prepared with the MgO source from Magchem (Supplier Martin Marietta Magnesia Specialties) with the highest quality (see Table 2 and 3 for the formulations) have been characterized by XRD after 7 and 28 days of curing time (Figure 1 and 2). The higher initial MgO content, the highest presence of MgO in the paste. We can observe the formation of a better crystallised K-Struvite with the increasing of curing time (from 7 to 28d). The main reaction product is the K-struvite (s) and the secondary reaction products are: unreacted MgO, periclase and rests of mullite (m), quartz (q) and Fe_2O_3 (h) from the fly ash.

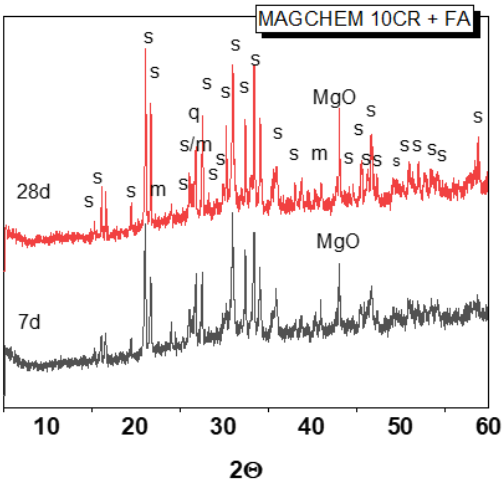


Figure 1. *XRD diffractogram for the paste prepared with the MgO source from Magchem (98.3%) and a MgO/KH_2PO_4 mass ratio of 0.3 after 28 days of curing (s: K-Struvite (COD 9010847); q: quartz (COD 9011492); m: mullite (COD 9001567); MgO (COD 9006456)).*

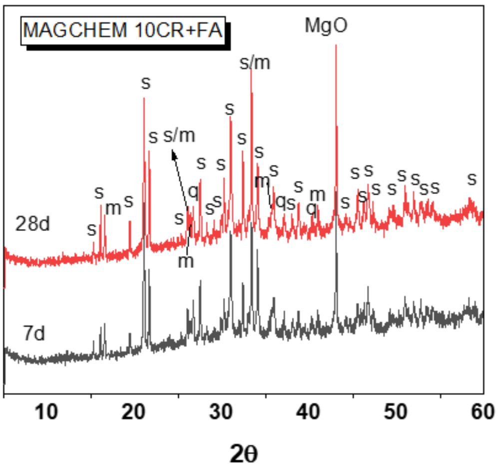


Figure 2. *XRD diffractogram for the paste prepared with the MgO source from Magchem (98.3%) and a MgO/KH_2PO_4 mass ratio of 0.5 after 28 days of curing. (s: K-Struvite (COD 9010847); q: quartz (COD 9011492); m: mullite (COD 9001567); MgO (COD 9006456)).*

The work is now focused on the mechanical (depending on the type of curing), chemical and mineralogical characterisation of selected cement pastes. The substitution of fly ash by pumice powder or also alternatives are also planned.

2.2 Optimization of the MPC cost

Most of the raw materials used for study on MPC are either of high purity (phosphates or the retarder), either from a few providers (the dead-burned MgO). The use of such raw materials is understandable for investigating a novel cement matrix and its applications, but from an industrial point of view, this can lead to an excessive price for the metric ton. While results have already shown the interest of using MPC for Al waste encapsulation, it is primordial to optimize their cost to consider them at an industrial scale.

A simulation approach has been adopted. An Excel spreadsheet has been developed to compute the mass and the price of each reagent in order to identify the most sensitive parameters to the overall price. Sourcing of MgO (from the price point of view) showed that magnesia price can slightly be lowered, but we do not expect to exceed 10%. This can have an impact only on high Mg/P formulations. The MPC price depends on the KH_2PO_4 and borax source but within the given technical criteria it will further allow optimization. Cement paste replacement with filler is one of the most promising development axes from the pricing point of view. The reference formulation is already optimized, with a filler/cement ratio equal to 2. Still, it is hard to believe that one can go further than a ratio of 3. Even thus, it can allow an important price optimization, at least 15%. Function of results, after all the raw material prices were studied (cements, fillers and retarders). Formulations will be proposed and tested, aiming high hydration, similar strength to the reference and long-term durability.

An experimental approach has also been undertaken. Keeping the same MPC formulation reported Table 1, the influence of the nature of the filler has been studied. The density and the compressive strength have been measured for three filler natures: fly ash, blast furnace slag or a half of fly ash and a half of blast furnace slag. The results reported Table 2 show that both density and compressive strength is increased by replacing fly ash by blast furnace slag.

***Table 4**. Density and compressive strength values according to the nature of the filler in the MPC.*

Filler	**Density (g/cm^3)**	**Compressive strength after air curing (MPa)**		
		7 d	14 d	28 d
Fly ash	1.9	8	10	15
Blast furnace slag	2.1	16.5	18.8	21.6
½ fly ash + ½ blast furnace slag	2.0	9.6	12.8	17.2

2.3 Behaviour of MPC under leaching

Information on the behaviour of MPC materials under leaching by alkaline solutions is scarce. Most data are relative to materials with high Mg/P ratio and / or prepared using $(NH_4)H_2PO_4$ instead of KH_2PO_4. Amorphization of K-struvite can be expected at high pH, as well as porosity increase. The objectives of the leaching studies are twofold: (1) assess the behaviour of MPC pastes / mortars under leaching by demineralized water (reference) and by an alkaline solution representative of the pore solution of conventional concrete placed in the near field of the cemented waste packages; (2) understand and model the degradation processes of the MPC matrix under well-controlled conditions. These results should help assessing the extent of degradation of the material as a function of time and pH.

Two experimental approaches will be used:

- “practical” approach, using ANSI ANS 16.1 test: The leachability index will be calculated from the diffusivities of the different species released in solution. The results obtained for the different MPC formulations will be compared between each other, and to conventional cement-based matrices.
- ‘fundamental” approach: Leaching will be performed under dynamic and well-controlled conditions (pH maintained constant, renewal of the leaching solution, controlled atmosphere and temperature). Both the composition of the leachates and of the solid (from the leached surface to the sound core) will be characterized as a function of time. These results will be used as input data for reactive transport modelling. The first step, which is to build a consistent thermodynamic database containing all the relevant phosphate minerals and aqueous species, has been completed. This database will then be used with the Hytec code. In this code, transport and chemistry are coupled through a sequential iterative algorithm. Moreover, the effective diffusion coefficients change when mineral precipitation or dissolution modifies the local porosity. A modified version of the Archie’s law will be used in a first attempt at modelling the feedback of chemistry on mass transport.

2.4 Behaviour of MPC under irradiation

The literature on the behaviour of MPC under irradiation is relatively scarce. [8-11] Water radiolysis from pore solution and hydrates must be considered for the conditioning of radioactive waste in cement materials, since hydrogen is produced. Therefore, its ability to withstand representative levels of irradiation has to be evaluated carefully to validate the use of such a matrix and its compliance with WAC. The samples will be irradiated by using either Cs-137 or Co-60 gamma-emitting sources characterized by different dose-rates up to relevant absorbed doses.

The installation at IMT and POLIMI will allow several studies on irradiated samples, such as:

- The analysis by gas chromatography of H_2 produced during the radiolysis of the cement.
- The determination of the mechanical properties at the macroscopic scale (elastic, plastic, creep, strength) and at the nanoscale (local hardness, elastic, topography).
- The characterization, structure and composition, of the samples by TEM, SEM, µRaman, FTIR and XRD.

The leaching properties of irradiated solids (gas and solution analyses via gas/liquid chromatography, high-resolution ICP-MS, radiochemical analyses, etc.) will also be considered.

2.5 Al corrosion

The aim is to confirm the possible use of MPC as matrices for Al waste encapsulation. The aim is to determine the Al corrosion mechanism and kinetics as a function of the formulation and the Al grade, Al metal or Al-Mg alloys, and compared the results to the ones obtained in Portland based cements. This study is carried out by electrochemistry (Corrosion potential, Cyclic voltammetry, Linear polarization curve and Electrochemical impedance spectroscopy) and gas chromatography. The pH of the media was also evaluated.

The set-ups for electrochemical and chromatographic measurements have been developed. For the electrochemical experiments in mortars, pseudo-reference electrodes (Pt, TiO_2 and MnO_2) have been selected and calibrated against classical reference electrodes (saturated calomel electrode or Ag/AgCl electrode).

Preliminary studies have been focused on the variation of the Al and Al-Mg alloy corrosion potential in different pH and ions type solutions, in simulated binder pore solutions (filtrated suspensions) and in different mortars (MPC, CEM I and CEM IV). The pH evolution of the solution or the cement pastes have also been followed to be able to report the results on a potential – pH diagram for Al. Al is only in the passivity zone for the solution containing phosphate ions or for a mortar composed of MPC (Fig. 3 and 4). The results also confirm that Al and Al-Mg are in the passivity zone when they are encapsulated in a MPC reference mortar (Fig. 5).

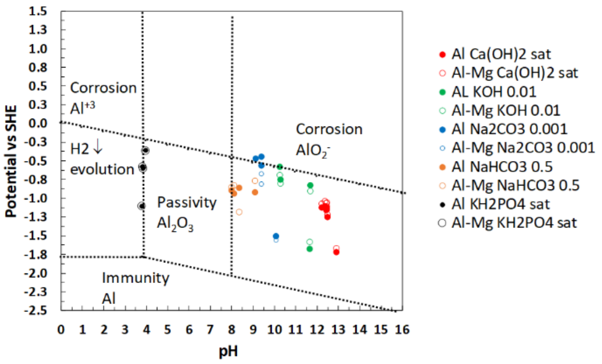


Figure 3. *Stability diagram of Al in solutions of different compositions, as a function of the potential and the pH.*

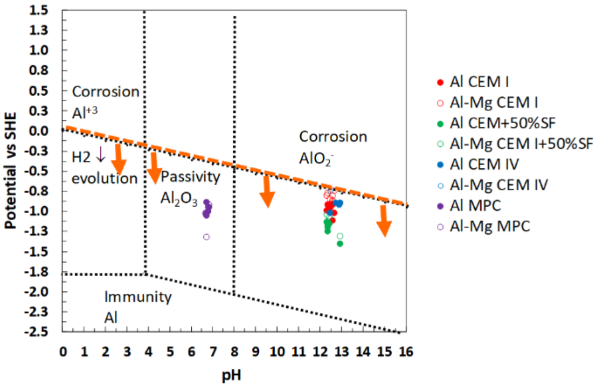


Figure 4. *Stability diagram of Al in simulated binder pore solutions of different compositions, as a function of the potential and the pH.*

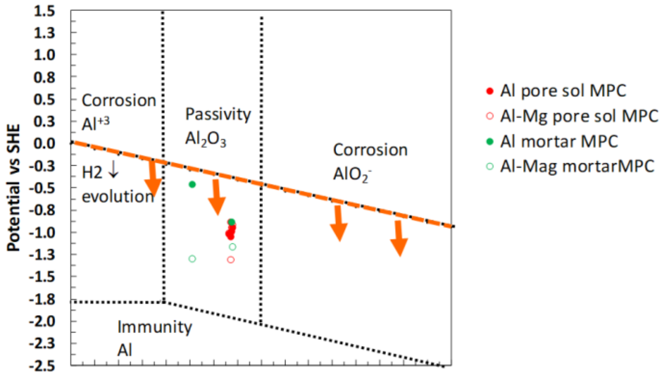


Figure 5. *Stability diagram of Al and Al-Mg in MPC reference mortar, as a function of the potential and the pH.*

An Al-Mg3 alloy corrosion rate of 5.28 mm/y has been evaluated in saturated Portlandite solution by potentiodynamic polarisation, from the Tafel slope (Fig. 6). The Al corrosion rate has also been evaluated in solution from neutral to highly alkaline solutions, by gravimetric solutions (Fig. 7). The results confirm that Al is protected against the corrosion until pH 11, while it is highly corroded at pH higher than 12.

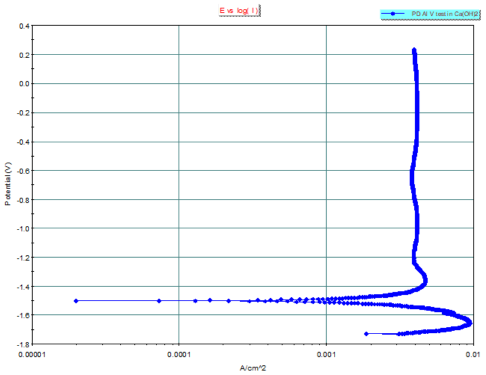


Figure 6. *Potentiodynamic polarization (+250mV up to +600mV/SCE) on Al-Mg3 electrode in Portlandite solution, at a scan rate of 0.5 mV/s.*

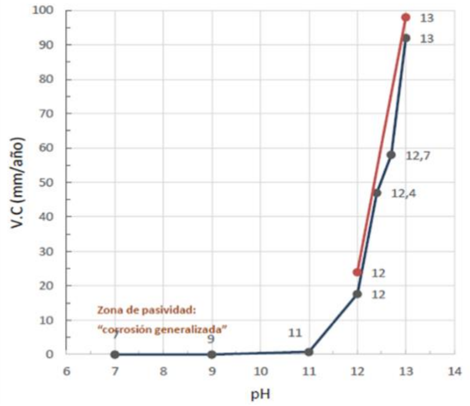


Figure 7. *Corrosion rate of Al, determined by gravimetry, in aqueous solution as afunction of the pH.*

The composition of the synthetic OPC solutions for future study on the Al corrosion under leaching conditions have been determined (Table 5 and 6). The Al corrosion will be studied in these two solutions.

Table 5. *Composition of the leaching solution in the case of a package made of the CEM II BL 32.5 concrete*

Ca^{2+}	579 mg/L
Mg^{2+}	<1 mg/L
K^{+}	116 mg/L
SiO_2	0.6 mg/L
Na^{+}	32.1 mg/L
Cl^{-}	<5 mg/L
PO_4^{3-}	<0.5 mg/M
SO_4^{2-}	<5 mg/L
Al	0.7 mg/L
Fe	<0.02 mg/L
pH	12.4

Table 6. *Composition of the leaching solution in the case of a package made of the El-Cabril mortar CEMI SRS 42.5*

Ca^{2+}	719 mg/L
Mg^{2+}	<0.5 mg/L
K^{+}	102 mg/L
SiO_2	0.3 mg/L
Na^{+}	40.6 mg/L
Cl^{-}	<2 mg/L
PO_4^{3-}	<0.5 mg/M
SO_4^{2-}	<2 mg/L
Al	0.4 mg/L
Fe	<0.02 mg/L
pH	12.4

2.6 Steel corrosion

Since steel drums are widely used containers for cemented waste, the objective is to determine the steel reactivity in contact with MPC used as matrix for Al waste encapsulation. It is important to evaluate the H_2 release by aqueous corrosion and the drum degradation by reaction with additives or impurities in the MPC.

MPC have been tested as anti-corrosive coating on C-steel. [12] The coating increases the steel corrosion resistance and dissolved phosphate ions further enhance the steel protection. The literature on the steel corrosion in contact with MPC concerns mainly the development of reinforced concrete. [13-15] The studies revealed that MPC can be used as an alternative for the OPC. The steel passivity in the MPC increases with increasing M/P ratio. The formation of iron phosphate made additional contribution to the steel protection.

The first studies have been focused on the role of boric acid on the steel reactivity. The experiments have been carried out in solution at pH 8, which is the pH of MPC after several days. The gravimetric analysis clearly shows a linear loss of steel mass at pH 8 and almost none variation with boric acid (Fig. 8). Moreover, the steel open circuit potential is lower in absence of boric acid than in presence of this acid (Fig. 9). The steel is then highly corroded in solution at pH 8, while the steel corrosion is inhibited in presence of boric acid.

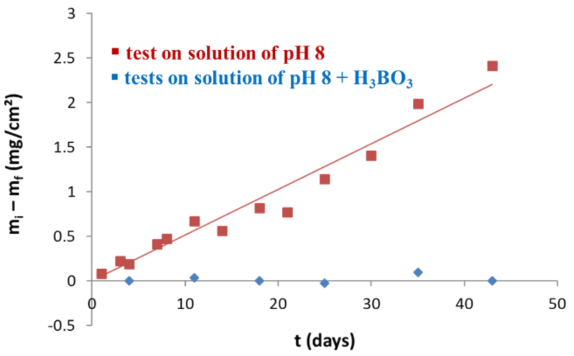


Figure 8. *Variation of the steel mass as a function of time immersion in a pH 8 solution without or with boric acid.*

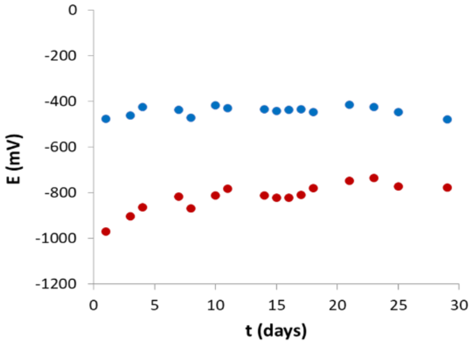


Figure 9. *Variation of the open circuit potential of steel with the time immersion in a pH 8 solution without or with boric acid.*

The steel corrosion has also been studied in MPC. The OCP of steel in MPC is lower in absence than in presence of boric acid during the first ten days, while it remains at an almost constant value with and without boric acid for the rest of the immersion duration (Fig. 10). The electrochemical impedance spectroscopy put in evidence a more capacitive behaviour, like an inert electrode, for the steel immersed in a MPC containing boric acid than in MPC (Fig. 11). All results suggest that boric acid has an inhibition effect against the steel corrosion.

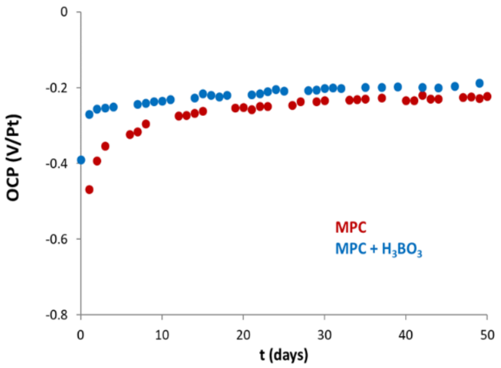


Figure 10. *Variation of the steel open circuit potential with the time immersion in MPC without or with boric acid.*

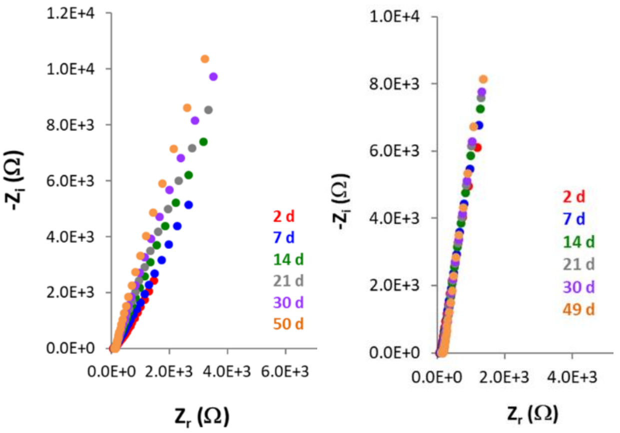


Figure 11. *Nyquist diagrams recorded with a steel electrode as a function of time immersion in MPC without or with boric acid, at OCP, from 10^5 to 10^{-1} Hz.*

The work is now focused on the determination of the steel corrosion mechanisms and kinetics in MPC depending on the formulation.

2.7 Be corrosion

Experiments and protocol have been defined to study the behaviour of Be embedded in MPC and, for comparison, in Ordinary Portland Cement (OPC). Leaching experiments are also planned in solutions mimicking OPC- and MPC-pore water for investigating the main factors affecting the Be corrosion.

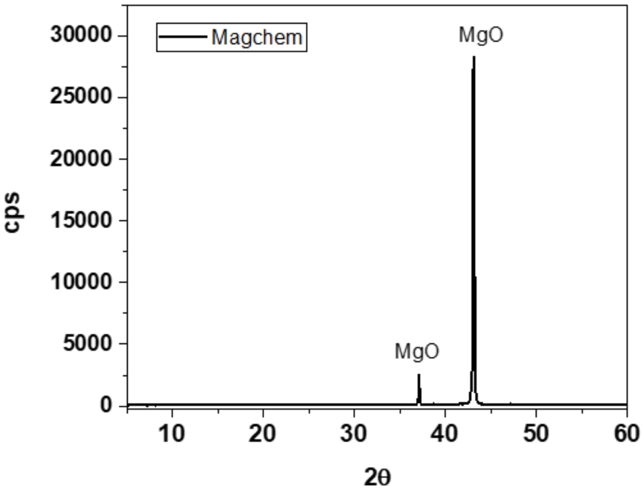
3. Materials and methods

3.1 Chemical reagents and metals

MgO sources:

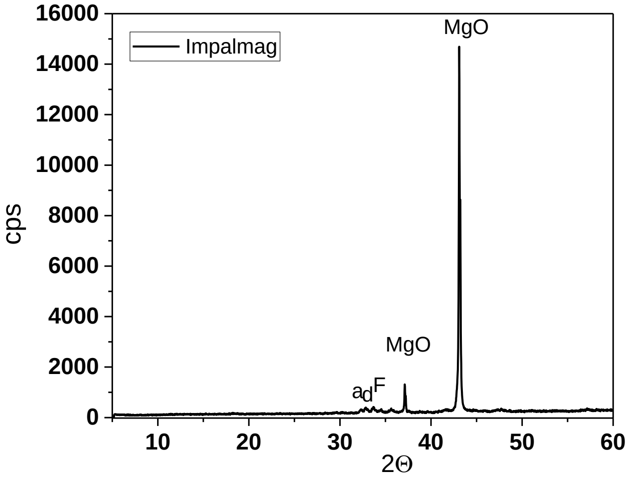
MAGCHEM

Hard Burnt MgO
98.3 % MgO (COD 5000225)



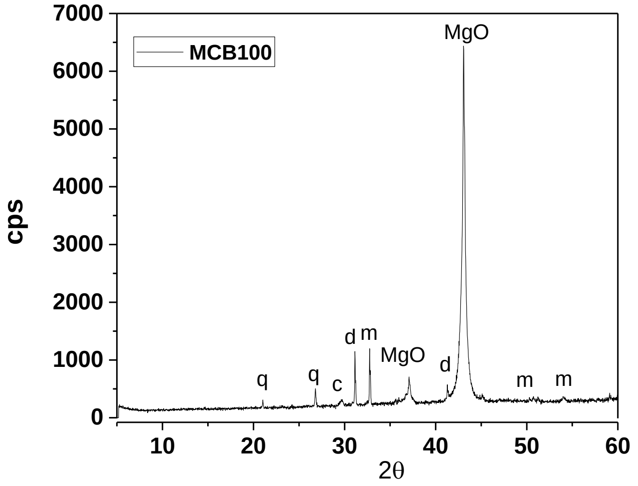
IMPALMAG

Dead Burnt MgO
83% MgO (COD 1011117)
Minor components: Dolomite (d) (COD 9000887), aragonite (a) (COD 9016232), Fe_3O_4 (F) (COD 1526955)



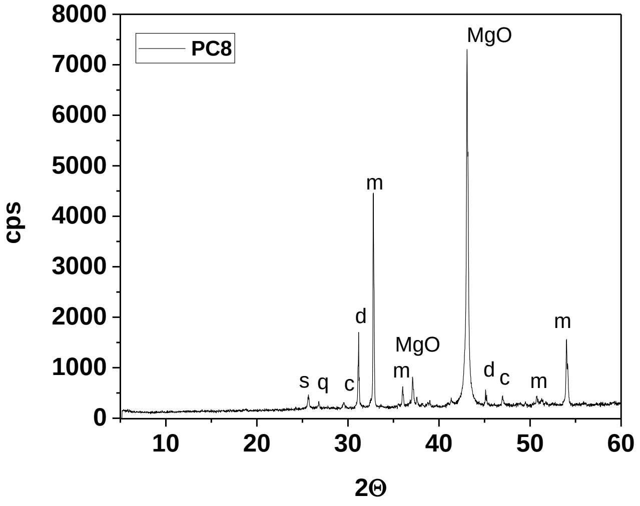
MCB100

Calcined MgO
87 % MgO (COD 9006747)
Minor components: Dolomite(d) (COD 5000116), calcite (c) (COD 9016706), magnesite (m) (COD 9000096), quartz (q) (COD 1536389)



PC8

Semicalcined MgO
60 % MgO (COD 9006796)
Minor components: Dolomite (d) (COD 9004932), calcite (c) (COD 9014415), magnesite(m) (COD 9000380), anhydrite (s) (COD 9004096, quartz (q) (COD 9013321)



Metal composition

Al grade: Al metal (99.5%) and Al-Mg alloy (2.6, 3 and 3.6).
Be grade used at SCK CEN: S-200-F, metallic beryllium rods (not irradiated) from the BR2 1980's campaign. As Be is a highly toxic reagent, the experiments have to be carried out in an isolated zone (glove bag or box).
Steel grade: S235JR.

3.2 Leaching experiments

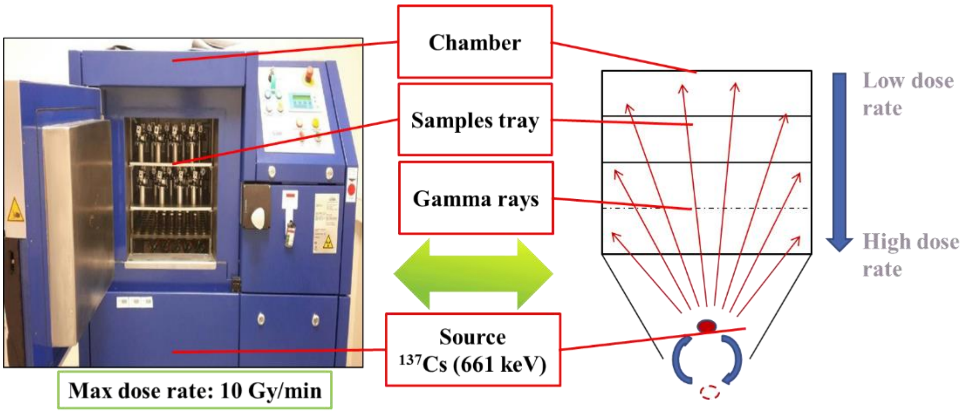
Static tests:
The ASTM standard ANS 16.1 "Measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure" will be applied on the reference and the optimized formulations MPC mortars. The specimens will be immersed in deionized water at 20°C. The leaching solution will be renewed after increasing periods of time.

Dynamic tests:
The reference MPC paste will be immersed in the leaching solutions, deionized water (pH 7, reference) or alkaline solution (pH ≈ 13.2) mimicking the pore solution of conventional concrete present in a repository. The external conditions will be maintained as constant as possible (20°C, N_2 atmosphere, constant pH by automatic addition of acid or base – renewal of the leaching solution when the amount of acid or base exceeds 1% of the total volume of leachate).

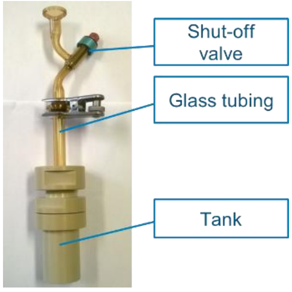
The leachates will then be analysed by ionic chromatography and ICP-AES and the post mortem specimen will be characterized by XRD, TGA and SEM-EDX and 31P MAS-NMR.

3.3 Irradiation experiments

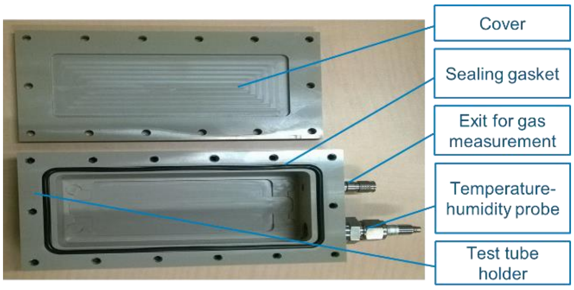
The irradiation device at IMT that will be used is a Cs-137 gamma source. Dose rate mapping inside the irradiator has been studied in an earlier project using experimental and Monte Carlo simulation.



Two different cells can be used according to the sample form (powder or cement). We will study the evolution of the chemical, physical and mechanical properties of the irradiated cement. Leaching of the irradiated cement will give insights on the chemical stability of the cement. The used reactors will also allow the analysis of gas produced by the water radiolysis process.



Irradiation cell for powdered sample

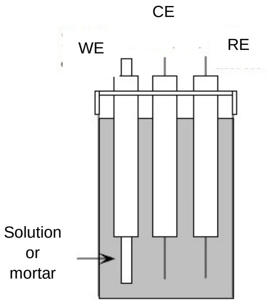


Irradiation cell for cement specimens

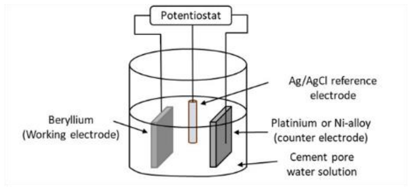
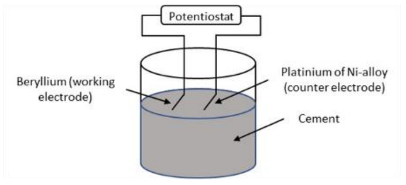
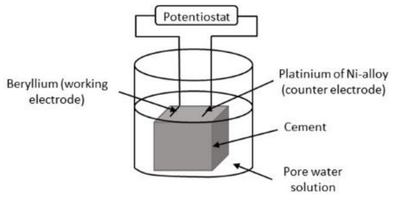
Electrochemical experiments

For Al and steel corrosion studies, a similar electrochemical set-up is used:

WE: working electrode, Al or steel
CE: counter electrode, Pt
RE: reference electrode, SCE, Ag/AgCl, Pt, Mn, Ti

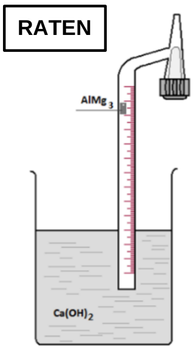
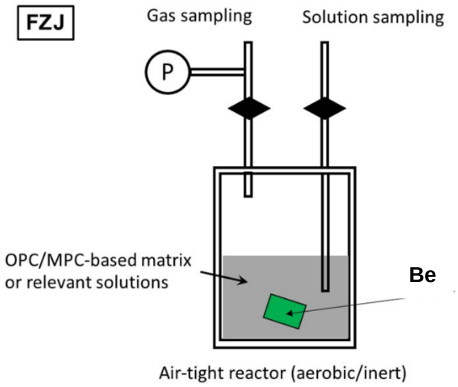
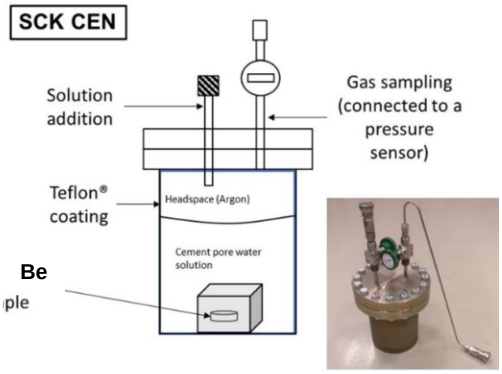


For electrochemical measurements on beryllium, three different cells will be used according to the experimental conditions of the studies:

		
Be in representative cement pore solution	Be embedded in OPC or MPC	Study of the cement resaturation

Analysis by chromatography

Three devices have been developed for the analysis by gas chromatography:

RATEN 	**FZJ** 	**SCK CEN** 

4. Conclusions

Magnesium phosphate cements have been studied to propose them as a matrix for the aluminium and beryllium waste conditioning. For that purpose, work has been done on the formulation by testing different MgO sources (different qualities and different modes of calcination) and different fillers (fly ash, blast furnace slag, pumice powder). The MPC mortars have been characterized to determine their mechanical properties. The economical aspect is also considered since their cost is too high for an industrial scale use. The magnesia price can be lowered but no more than 10%. Cement paste replacement with filler seems a more promising way to decrease the cost. Work has also done to define the methodology and the devices for the leaching and the irradiation studies. The set-ups for the electrochemical and chromatographic measurements have been developed for the corrosion of Al, Be and steel-drum studies. Preliminary results have shown that Al and Al-Mg alloy are protected by a passivation layer only in solutions containing phosphate ions or in MPC mortars. The study has also put in evidence that the boric acid, used as a retarder for MPC, is an efficient corrosion inhibitor for the C-steel in neutral media (solution or MPC).

References

[1] M. Pourbaix, Atlas des équilibres électrochimiques, Gauthier-Villars & Cie, Paris, 1963.

[2] 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, p. 31-40, 2014.

[3] M. Nicu, L. Ionascu, C. Turcanu, F. Dragolici, Use of lithium nitrate as a potentially corrosion inhibitor for radioactive aluminium in cementing systems. Romanian Journal of Physics p. 1193-1202, 2015.

[4] S. Delpech, C. Cannes, N. Barré, Q. Thuan Tran, 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 p. C717-C727C, 2017.

[5] B. Grambow, M. Lopez-Garcia, J. Olmeda, M. Grivé, N. C.M. Marty, S. Grangeon, F. Claret, S. Lange, G. Deissmann, M. Klinkenberg, D. Bosbach, G. Bucur, I. Florea, R. Dobrin, M. Isaacs, D. Read, J.

Kittnerova, B. Drtinova, D. Vopalka, N. Cevirim-Papaioannou, N. Ait-Mouheb, X. Gaona, M. Altmaier, L. Nedyalkova, B. Lothenbach, J. Tits, C. Landesman, S. Rasamimanana, S. Ribet, Retention and diffusion of radioactive and toxic species on cementitious systems: Main outcome of the CEBAMA project. Applied Geochemistry p. 104480-104493, 2020.

[6] N. Çevirim-Papaioannou, X. Gaona, M. Böttle, E.Y. Bethune, D. Schild, C. Adam, T. Sittel, M. Altmaier, Thermodynamic description of Be(II) solubility and hydrolysis in acidic to hyperalkaline NaCl and KCl solutions. Applied Geochemistry p. 104601-104612, 2020.

[7] L. Gardner, Ph.D Thesis, Assessment of magnesium potassium phosphate cements for radioactive waste encapsulation, University of Sheffield, 2016.

[8] D. Chartier, J. Sanchez-Canet, P. Antonucci, S. Esnouf, J-P. Renault, O. Farcy, D. Lambertin, S. Parraud, H. Lamotte, C. Cau Dit Coumes, Behaviour of magnesium phosphate cement-based materials under gamma and alpha irradiation. Journal of Nuclear Materials p. 152411-152420, 2020.

[9] G.L. Bykov, V.A. Ershov, B.G. Ershov, Radiolysis of the magnesium phosphate cement on γ-irradiation. Construction and Building Materials p. 119156-119162, 2020.

[10] D. Leng, X. Li, Y. Lv, H. Tan, N. Li, Z. Liu, W. Jiang, D. Jiang, Cesium immobilization by K-struvite crystal in aqueous solution: Ab initio calculations and experiments. Journal of Hazardous Materials p 121872-121883, 2020.

[11] L. Acher, PhD Thesis, Etude du comportement sous irradiation γ et électronique de matrices cimentaires et de leurs hydrates constitutifs, Paris-Saclay University, 2017.

[12] S. Yin, H. Yang, Y. Dong, C. Qu, J. Liu, T. Guo, K. Duan, Environmentally favourable magnesium phosphate anti-corrosive coating on carbon steel and protective mechanisms. Scientific Reports 11/197, 2021.

[13] H. Tang, J. Qian, Z. Ji, X. Dai, Z. Li, The protective effect of magnesium phosphate cement on steel corrosion. Construction and Building Materials p. 119422-119432, 2020.

[14] H. Pei, Z. Li, J. Zhang, Q. Wang, Performance investigations of reinforced magnesium phosphate concrete beams under accelerated corrosion conditions by multi techniques. Construction and Building Materials p. 989-994 (2015).

[15] D. Wanga, Y. Yueb, T. Mia, S. Yanga, C. McCaguea, J. Qian, Y. Bai, Effect of magnesia-to-phosphate ratio on the passivation of mild steel in magnesium potassium phosphate cement. Corrosion Science p. 108848-108850 (2020).

11. WP5: Progress on experimental protocols, formulation of conditioning materials and performance assessment for the direct conditioning of RLOW

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Abstract

WP5 proposes to investigate a *direct route* for the conditioning of Radioactive Liquid Organic Waste (RLOW). After a short state-of-the-art, which highlights the high potential of alkali-activated materials (AAM) for organic liquid encapsulation, this article presents the main findings of the partners involved in Task 5.3 (NUCLECO/SOGIN, NNL/USFD, CIEMAT, POLIMI, SCK CEN, KIPT, RATEN) to this date. Other Tasks relate to WP management (T5.1), RLOW inventory (T5.2) and durability assessment (T5.4 – not started yet). Task 5.3 (T5.3) aims to design reference formulations of conditioning materials for the immobilization of RLOW, prior to Task 5.4, which focuses on the durability assessment of conditioned RLOW by the direct route. Since the start of PREDIS, the partners in T5.3 have proposed varied AAM formulations, based on metakaolin, blast furnace slag, volcanic tuff or their mixes as alumino-silicate solid precursors. The latter are alkali-activated with NaOH, KOH or metasilicate (sodium or potassium based). Varied RLOW are incorporated in the AAM, the most viscous and chemically simple RLOW being those with the greatest incorporation rate. For highly fluid RLOW (e.g. TBP, kerosene or scintillating cocktails), the use of a surfactant proves necessary. Optimizations of the RLOW/AAM mixes are still on going to this date, with already very promising preliminary results.

Keywords: Direct conditioning, Alkali-activated cement, Geopolymer, encapsulation, cementation

1. Introduction

Industrial background

Radioactive Liquid Organic Waste (RLOW) can be generated in different fields, including industrial nuclear activities, nuclear research centres and medical applications. While the volume of these waste is small compared to other classes of radioactive waste, the range of RLOW is highly variable, with typical examples such as oils, scintillation liquids, extraction solvents and miscellaneous solvents (e.g. those involved in decontamination operations). Although they may be kept separated during collection and storage, RLOW are also frequently multiphasic mixes, and may contain significant quantities of water and sludge. They may display a high diversity in radiological features, from VLLW to HLW, still with a major part belonging to VLLW/LLW/ILW categories. Their chemical and radiological compositions often lack detailed information. RLOW require dedicated management steps, considering both their radioactivity and their chemical content, because both can affect nuclear safety and have detrimental effects on human health and the environment.

In many European countries, the management of RLOW is still an issue. Currently, several industrial treatment units (e.g. incineration plants) are operated in various European countries and can process a part of RLOW produced. However, these industrial treatment units have limited acceptance specifications from radiological and physicochemical points of view. In particular, a key issue is that a significant part of these RLOW include organic components with heteroatoms such as Cl, F, P and S, which may be penalizing in incineration and more generally mineralization processes. As a consequence, many RLOW do not meet the acceptance specifications of these industrial treatment plants and as such constitute radioactive waste without management route. Consequently, these RLOW are stored in various sites on the European territory.

In this context, Work Package 5 (WP5) of the PREDIS project aims to address the issue of RLOW disposal or treatment route by focusing on *a direct conditioning route*. Direct conditioning is the simplest route for industrial purposes in a radioactive environment. It consists in encapsulating the RLOW in a solid matrix in order to obtain a composite material (conditioning and stabilizing the organic liquid). This can constitute the base of a radioactive waste package, that could fulfil the requirements of disposal facilities. Direct conditioning may be performed after an optional limited pre-treatment (neutralization, decontamination, evaporation, etc. but not mineralization).

Scientific background

The first study related to the direct cementation of RLOW was carried out in the USA in 1985 [Greenhalgh-1985]. A pump oil and a TBP/dodecane mixture were encapsulated in Portland cement with an emulsifier and setting accelerator additions. Studies devoted to the study of the influence of organic liquids on Portland cements, have shown that the presence of organics in Portland cement pastes causes retardation of hydration and structural defects, that can cause significant leaching of organic compounds [Pollard-1991, Montgomery-1991, Nestle-2001]. To overcome this problem, an absorption step may be used before the immobilization of RLOW in a Portland cement [Montgomery-1991; Sazonov-2009; El Naggar-2018; Cuccia-2020]. However, this mechanism of immobilization is not encapsulation. Rather, the process converts the liquid material into a solid material via a preliminary step consisting of inter-molecular bonding (adsorption). It can be further combined with cement powder to produce a final waste form (i.e. a solidified product embedded in a cement matrix or a homogeneous waste form) [Galkin-2015], but in at least two or more steps, which increases significantly the waste management cost.

More recently, *direct conditioning* of radioactive waste has been proven effective by using alcali-activated materials (AAM) and in particular geopolymers (GP) [Seo-2013; Medpelli-2014; Cilla-2014; Shi-2019; Reeb-2021], which limits and even possibly removes chemical interactions between waste and binder. They have already shown strong interest from the radioactive waste community [Marchon-2013; Cantarel-2018; Davy-2019]. For instance, for the application targeted in WP5, preliminary experimental studies for the direct conditioning of viscous oils using geopolymers based on metakaolin have shown efficient encapsulation at up to 20%vol oil [Davy-2019; Planel-2020]. The principle described is based on the emulsification of RLOW in an alkaline silicate solution (i.e. the activation solution) followed by the addition of an alumino-silicate source (i.e. metakaolin) leading to the setting of the RLOW/geopolymer composite. For successfully incorporating a range of organic liquids in AAM, surfactants are often necessary [Reeb-2021]; they contribute to homogenize and stabilize the organic liquid emulsion, prior to cement setting.

These results are a starting point for WP5 which aims at investigating, developing and assessing the direct conditioning solutions for RLOW based on AAM, by exploring all possibilities and options of this mineral binders family [Davidovits-1985; Provis-2009; Provis-2014; Shi-2019]. This includes the choice of the aluminosilicate precursor, of the alkaline activators and even blended binder systems, and the additives facilitating the oil emulsification (surfactants), in order to tune materials properties to the relevant RLOW of the different partners.

In this article, the main findings of WP5 since the start of the PREDIS project (September 2020) are presented. They mainly relate to Task 5.3, and include the description of the work and main findings of the partners involved in Task 5.3 (NUCLECO/SOGIN, NNL/USFD, CIEMAT, POLIMI, SCK CEN, KIPT, RATEN), the materials used, and more details on the main results to this date (webinar of May 5th, 2020).

2. Description of work and main findings

NUCLECO/SOGIN

Laboratory work was carried out starting with the study of the geopolymer formulation without ROLW to select the reference formulation to be tested with the addition of different surrogated wastes. Promising results were obtained with Shellspirax oil and further investigations are needed to find suitable additive/surfactant/emulsifier mainly with solvent waste. Cooperation and exchange of information between all the other Partners helped to drive the experimental activities and to find solutions for common issues.

NNL/USFD

Small-scale laboratory work (~160 mL) studies have been undertaken in which both Nevastane EP 100 paraffin oil and TBP have been incorporated in two different geopolymer systems using two different metakaolin powders over a range of formulations developed in previous UK studies. The aim of these trials was to assess likely RLOW loadings for both organics tested and if there is a preferred order of addition for incorporating the RLOW into the system for subsequent scale-up studies.

Promising results have been obtained for Nevastane EP 100, in that 50 vol% has been incorporated into both geopolymer systems and therefore loadings up to this vol% will be assessed in the next phase of scale-up studies to measure product properties & retention characteristics. Trials with TBP have been less successful, and in common with other partners the incorporation of surfactants appears to be required to obtain a stable product. Scoping trials are currently on-going to identify a suitable surfactant and level and order of addition, prior to scale-up to obtaining product evolution data.

CIEMAT

The laboratory work that is being carried out consists in the study of different commercial metakaolin and activators with different concentrations of NaOH and water glass, in order to find the most suitable geopolymer formulation to later incorporate ROLW. To date, mechanical resistance has been tested, but no suitable formulation has been found, so further trials are needed.

POLIMI

i) The pozzolanic reactivity (dissolution of Al and Si in alkaline medium) of VT has been determined and compared with metakaolin (MK, IMERYS) in order to identify the optimal geopolymerization conditions. The optimal volcanic tuff-based geopolymer formulation was first studied without waste encapsulation on a visual inspection basis. Afterwards, the most promising one was tested with some surrogate RLOW, with addition of surfactants when needed.

ii) RLOW pre-absorption on polymers before cementation
The reference NOCHAR N910 and a novel polyurethane (PU)-based polymer have been characterised with/without surrogate RLOW by means of FT-IR, Raman, TGA, XRD, DSC, CHNS techniques to understand the binding mechanism.

SCK CEN

Study on reference geopolymers without waste was implemented by testing the fresh and hardened properties as well as the durability of geopolymers with various water/binder ratio and precursors (BFS and Metakaolin). The results showed that the reference geopolymers had a good performance and potential to incorporate the liquid waste in their structures. Further, the encapsulation capacity of reference geopolymers with TBP and ionic liquid was investigated with and without using surfactant. MK-based geopolymer showed an impressive mixing capacity with all examined waste when using 1 wt. % Tween 80 as surfactant.

KIPT

Laboratory research was carried out starting with the study of the geopolymer formulation without ROLW to select the optimal formulation to be tested with the addition of different simulated ROLW. First results were obtained with pump oil (Ukrainian production) and Shellspirax oil and further researches are needed to find suitable additive/surfactant mainly for obtaining geopolymers with homogeneous structure, accepted setting time as well as compressive strength.

RATEN

Preliminary laboratory work was performed to optimize the geopolymer formulation based on BFS and volcanic tuff before to select the proper formulation for testing the surrogated waste incorporation. Two formulations were selected for further test the incorporation of oil (Shellspirax) and scintillator cocktail (Ultima Gold AB): one formulation based only on BFS activated using an alkaline solution and one with BSF and 22% volcanic tuff (reported at the ligand total mass). For both types of RLOW, without any additive, surfactant or emulsifier it was not possible to obtain a matrix with good workability for waste loading higher than 10% (wt.%). Sodium phosphate was tested as emulsifier but the emulsions was not stable more than 15 minutes. Regardless of the order of addition, the GP matrix with oil/scintillator is not homogeneous and after a short time, the waste is separated. Other inorganic surfactants or emulsifiers will be tested to allow a higher waste loading. Also, the percentage of added sand will be decreased to 20-30 wt. %.

3. Materials

All raw materials for laboratory trials have been detailed in Table 1.

Table 1. *Raw materials used by all partners for oil incorporation*

Partners	Raw Materials
NUCLECO/SOGIN	BFS: Fos-sur-Mer (France) Specific Surface Blaine: 4450±250 cm2 Average diameter: 11 µm Oil: Shellsprirax Solvent: TBP and Dodecane

Partners	Raw Materials
NNL/USFD	MetaMax Rotary Calcined MK, SSA Rigden: 3851 m2/kg, D_{50} 3 µm Argicem Flash Calcined MK: SSA Rigden: 605 m2/kg D_{50} 41 µm Activator solution: K2SiO3/KOH Oil: Nevastane EP 100 Solvent: TBP
CIEMAT	Commercial MK X-Ray fluorescence under study Activator solution: Na_2SiO_3/NaOH Oil: Repsol Super Tauro Grade ISO 100
POLIMI	VT: Salerno (Italy) NOCHAR N910 (USA) Recycled PU (Italy) Scintillation cocktail: Ultima Gold (PerkinElmer) Solvent: TBP and Kerosene
SCK CEN	BFS: Ecocem Benelux MK: BASF (Metamax) TBP (Merck) Ionic liquid: Sigma-Aldrich
KIPT	MK: from Ukrainian deposit BFS, FA: from Ukrainian power stations All raw materials sieved (≤500 µm) Oil : Pump oil (Ukrainian production), Shellsprirax Surfactant: Castament FW-10 (BASF)
RATEN	BFS: Liberty Steel Galati, *dried, grounded and sieved (<125 µm)* Volcanic tuff from Barsana, calcined (80°C) and sieved (<125 µm) Sand: certified CEN, EN 196-1 Oil: Shellsprirax Scintillator: Ultima Gold AB

4. Methods

NUCLECO/SOGIN

Geopolymer preparation without surrogated waste: the alkaline activator is added to the water under mixing and then the solution is added to the BFS powder (+ additives in some cases) under mixing (10 minutes mixing).

Geopolymer preparation with surrogated waste

- Without emulsifier (surfactant): the alkaline activator is added to the water under mixing and then the organic liquid is added to the solution. Finally, the BFS powder (+ additives in some cases) is added under mixing (10 minutes mixing).
- With emulsifier (surfactant): surfactant is dispersed in water and then organic liquid is added to obtain the emulsion under mixing. Alkaline activator is added and finally the BFS powder is added under mixing (10 minutes mixing).

NNL/USFD

RLOW addition to activator solution and then form geopolymer: KOH is mixed with water and K_2SiO_3 of appropriate molar ratios and allowed to cool to 20 °C. An appropriate vol% of RLOW (10-50 vol% of total wasteform mix volume) is added to the activator solution and mixed using a Silverson high shear mixer at 2000 rpm for 1 min. The required quantity of metakaolin powder is then added for the formulation under test and mixed using a Kenwood hand mixer at ~700 rpm for 2 min.

RLOW addition to Pre-formed geopolymer: KOH is mixed with water and K_2SiO_3 of appropriate molar ratio and allowed to cool to 20 °C. The required quantity of metakaolin powder is added for the formulation under test and mixed using a Kenwood hand mixer at ~700 rpm for 1 min. The appropriate vol% of RLOW (10-50 vol% of total wasteform mix volume) is added and mixed using a Kenwood hand mixer at ~700 rpm for a further 1 min.

Resultant mixes at culmination of mixing are tested for:

- Viscosity by ASTM C1749 up to 100 s^{-1}.
- Bleed on the surface of the sample at 24 h curing at 20 °C and >90%RH.
- Initial and final set of the sample on curing at 20 °C and >90%RH.

CIEMAT

Geopolymer preparation: Different NaOH concentrations and silicate ratios are mixed and when the mixtures reach the proper temperature, metakaolin powder is incorporated. Additional water may be added if the geopolymer has not the adequate physical properties (Table 2).

Table 2. *Mixtures used for geopolymer preparation*

			ACTIVATOR				
NaOH (M)	**MK (% w)**	**Total Activator (% w)**	**NaOH (% w)**	**Sodium Silicate (% w) ($Na_2O·nSiO_2$)**	**H_2O (% w)**	**$R_{Act/MK}$**	**$R_{L/S}$**
20	42	42	23	19	17	1,0	1,4
20	43	43	22	22	13	1,0	1,3
20	42	42	19	23	17	1,0	1,4
13,5	45	45	25	20	9	1,0	1,2
13,5	45	45	23	23	9	1,0	1,2
13,5	45	45	20	25	9	1,0	1,2
25	43	43	24	20	13	1,0	1,3
25	45	45	23	23	9	1,0	1,2
25	45	45	20	25	9	1,0	1,2
13,5	50	50	25	25	0	1,0	1,0
8	42	43	31	12	15	1,0	1,4
13,5	50	50	25	25	0	1,0	1,0
13,5	45	45	23	23	20	1,0	1,5
13,5	43	33	67	33	24	0,8	2,9

Three samples of each mixture are tested for mechanical performance at 48 h, 7 and 28 days.

POLIMI

i) RLOW direct encapsulation in volcanic tuff geopolymer

Pozzolanic reactivity of VT: Both thermal and mechanical pre-treatments were considered to enhance VT pozzolanic reactivity: calcination up to 800 °C and grinding. The pozzolanic reactivity of both treated and untreated VT in alkaline solutions has been determined by two different methods:

- **Chemical method**: to quantify the amount of dissolved Al and Si by ICP-OES and estimate the reacted fraction by gravimetry [Liguori-2017]
- **Conductivity method**: to estimate pozzolanic reactivity by monitoring conductivity change in time [Uzal-2010]

GP preparation without surrogate waste: The alkaline activator is added to water under mixing some hours before GP preparation. Then the solution is added to VT powder (10 minutes mixing). The GP grout is cured for 2 days at different temperatures between room temperature (20 °C) and 70 °C.

GP preparation with surrogate waste:

- Without surfactant: the surrogate RLOW is directly added to the GP grout (10 minutes mixing).
- With surfactant: the GP grout is prepared with 70% of the total amount of water. The surfactant is dissolved in the remaining 30% of water (10 minutes mixing) and is then poured into the GP grout. Finally, the surrogate RLOW is added to the mixture (10 minutes mixing).

ii) RLOW pre-absorption on polymers before cementation

The surrogate RLOW is added to the polymer (same procedure for NOCHAR N910 and recycled PU) under vigorous mixing before FT-IR, Raman, TGA, and DSC (just for PU polymer) analyses. XRD and CHNS analyses have been performed on NOCHAR N910 polymer without waste.

SCK CEN

Reference geopolymers preparation: Solid sodium silicate is added gradually into the mixture of sodium hydroxide solution and additional water and mixed until achieving a homogeneous solution, then BFS is added and mixed for 2+1 minutes. River sand is then added and mixed for 2+2 minutes more.

Waste-forms (geopolymer+waste) preparation: Surfactant is dissolved in waste for around 5 minutes to obtain mixture 1. In the meantime, geopolymer (mixture 2) is prepared using the same procedure for the reference geopolymers preparation, but reduce the mixing time with sand to 2 minutes. The mixture 1 is then poured into mixture 2 and mixed for 2+1 minutes more.

KIPT

Geopolymer preparation without surrogated simulated waste: The alkaline silicate aqueous solution is prepared by adding Na/KOH and Na/KSiO$_3$ to the water and then the sieved raw materials (MK+BFS+FA) are added to the alkaline silicate aqueous solution under mixing (60 minutes mixing in planetary mill, volume of container 250 ml) and forming (casting) of samples into plastic molds.

Geopolymer preparation with surrogated simulated waste

- Without surfactant: preparation of alkaline silicate aqueous solution and then the simulated ROLW is added to the solution. Finally, the sieved raw materials (MK+BFS+FA) are added to the solution under mixing (60 minutes mixing in planetary mill, volume of container 250 ml) and forming (casting) of samples into plastic molds.
- With surfactant: surfactant is dispersed in water and added to prepared the alkaline silicate aqueous solution, then the simulated wastes are added to that solution. Sieved raw materials (MK+BFS+FA) are added to the solution under mixing (60 minutes mixing in planetary mill, volume of container 250 ml) and forming of samples into plastic molds.

RATEN

Geopolymer preparation without surrogated waste: The alkaline activator (based on a mixture of commercial Na$_2$SiO$_3$ solution and 8 M NaOH solution) is added to the solid materials (BFS + sand and respectively BFS+ volcanic tuff + sand) under mixing for standard time under standard shear.

Geopolymer preparation with surrogated waste

- Without emulsifier (surfactant): the mixture of alkaline activator is added under mixing to the surrogated waste and the mixture is added to the solid materials (BFS + sand and respectively BFS+ volcanic tuff + sand) under mixing for standard time under standard shear.
- With emulsifier (surfactant): the emulsifier is added to the surrogated waste and mixed to form an emulsion that is after that added to the solid materials (BFS + sand and respectively BFS+ volcanic tuff + sand) under mixing for standard time under standard shear.

5. Results

NUCLECO/SOGIN

Geopolymer formulation was tested with different Water/BFS ratio, different types of alkaline activators (NaOH, KOH and $Ca(OH)_2$) and with the eventual addition of silica fume. $Ca(OH)_2$ did not work as an alkaline activator like NaOH and KOH. The increase in the percentage of NaOH or KOH in the mixture improved hardening and compressive strength, up to a maximum value of 4% (for NaOH) or 5% (for KOH). Over these percentages there were no effects. Water reduction led to an increase in compressive strength. The optimum W/B ratio was 0.3. The addition of silica fume led to an increase in compressive strength, proportional to the amount of additive up to a maximum percentage of 15%.

Addition of Shellspirax oil (Figure 1)

- Oil increased workability, therefore W/B ratio was reduced to 0.15;
- The use of KOH as activator led to higher compressive strength than NaOH;
- About 60% (vol.) was loaded without bleeding but no hardening was checked even after one week
- Bleeding was observed only with the addition of silica fume
- With about 30% (vol.) it was possible to obtain formulations that allow hardening of the specimens, up to compressive strength values of about 8 MPa (after 28 days);

60% (vol.) Oil Oil bleeding with silica fume 30% (vol.) Oil with KOH as activator

Figure 1. *Geopolymer formulations with Shellspirax oil.*

Addition of TBP and/or Dodecane

TBP and dodecane were not incorporated into the mixture, even at low percentage. The need to use an emulsifier was highlighted. Triton X (non-ionic) and Sodium Lauryl Sulfate (anionic) were tested. No good results with Triton X. With Sodium Lauryl Sulfate (about 3% by weight):

- Shellspirax oil:
    - the workability of the mixture decreased but the mixture was much more homogeneous (no bleeding even if subjected to vibration);
    - the compressive strength values were similar to those determined without Surfactant
- TBP, Dodecane and TBP/Dodecane (30%)
    - With the use of SLS, in all cases it was possible to obtain good geopolymer formulations (no segregation of the liquid, no bleeding and good workability) with a WL of about 30% (vol.)
    - Low compressive strength values were obtained after 7 days: 5 MPa with Dodecane, 2 MPa with TBP, 3 MPa with TBP/Dodecane

NNL/USFD

The baseline geopolymer formulation ranges tested, based on adequate setting and segregation results were as follows:

MetaMax GP:

- SiO_2:K_2O (1.0 – 1.4)
- K_2O:Al_2O_3 (1.0 - 1.5)
- H_2O:K_2O (11-15)

Argicem GP:

- SiO_2:K_2O (1.0 – 1.4)
- K_2O:Al_2O_3 (1.0 - 1.35)
- H_2O:K_2O (11-14)

Addition of Nevastane EP 100 Oil

Nevastane EP 100 was incorporated into both geopolymer systems at up to the tested 50 vol% of the total wasteform volume with minimal bleed and viscosities, typically < 1000 mPa·s at 100 s^{-1}. The products generally set within 24 hours (Figure 2) and no significant difference was apparent in the order of RLOW addition to the system:

Figure 2. *50 vol% loading of Nevastane EP 100 in MetaMax geopolymer (left) and Argicem geopolymer (right).*

These formulations will therefore be scaled up to 3 L in the next phase of study to assess longer term product properties and retention characteristics.

Addition of TBP

Preliminary results for the TBP solvent have been less successful in that incorporation rates for the solvent into the Metamax geopolymer system at levels of addition of only up to 20 vol% have been achieved, irrespective of the order of RLOW addition, producing low viscosity mixes (< 300 mPa·s at 100 s^{-1}) which set within 24 h with a small amount of residual bleed (Figure 3). However, at higher TBP incorporation rates, and for all levels of incorporation rates studied for the Argicem geopolymer system, the TBP sat on top of the geopolymer mixture suggesting little to no incorporation of the oil (Figure 2). In addition, the top of the geopolymer product produced using Argicem appeared more porous with the addition of TBP and this became more prominent with increased TBP addition (Figure 3). Further, after some time the MetaMax GP samples have shown signs of a substantial increase in the measured bleed volume, suggesting that longer term retention has not been achieved.

As a result, the addition of surfactants into the mix design (non-ionic (L35) and cationic (CTAB)) is currently being investigated to assess if a stable emulsion with the geopolymer activator solution can be attained, thereby increasing the probability of producing a stable wasteform with higher incorporation rates than those achieved thus far.

Figure 3. *20 vol% loading of TBP in MetaMax geopolymer (left), 10 vol% loading of TBP in Argicem geopolymer (centre) and 20 vol% loading of TBP in Argicem geopolymer (right).*

CIEMAT

Although sample tests show interesting properties, are not enough to start with the addition of ROWL. The ideal geopolymer formulation is still being studied.

POLIMI

i) RLOW direct encapsulation in VT-GP

Pozzolanic reactivity of VT

These experiments showed that VT is less reactive than MK in the same conditions. It was shown that at the same reference conditions (*i.e.* in 3 M NaOH solution, room temperature), the reacted fraction of VT is far below that of MK, regardless of any thermal and mechanical pre-treatment. If NaOH concentration is increased, the VT reacted fraction increases too. If also temperature is increased above 50 °C, the VT reacted fraction reaches about 37%w, approaching 42%w of MK at reference conditions. These results were confirmed by measure of conductivity changes and of dissolved Si and Al in the filtered solutions.

The improved VT reactivity at higher NaOH concentration and temperature suggests some more suitable experimental conditions for GP preparation, such as: optimal composition of the activation solution and curing temperature. Nevertheless, the lower reactivity of VT may encourage the addition of other raw materials (BFS and/or fly ashes) together with VT to improve the final mechanical properties of the manufacts.

GP preparation without surrogate waste

Different types of alkaline activators (NaOH, KOH, Na silicate) have been tested. The optimal amounts of water, activator, VT have been determined on the basis of literature [Davidovits-1991] and experimentally verified. Both NaOH and KOH activation solutions allowed the GP grout to harden at curing temperature above 50 °C, while the NaOH and Na silicate mixture did not at all. The hardened specimen activated by KOH presented some cracks, so NaOH was identified as optimal activation solution (see Figure 4). Attempts to improve mechanical resistance were done by partially replacing VT with amounts of alumina or mullite. In all cases, the workability was very high. Some preliminary compression tests proved that the addition of alumina is worthless. Moreover, unsatisfactory compressive strength values of about 1 MPa were registered on specimens cured for 28 days.

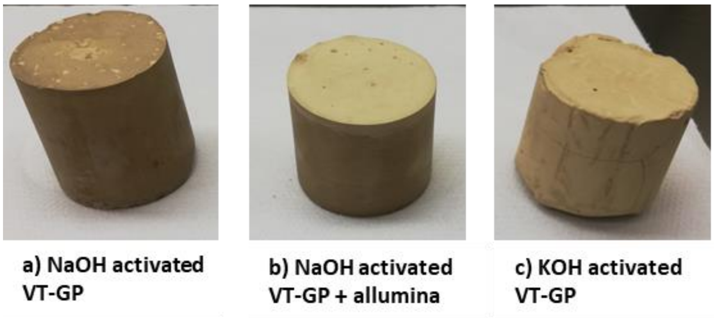

Figure 4. *VT-GP activated with NaOH (a) and KOH (c), VT-GP + alumina activated with NaOH (b).*

GP preparation with surrogate waste

- Vacuum Pump Oil (Alcatel120): 40%v loading can be achieved without employing any surfactant.
- Scintillation cocktail (Ultima Gold, UG-AB): at least 30%v loading can be achieved using a surfactant.
- 30%v TBP in kerosene (TBP/K): about 25%v loading can be achieved thanks to a surfactant.

In all cases, the addition of surrogate RLOW to VT-GP further improved workability. No bleeding was observed, and the specimens hardened within few days (see Figure 5).

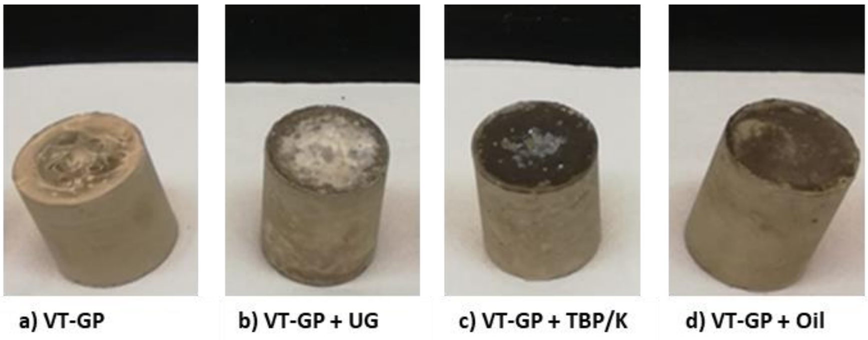

Figure 5. *VT-GP without waste (a) and with scintillation cocktail (b), TBP/K (c), and Vacuum Pump Oil (d) surrogate waste.*

In the case of UG-AB (scintillating cocktail) and TBP/K (TBP/Kerosene) the use of a surfactant was necessary to optimize or allow mixing with the GP grout respectively. Some surfactants were tested, but non-ionic Poloxamer copolymers resulted the more effective. About 2%w of Pluronic F-127 allowed UG-AB and TBP/K to be mixed with the GP grout allowing the specimens to harden without any bleeding.

Preliminary compression tests proved that the addition of surrogate RLOW worsens compressive strength values from 1 MPa to about 0.6 MPa (at 28 days of curing). Immersion tests following ANSI-ANS 16.1 leaching protocol are on-going on VT-GP specimens with/without oil, UG-AB, and TBP/K surrogate waste to determine stability and retention capability of the GP towards RLOW surrogate and contaminants.

ii) RLOW pre-absorption on polymers before cementation

NOCHAR N910: Preliminary XRD, ATR-IR, FT-Raman, CHNS, DSC, and TGA analyses on N910 polymer without surrogate waste were conducted in order to characterize the material. In particular, the XRD analysis showed that N910 is amorphous without any crystalline phase. ATR-IR and FT-Raman analyses allowed to identify the main functional groups of the polymer that may participate in the RLOW binding. TGA and DSC analyses were performed to further characterize the material and evaluate its thermal stability.

Furthermore, ATR-IR, FT-Raman, and TGA analyses were performed on N910 polymer loaded with some surrogate RLOW, such as kerosene and the TBP/K mixture. Both ATR-IR and FT-Raman analyses suggested that no chemical bonds occur between polymer and waste, but the interaction is just due to physical absorption in the polymer cavities. This is in agreement with the partial RLOW release that can be observed once the loaded material is slightly compressed. A further confirmation of this hypothesis comes from the TGA experiments. They showed that a first weight reduction stage could be related to surrogate RLOW loss from the material, followed by the weight losses attributed to complete degradation of the N910 polymer.

Recycled PU: Similar investigations were carried out with an alternative polymer to be employed for the pre-absorption of RLOW before cementation. So far, the identified material is a recycled PU-based polymer. It is a greener and cheaper alternative to N910. The absorption mechanism is similar to the one hypothesized for N910 polymer, excluding the formation of chemical bonds between RLOW and polymer.

The capability of recycled PU of absorbing different types of surrogate RLOW (vacuum pump oil, scintillation cocktail, TBP/K) were studied. Absorbent capacity of up to 15:1 (RLOW to polymer ratio by weight) was obtained. The composite material (PU polymer and RLOW) would be then cemented, similarly as already reported in the literature for N910 [Galkin-2015].

SCK CEN

Reference geopolymers: With the aim of obtaining reference geopolymers with good performance and appropriate matrix for immobilizing the organic liquid waste, both BFS and MK precursors are used to investigate whether C-A-S-H or N-A-S-H is more beneficial in waste encapsulation. The water to binder ratios (w/b) were also examined, and the results showed that the w/b of 0.35, 0.45 and 0.55 are suitable BFS geopolymers, while the higher w/b of 0.75, 0.85 and 0.95 can provide good MK-based polymers. Herein, the mixture of NaOH and $Na_2Si_3O_7$ are used as alkaline solution for both types of precursors. However, a higher silicate content in the mixture is needed for the activation of MK compared to BFS.

Geopolymers showed a high compressive strength at 28 days of curing, up to 60 MPa in BFS geopolymers and 40 MPa in MK ones. The mineralogy, microstructure and transport properties of obtained geopolymers were also identified by using multiple characterization technique such as XRD, MIP, BET, SEM, NMR. The MK geopolymer showed its significantly higher porous matrix than BFS gels, leading to a higher transport property, which could affect the durability of geopolymer [Nguyen-2021].

To understand the durability of geopolymers, ASR, carbonation and leaching tests have been carried out. Geopolymer from MK witnessed an excellent ASR resistance with a low expansion of about 0.08% as maximum value after 14 days in 1M NaOH. Although alkali activated BFS was more vulnerable to ASR than MK gels, its expansion is still acceptable as around the standard threshold (ASTM 1260) of 0.1%. BFS geopolymer was also susceptible to be carbonated, even rather than OPC system with the same w/b ratio, whilst carbonated MK geopolymer still need to be characterized further as the carbonation mechanism is very different. Leaching test has been ongoing, even though the preliminary results showed a relative loss of Na and Ca from geopolymer matrix under aggressive environment with 6M ammonium nitrate solution.

Geopolymer – liquid waste: TBP and ionic liquids including Aliquat 336 and Trifluor were mostly not encapsulated in both geopolymers from BFS and MK without surfactant. A very limited amount of waste incorporated in the matrices was quantified as 11 wt% as maximum percentage in case of Aliquat 336. In general, the separation was observed clearly. To deal with this issue, adding surfactant could be a good choice (Figure 6). The action in changing surface tension helps to improve the mixing capacity between geopolymer and waste. Amongst several surfactants used, Tween 80 showed the best efficiency on both MK and BFS matrices. BFS-based geopolymers can incorporate 20 wt.% (36 vol.%) TBP and 25 vol.% Trifluor when using 5% (of waste) Tween 80, while MK-based geopolymers could encapsulate 32.5 vol.% with all examined waste and using only 1% surfactant. In addition, the compressive strength of all waste-forms were determined. Results revealed that waste-forms of MK achieved a relatively high compressive strength of around 5 MPa after only 4 days of curing under ambient conditions, whereas the waste-forms with the highest amount of incorporated waste of BFS show a lower strength of 3 MPa after 19 days of curing. This implies that the MK geopolymers showed a higher potential for immobilizing waste rather than BFS geopolymers. The formulation of MK geopolymers with waste will be studied further while the waste-form recipes for BFS should be improved.

Figure 6. *State of BFS geopolymer-waste (left) and MK geopolymer-waste (right) with the addtion of surfactants after 3 days of mixing.*

KIPT

Geopolymer formulation was tested with different ratio of raw materials, different types of alkaline activators. As a result the optimal formulation of geopolymer with best properties was established (composition No.5). Ukrainian pump oil was tested as simulant of ROLW. It was set that the content of pump oil from 10 to 30 %wt in geopolymer does not essentially decrease the compressive strength of samples (comp. No.6-8).

Table 2. *Compositions and properties of KIPT trials.*

Component			**Content, %wt**							
			Composition No							
			1	2	3	4	5	6	7	8
FA						34	34	34	34	34
BFS						20	20	20	20	20
MK			36	36	26,5	14	14	14	14	14
Sand					26,5					
Na_2SiO_3			46			11				
K_2SiO_3				46	33		11	11	11	11
NaOH			6			9				
KOH				6	6		9	9	9	9
H_2O			12	12	8	12	12	12	12	12
Pump Oil (%vol)								10	20	30
Properties	Setting time, h Start / finish		Cracks	Cracks	8/48	4/24	4/20	5/22	5/24	5/24
	Density, g/cm^3				1,75	1,83	2,15	2,00	1,95	1,95
	Comp. strength, MPa	7 d			12	13	22	22	20	21
		14 d			15	21	28	25	22	24
		28 d			24	25	31	29	28	28

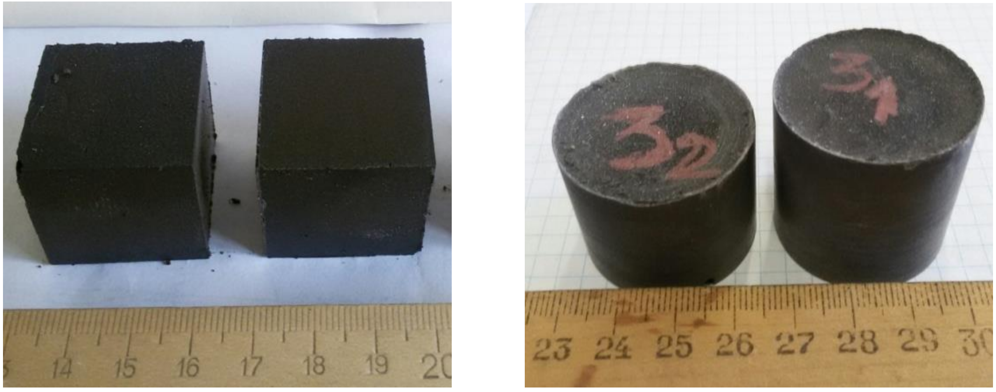

Figure 7. *Geopolymer samples (curing 24h): comp. No.5 (left), and the same with pump oil content of 30 %wt (comp. No.8) of pump oil (right).*

Addition of Shellspirax oil

It was shown that when adding Shellspirax oil in an amount of (10 - 30) %vol, it is possible to obtain solid samples with compressive strength values of (8 - 16) MPa (after 28 days of curing, Fig. 8). The addition of 40%vol of oil to geopolymer requires the use of surfactant because of bad fluidity.

Figure 8. *Geopolymer samples with 30% of Shellspirax oil.*

The addition of Castament FW-10 (a polyethylene glycol dispersant) improved the flowability of the paste and aided in obtaining appropriate samples with a uniform structure (Fig. 9, no large pores) and acceptable characteristics, in particular, setting time and compressive strength of the order of 10 MPa after 28 days of curing.

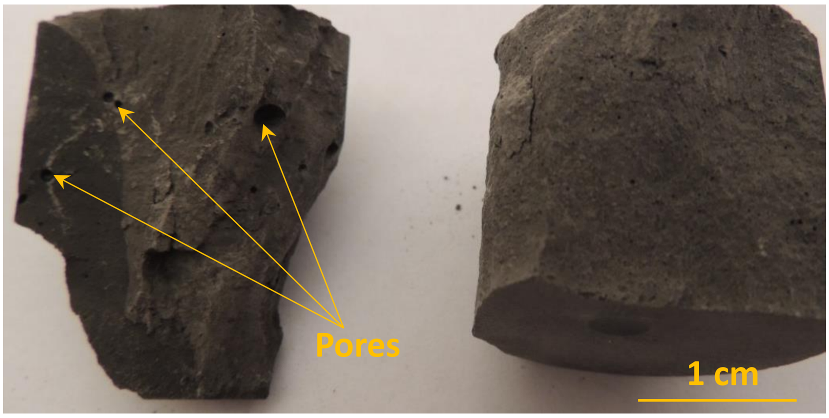

Figure 9. *Castament FW 10 influence on homogeneity of the samples with 40% of Shellspirax oil: left – without FW-10, right – 0,5% FW-10.*

RATEN

For selecting the geopolimer formulations to be further used to incorporate the surogated waste, tests were performed on BFS with different amounts of volcanic tuff addition and different composition of alkaline activator

(Na_2SiO_3 and 8 M NaOH solution). The best results, in terms of workability, setting time and bleeding were obtained for a geopolymer based only on BFS and for one with BFS and volcanic tuff. The composition and characteristics of the two selected formulations are reported in Table 3 and Table 4.

Table 3. *Composition of two selected formulation with BFS and VT.*

composition		**wt.%**	
		GP1	**GP2**
BFS		20.45	15.91
volcanic tuff		-	4.55
sand		61.36	61.36
activator	NaOH	9.09	9.09
	Na_2SiO_3	4.55	9.09
	added H_2O	4.55	-
W/B		0.70	0.62
SiO_2/CaO		0.74	1.27
SiO_2/Al_2O_3		4.8	5.82
SiO_2/Na_2O		16.23	11.73
H_2O/Na_2O		39.32	17.47

Table 4. *Characteristics of the selected geopolymer formulations*

Characteristics		**GP1**	**GP2**
setting time	***initial***	*45 min*	*2h 40 min*
	final	*2h 15 min*	*4h 15 min*
Density, g/cm^3		*2.113*	*2.107*
Mechanical strength after 28 days of curing, MPa		*19.34*	*34.97*

Surrogate waste incorporation

For both types of RLOW, without any additive, surfactant or emulsifier, it was not possible to obtain a matrix with good workability for waste loading higher than 10%. Sodium phosphate (Na_3PO_4) was tested, but the emulsions were not stable for more than 15 minutes. Regardless the order of addition, the GP matrix with oil / scintillator is not homogeneous and after short time the waste is separated.

6. Conclusions / Summary / Way forward

All partners of Task 5.3 have shown that different AAM formulations may be used for RLOW encapsulation, either based on metakaolin, or on BFS or volcanic tuff, or mixes of these alumino-silicate precursors. Alkaline activation is achieved either with NaOH, KOH or metasilicate (sodium or potassium based). In general, the RLOW is added to the alkaline activating solution, before the liquid mix is added to the solid alumino-silicate precursor. For a number of RLOW, the use of surfactants is compulsory to achieve minimal incorporation rates.

In terms of perspectives to these ongoing investigations, several partners have proposed the following:

POLIMI

Concerning RLOW direct encapsulation in VT-GP, preliminary results confirm that modifications of GP formulation are necessary to improve mechanical properties. Further studies are needed to identify cheaper and more effective surfactants for the emulsification of surrogate RLOW in the GP grout.

Concerning RLOW pre-absorption on polymers before cementation, the next studies would be focused on the optimization of the cementation stage. The so-obtained specimens will be characterized in terms of mechanical, thermal, and immersion stability.

RATEN

Further tests will be carried out with lower amounts of sand (~ 20-30%), while the BFS and the volcanic tuff will be more finely ground to get most of the particles less than 0.45 μm. To obtain higher waste loading other inorganic surfactants/emulsifiers, including monobasic sodium phosphate (NaH_2PO_4) will be tested.

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References

[Cantarel-2018] Cantarel et al. Ceram Int (44) 10558-10568, 2018

[Cilla-2014] Cilla et al. J Eur Ceram Soc (34) 3133-3137, 2014

[Cuccia-2020] V. Cuccia, C.B. Freire, A.C.Q. Ladeira, Prog. Nucl. Energy 122 (Apr. 2020) 103246, https://doi.org/10.1016/j.pnucene.2020.103246

[Davidovits-1985] J. Davidovits, J. L. Sawyer, US Patent n. 4,509,985, Apr. 9, 1985

[Davidovits-1991] J. Davidovits, Geopolymers. Journal of Thermal Analysis, Vol. 37, p. 1633-1656, 1991

[Davy-2019] Davy et al. J Am Ceram Soc (102) 949-954, 2019

[El Naggar-2018] M.R. El-Naggar, E.A. El-Sherief, H.S. Mekhemar, J. Hazard Mater. 360 (Oct. 2018) 670–680, https://doi.org/10.1016/j.jhazmat.2018.08.057.

[Galkin-2015] A. Galkin, et al., Dual solidification process of BN-350 liquid radioactive waste using high technology polymers and newly designed encapsulation techniques. INIS-US-19-WM-15198, 2015

[Greenhalgh-1985] W. O. Greenhalgh, Report HEDL-SA--3377-PP, DE86 009414, Aug. 7, 1985, Waste Management '86, March 2-6, 1986, Tucson, Arizona, USA

[Liguori-2017] B. Liguori, I. Capasso, M. De Pertis, C. Ferone, R. Cioffi, Geopolymerization Ability of Natural and Secondary Raw Materials by Solubility Test in Alkaline Media. Environments, Vol. 4, p. 56-68, 2017

[Marchon-2013] Marchon et al. Soft Matter (9) 10719-10728, 2013

[Medpelli-2014] Medpelli et al. J Am Ceram Soc (97)1 70-73, 2014

[Montgomery-1991] D.M. Montgomery, C.J. Sollars, R. Perry, Waste Manag. 9 (1991) 21–34.

[Nestle-2001] N. Nestle, C. Zimmermann, M. Dakkouri, R. Niessner, Environ. Sci. Technol. 35 (24) (Dec. 2001) 4953–4956, https://doi.org/10.1021/es015528y.

[Nguyen-2021] Nguyen, T.N., et al., in The 4th International RILEM conference Microstructure Related Durability of Cementitious Composites. 2021: Delft, The Netherlands. p. 10.

[Planel-2020] B. Planel, C. A. Davy, P. M. Adler, G. Hauss, M. Bertin, V. Cantarel, D. Lambertin, Cement and Concrete Research, Volume 135, September 2020, 106108

[Pollard-1991] S.J.T. Pollard, D.M. Montgomery, C.J. Sollars, R. Perry, J. Hazard Mater. 28 (3) (Nov. 1991) 313–327, https://doi.org/10.1016/0304-3894(91)87082-D.

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

[Provis-2014] J.L. Provis, S.A. Bernal, Geopolymers and related alkali-activated materials, Annu. Rev. Mater. Res. 44 (1) (2014) 299–327, https://doi.org/10.1146/ annurev-matsci-070813-113515.

[Reeb-2021] C. Reeb, C. Pierlot, C. A. Davy, D. Lambertin, Ceramics International, Volume 47, Issue 6, 15 March 2021, Pages 7369-7385

[Sazonov-2009] A.B. Sazonov, A.V. Aleshina, E.P. Magomedbekov, Radiochemistry 51 (4) (2009) 412–414, https://doi.org/10.1134/S106636220904016X.

[Seo-2013] Seo et al. U.S. Patent No. US20130055924 A1, 2013

[Shi-2019] Shi et al. Cem Con Res. (122) 227-250, 2019

[Uzal-2010] B. Uzal, L. Turanli, H. Yücel, M.C. Göncüoğlu, A. Çulfaz, Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan. Cement and Concrete Research, Vol. 40, p. 398-404, 2010

12. Thermal treatment of the radioactive waste forms and characterization of the treated / reconditioned wastes

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Abstract

The task of work package 6.3 is devoted to the thermal treatment of RSOW aiming to change their chemical composition and to reduce significantly the volume. For this, the existing thermal processes will be adapted in function of the types of wastes (Resins, Polymers and Bituminized) or will be developed. In addition, the thermally treated wastes will be delivered according to the project planning, in the necessary and sufficient quantity for the immobilisation work (Task 4 and 5) or the physico-chemical characterisation investigation (Task 6).

Keywords: Thermal treatment, waste form, characterization

1. Introduction

This task, led by CEA, involves six partners (CEA, USFD, SIIEG, POLIMI, CVREZ, NNL, VTT) having installations to treat the RSOW or able to provide existing treated wastes coming from their "own stock" produced during previous projects. The objectives are to establish, in collaboration with the laboratories / industrial facilities able to treat the RSOW, an inventory of the treated wastes (ashes, residues, plasma slags…) already available or that will be made available during the first year of the project.

The processes involved are "Plasma incineration" (CEA, USFD, NNL, SIIEG) "Incineration / Gasification" (VTT, POLIMI, SIIEG), "Molten Salt oxidation" (CVREZ) and "Wet Oxidation" (USFD, POLIMI).

According to the recommendations made in the Task 2 (Strategic overview) and the project partners competences, distribution of the thermally treated samples will be provided to the project partners for the immobilization step in Task 4 (Encapsulation) or Task 5 (Densification) if an immobilization step is needed. If not, the treated wastes will be directly tested in Task 6 in order to assess their durability and their stability.

2. Description of work and main findings

A database gathering the information concerning the treated waste has been established by the six partners. It includes a detailed description of the thermal process used, the nature of the initial and final waste, and the quantity available for the project.

The French Alternative Energies and Atomic Energy Commission (CEA) will provide and characterize ashes coming from the IRIS pilot (Installation de Recherche en Incinération des Solides – treating mixed plastic, cellulose and ion exchange wastes). Around 5 kg are available for the project and a first batch of 350 g have been sent to the University of Sheffield (USFD) for hot isostatic pressed tests.

Elementary chemical analysis of the IRIS ashes have been done. They are mainly composed of a mix of oxides, mainly alumina and silica.

The **University of Sheffield (USFD)** has sourced plasma incineration slag material from an industrial partner. This material arose from inactive trials of simulant plutonium contaminated material, plasma melted in steel drums. This material will be characterised, and will undergo leach testing without further conditioning steps. USFD are also providing sludges from processing mixed ion exchange resins via Fenton-like wet oxidation. Currently a small research rig is operational within a fume hood, processing small quantities of resin with varying operational parameters, over 3-4hrs runtime [1]. Utilising a mixed Fe + Cu catalyst at 90-95 °C processing temperature, organic resins are decomposed into inorganic sulfates, phosphates and metal oxides, dependant on catalyst concentration, resin loading and additions of antifoaming agents. These sludge materials are due to be processed via Hot Isostatic Pressing (HIP) within a separate workpackage, after extensive characterisation.

The CVRez has equipment for a high-temperature process in molten salt (MSO). On a laboratory scale, we perform process validation for specific types of waste. In this case, it is solid organic waste containing polymers (resins, PPE). Laboratory tests also allow verification of the applicability of new melting salts and construction materials of the device.

The pilot scale verifies the process with a higher mass flow of waste. The device is already equipped with autonomous dosing and control, a two-reactor system in series, flue gas cleaning lines and field instrumentation to monitor process phenomena and chemical composition of products / intermediates (infrared gas analyzer, XRD, MS). This device will be the main source of waste salt melt, which is and will be available throughout the project solution to all partners from WP6 (up to 200 kg). For the purpose of verifying the immobilization from T6.4, the waste salt has already been sent to SCK CEN and CSIC.

VTT has gasification residue from previous project available. These residues are from gasification of organic anionic/cationic ion exchange resins. Before gasification, resins were doped with non-active tracers. This residual stock has been well analyses for chemical and physical properties. VTT has as the moment about 1.3 kg available for their own tests in tasks 6.4 and 6.6.

The Scientific and Research Group of the Institute of Environmental Geochemistry (SIIEG) has developed new and innovative mobile equipment for safe and efficient deep processing of thermal treatment of the RSOWs (polymer products of any chemical composition), and design with obtaining useful energy products (electricity, hot water, heating). The system for thermal treatment of radioactive waste consists of a thermal treatment unit, a heat exchanger and a control unit (fig 1).

Thermal treatment unit consists of a hopper for loading waste, a gasification chamber, a gas afterburner, a heat exchanger and a smoke exhauster. The frame parts are made of steel sheets. The lining is made of high-temperature ceramics, the composition of which was developed by the specialists of our institute. The heat exchanger is made of stainless steel.

Radioactive waste is loaded into a bunker. The hopper and the gasification chamber are preheated using a gas burner. Wood chips can also be used for heating. Polymer materials can be added to intensify the process. The gasification process and stability of oxidative reactions can be controlled using an air damper 1. Then the gasification products pass into the gas afterburner. Afterburning of gases is controlled by an air damper 2. Also, this damper makes it possible to increase the temperature of the gas chamber using warm air.

The heated air is cooled using a heat exchanger. The role of the coolant is played by water. Hot water is supplied to the air convectors or space heating system. The gas removal process is controlled by a smoke exhauster, the design feature of which is the impeller. This is also the development of our institute. The system has the ability to expand functions using a plasma torch. The plasmatron module is installed through hatch 1. Ash is removed through hatch 2. Ash after the gasification process is removed from the system and loaded into special steel containers for further disposal using concrete.

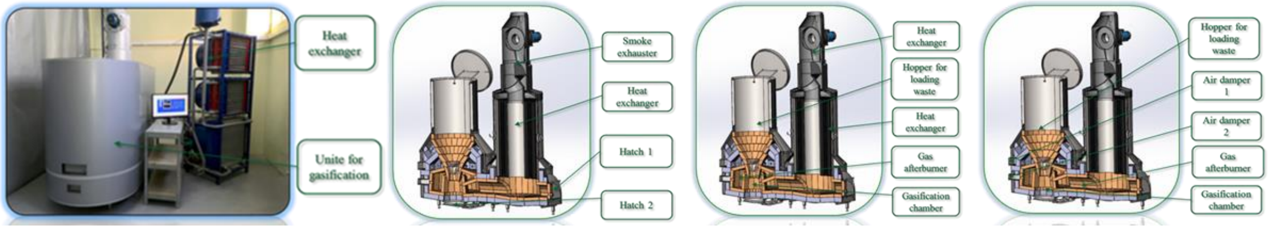

Figure 1. *Gas burner description.*

This system allows you to dispose of waste of various compositions, for example – IER, rubber, PVC, polyethylene, cotton, polypropylene, acrylic, surfactants (Humidity - 70%).

RWTP process is fundamentally new technology of multiloop circulating gasifier, which provides a complete thermal decomposition of radioactive wastes (RW) at high temperature in the reactor (1) without oxygen. Hazardous components of RW, which are formed as-gas mixture, circulates in multiloop system (5, 6, 7, 8, 9) until completely decomposed to low molecular components. The forming pyrolysis gas (2) burned in a special device, preventing the formation of toxic elements.

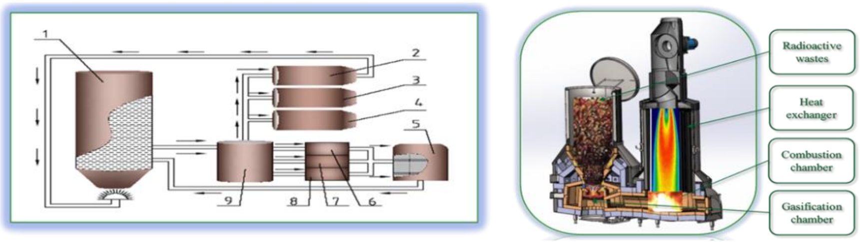

Figure 2. *Physical aspects of technological stages of the multiloop circulation gasifier in RWTP.*

1 - reactor, 2 - output circuit gaseous compounds, 3 - closed circuit solid compounds,

4 - output circuit for the solid residue, 5 - unit of catalyst, 6,7,8 - sectional contours

9 - Multiloop coolant distribution unit

The ecological safety is the primary requirement imposed on modern technological processes of Radioactive Solid Organic Wastes processing. The adoption of the multiloop circulation gasifier principle in waste processing allows fulfilling this requirement for the major part, in view of the deeper destruction of wastes. As a result, toxic high-molecular components are transformed into low-molecular ones, so that their toxicity reduces. Furthermore, toxic volatiles, which are present in the pyrolysis gas, are after-burned at a temperature of 1100–1400 C, so that provides dioxins and furanes completely decompose.

POLIMI is focusing its research activities on thermal incineration and Fenton-like wet oxidation of spent Ion Exchange Resin (IER). Both processes have been studied at laboratory scale. The spent IER incineration method is being optimized by slowing the gasification process to gradually convert mobile and volatile Cs species into inorganic and thermally stable compounds [2]. A simple surrogate waste has been used by loading nuclear grade cationic IER with stable Cs. The residence time and temperature ramp rate of the thermal process have been optimized by performing preliminary thermogravimetric analysis. Incineration has been conducted into a muffle furnace up to 800 °C. The obtained ashes shown in Figure 5 have been characterized by FT-Raman and X-Ray Diffraction (XRD) spectroscopy to demonstrate the complete decomposition of organic matter, while Cs retention efficiency has been calculated by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analysis.

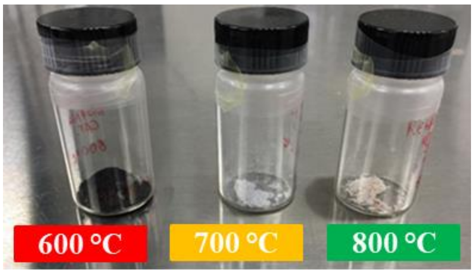

Figure 4. *Ashes of resin batches treated at 600, 700 and 800 °C by incineration process.*

Meanwhile, a more sustainable approach is being pursued at POLIMI. The wet oxidation process has been tested on a surrogate IER waste containing Cs, Co, Sr and Ni ions, as representatives of activation and fission products contamination. First research efforts were devoted to optimization of temperature, catalyst and oxidant concentration [3]. Figure 6 shows the temperature profile obtained from a lab scale wet oxidation.

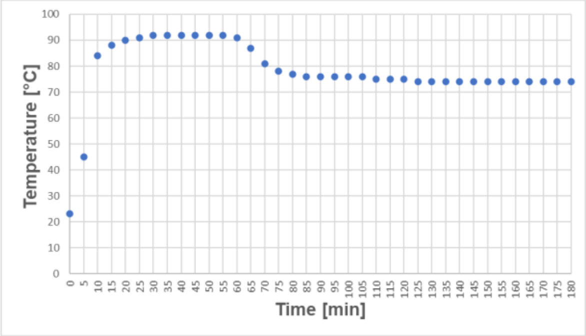

Figure 5. *Optimized temperature profile of a wet oxidation process performed at lab scale.*

FT-Raman and FT-IR spectroscopy techniques have been used with the purpose of monitoring IER decomposition. The colour change of the solution reported in Figure 7 is a straightforward proof of process evolution over time. In addition, XRD and ICP-MS analyses were conducted on the resulting solutions and residues to ascertain complete decomposition of organic matter and cations retention respectively, thus proving the process efficacy.

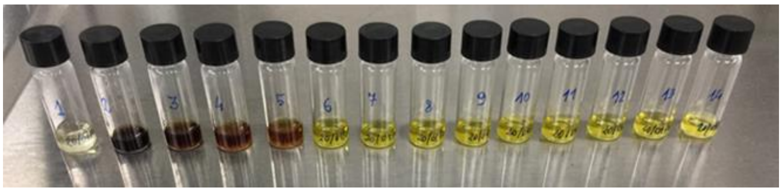

Figure 6. *Colour shift of resin solution over time for the Fenton-like wet oxidation process*

Both dry and wet oxidation treatments on surrogate IER showed a promising weight reduction and good decomposition of organic compounds. High caesium retention into the ashes was obtained for IER batches treated at 800 °C. Indeed, FT-Raman and XRD spectroscopy pointed out the favoured formation of the inorganic caesium sulphate compound. A homogeneous residue and a weight reduction rate of 40% have been obtained from wet oxidation tests.

3. Way forward

CEA will keep up characterizations of the IRIS ashes (SEM and XRD).

VTT will make new gasifications in near future for obtaining more materials for task 6.4. In addition, of ion exchange resin also solid organic maintenance waste will be gasified. This new type of waste form will consist mainly protective clothings, wipes and gloves. Non-active tracers and impurities will be added before gasification.

For SIIEG, in the current situation, the complete process of disposal of liquid organic radioactive waste has not been fully completed. The first task was to carry out full diagnostics, debugging and preparation of the system for work with this type of raw material. For this we needed money, which we received later than expected. The reason for this was problems with the transfer of money to the account of the institute. We received money, but many cities were in the red zone of the pandemic COVID-19 and as a result, many companies were closed. We had to wait for the delivery of some components. Our institute also worked in a remote communication mode. We lost about 6 months of working time. Now the situation has changed and we have embarked on large-scale tests and experiments.

POLIMI is going to scale up both incineration and wet oxidation treatment processes. An intermediate scale will be pursued by using at least 100 g of cationic IER containing Cs, Sr, Co, Ni and other activation, fission, and corrosion products representative ions. The ashes and sludges coming from the pre-treatment processes will be further characterized and finally conditioned into a geopolymer matrix. The physical and chemical stability of the final wasteform will be assessed and monitored for a long-term disposal.

Acknowledgements

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References

[1] Hyatt, N.C., Corkhill, C.L., Stennett, M.C., Hand, R.J., Gardner, L.J., Thorpe, C.L., The HADES Facility for High Activity Decommissioning Engineering & Science: Part of the UK National Nuclear User Facility. IOP Conference Series: Materials Science and Engineering, 818 012022, 2020

[2] HC. Yang, SY. Lee, YC. Choi *et al.* Thermokinetic analysis of spent ion-exchange resins for the optimization of carbonization reactor condition. *J Therm Anal Calorim* **127,** 587–595 (2017).

[3] L. Xu, X. Meng *et al.* Dissolution and degradation of nuclear grade cationic exchange resin by Fenton oxidation combining experimental results and DFT calculations. *Chem. Eng. J.* **361**, 1511-1523 (2019).

13. Immobilization of the treated wastes by geopolymer or cement-based materials encapsulation or by molten glass coating

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Abstract

The task 6.4 is to leverage the experience, know-how and equipment of each project partner in order to develop adequate formulations of geopolymer and cement-based materials for the immobilisation of thermally-treated surrogate or radioactive samples from T6.3.

The main objective of this task 6.4 is to design one or several geopolymer and cement-based materials formulations for the treated waste types. These recipes will be then considered for physico-chemical characterization in T6.6. In addition, this task demonstrates the Molten Glass Coating process for the immobilisation of treated waste from T6.3.

Keywords: immobilisation, geopolymer, cement, molten glass

1. Introduction

This task, led by CVRez, involves eight partners (CIEMAT, SCK CEN, CEA, POLIMI, SIIEG, VTT, CSIC, UAM) who have installations to immobilize the RSOW and demonstrate ability to apply the stabilization technique to selected wastes. Techniques include immobilization in a geopolymer / cement matrix and molten glass coating.

After the first year of the project, an inventory of selected matrix patterns will be available, which the partners will characterize themselves or provide for the T6.6 task.

These are geopolymer matrices (CVRez, CIEMAT, SCK CEN, POLIMI, SIIEG, VTT, CSIC, UAM) and cement (CIEMAT, SCK CEN, SIIEG, CSIC, UAM). Furthermore, a special task is to demonstrate the possibility of molten glass coating (CEA).

Thermally treated inactive surrogate will be used during the optimization of the formulation. Once an optimal formulation obtained, radiotracers (e.g. ^{85,90}Sr, ^{137}Cs at POLIMI) will be added to the treated wastes before the immobilization.

The tasks include, among others feedback exchange with WP 5 (direct immobilization of the Radioactive Liquid Organic Waste using geopolymer matrices). The two WPs will surely benefit of a strong interaction and collaborative work despite the type of waste and the considered treatment route.

2. Description of work and main findings

Eight partners created a database gathering information on immobilization techniques. It includes a description of the production of the matrix, the appropriate type of waste, waste loading, the type of matrices, as well as the number of samples that the partners can provide, including their shapes and sizes.

The Research Center Řež (**CVRez**) works mainly on the immobilization of salt waste from MSOs in a geopolymer matrix. Over the course of 3 months, we prepared a total of 20 samples, which differ by the "waste loading" criterion from 10% to 45% and the presence of trackers (Cs, Sr, Co) in their constant amount of 1%w_i. The next step will be an inventory of samples that differ in the composition of the binder in the matrix. Leachability was assessed, structure, mechanical strength and radiation aging.

SIIEG is focused on thenovel techniques, such as gasification / incineration, plasma incineration of the RSOW could lead to more stable reconditioned waste forms. Incineration techniques produce ashes and / or residues that required further immobilization in stable and leach-resistant waste forms.

VTT is focused on formulations for immobilisation of gasified waste using different locally available raw materials. The target is to develop different recipes for different applications. In the task 6.4 main part is to concentrate on fresh and hardened mechanical performance in immobilization process. Different immobilization recipes are behaving much differently.

CSIC has been working in the development of "one part geopolymer" based on a mixture of precursors (metakaolin + blast furnace slag) and solid activators (NaOH+ Sodium metasilicate). During this term, more than 24 geopolymer mixtures have been designed and tested and the most promising systems has been selected. In parallel two Portland based cement systems (CEM I and CEM III) have been selected and characterized. The CEM I mix will be tested and used as a reference and CEM III as a special binder. All these cementitious systems have been designed to immobilize the thermally treated ion exchange resins (calcined IERs), prepared by CIEMAT. In addition, a collaboration with CVRez to immobilize the molten salt waste (provided by CVRez) is planned.

CIEMAT is working together with CSIC and **UAM** in the conditioning of thermally-treated IERs on geopolymer and cement-based matrices. CIEMAT continues with the preparation of the surrogates to be used by CSIC and UAM in WP6. These surrogates consist of a mixed form of Ionic Exchange Resins (IERs), that have been doped according to the specifications provided by 2 of the Spanish NPPs. The resins have been saturated mainly with boron and traces of Sr, Cs and activation products (i.e. Co, Cr, Zn, Fe….). For the thermal treatment of the doped IERs, a low temperature range has been selected (450ºC) in order to avoid the release of volatile elements, i.e. Cs. After the thermal treatment, a volume reduction factor of 8 has been achieved. In order to assess the compatibility of the thermally-treated waste with the chosen matrices, CIEMAT and UAM, are carrying out the physico-chemical characterization of the residue (elemental analysis, FTIR, BET, LS particle size). Complementarily, a leaching test series at pH 7 and pH 13 is running in order to evaluate the residue's behavior under hyperalkaline media and the impact its degradation may have on the performance of the wasteform.

Belgian Nuclear Research Center (**SCK CEN**) is dealing with the immobilization of molten salt waste shared by CVRez in both geopolymer matrix and blended cementitious materials. The recipes was proposed based on the formulations developed in previous studies [1, 2].

POLIMI activity is focused on the confinement of surrogate IER ashes from incineration treatments in a geopolymer matrix. Some attempts are being dedicated to encapsulation of sludges produced by wet-oxidation treatment of surrogate IERs. A novel geopolymer matrix based on volcanic tuff (VT) as raw material is being developed and the main outcomes are also described in proceedings of WP5. In particular, POLIMI is investigating pozzolanic reactivity and cation exchange capacity (CEC) of VT in comparison with metakaolin. Since VT under investigation is highly zeolitized, it may present promising CEC towards some relevant cations, thus contrasting their leaching. In addition, the formulation of VT-based GP is under development. Loading of IER residues will be attempted.

The objective **CEA** is to demonstrate the immobilization of treated waste coming from the Task 3 by Molten glass coating. The aim will be to make a selection of the treated waste according to the specifics of the immobilization techniques. The implementation of a coating technique using molten glass to get an effective binder, resistant and allowing high waste loadings, will be tested to obtain a monolithic waste form (laboratory scale samples). Finally, the reconditioned waste will be characterize by the determination of the chemical composition, mineralogy, microstructure and mechanical properties. A complete characterization will be achieved by the exchange of the samples and by the use of specifics equipment from the project (list of equipment and availability will be establish before the start of the project). Preliminary tests have been performed and allow to select some glass compositions. The ashes coming from IRIS process have been characterized.

3. Materials

- CVRez mainly uses metakaolin, water glass and Dastite.
- CEA uses ashes coming from IRIS process and specific glass powder formulations.
- The CSIC has used as precursors several sources of metakaolin (MK) and a blast furnace slag (BFS). NaOH and Na_2SiO_3 laboratory grade reagents have been employed as solid activators.

- SIIEG NASU start development of cement-based and geopolymer matrices for treat waste. The based geopolymer matrices are mix slag-metakaolin with activators: sodium hydroxide + sodium silicate solution.
- VTT materials are in PREDIS metakaolin based with alkaline activators. Different types and qualities of metakaolin are under investigation to find suitable recipes for different applications. As reference material VTT is using OPC based material.
- SCK CEN uses two types of precursors were used including metakaolin and blast furnace slag. The activating solution contains sodium hydroxyl 10M and powder sodium silicate.
- CIEMAT, as well as UAM, will be using for the immobilization of the surrogates the geopolymer and cement-based matrices formulated by CSIC.
- POLIMI uses Italian volcanic tuff (VT), NaOH pellets as activator, blast furnace slag (BFS) and fly ash for the geopolymer formulation. The surrogate RSOW is IER residues from incineration and wet-oxidation treatments.

4. Methods

CSIC – More than 24 mixtures (one part geopolymers) with different proportions precursors (MK+ BFS) and activators (NaOH + Na_2SiO_3) were prepared, mixing the solids with water, and mechanical strength tested. Three different types of curing (1.) Climatic Chamber at 21°C, 99% RH, (2.) Laboratory conditions (21°C, 50% RH) and (3.) a soft thermal curing (60°C, 100% RH) were also analysed. The ratio w/s was around 0.42. From the several test, three promising dosages with ranges of MK (43-50 % wt.) + BFS range (35-40%wt.) + Solid Activators (HS + MS range 15-17% wt.) have been selected as representative matrix to incorporate the waste (next step).These mixtures were cured in the climatic chamber, at 21°C and 99 % RH, up to be mechanically tested at 3, 7 and 28 days. At 7 days, the compressive mechanical strengths range between 10-20 MPa. Consistency (minislump), Setting time (Vicat), Porosity (MIP), Microstructure analysis (BSEM), Stability of Volume (Drying Shrinkage at different RH conditions), Thermal behavior analysis (Temperature and Total Heat release) and Kinetics of chemical reactions (Isothermal calorimetry) on selected samples are on-going. Same experiments are being doing with the Portland based systems (CEM I and CEM III).

CVRez

- Consistency
- Setting times
- Water immersion
- Mechanical Strengths (2, 7 and 28 days)
- Porosity (MIP) and Microstructure (microindentation, FTIR, etc.)
- Stability of Volume (Drying Shrinkage at different RH conditions)

SIIEG – Test of hardened matrices for conditioning of residues and secondary wastes stemming from (thermal) treatment options. Compressive strength tests were performed using laboratory compression tester, at 7 and 28 days after casting for cement/slag and geopolymer matrices. The Compressive Strength was evaluated in accordance with the standard ASTM C109/C109M: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars or IAEA-TRS-222/1983 Conditioning of low and intermediate level radioactive waste.

VTT – Suitable recipe development start with the fresh material properties. Normally the material had to be flowable in consistency. This is measured using normal concrete technology test methods but also using rheological measurements. Strength target is not very important in immobilization itself. Strength is used to measure the quality of reactions. Dimensional stability in wet and dry condition is measured. Durability and long term aging of the developed material is in high important property. This will be measured with leaching tests coordinated with T6.6. In addition, accelerated chemical attack test are planned.

POLIMI uses its own protocol for determination of CEC of VT based on literature [3]. VT and single-cation solution are contacted. Once thermodynamic equilibrium is reached, the supernatant is separated and analyzed by ICP-MS to assess CEC of each cation of interest. The preliminary characterization of VT-based geopolymer grout (e.g. workability, setting time) and manufacts (e.g. compressive strength, water immersion, thermal stability) is not completely started yet, but will be performed following standardized methods.

SCK CEN – The first casting, we did preliminary small scale tests with the undried salt (52% water content). The main conclusion from this was that the workability was reasonable and that the 14 day strength was especially promising for metakaolin based samples, which showed an increase of compressive strength with increased waste loading. The second casting, we used the room temperature conditioned salt (16% water content instead of 52%). The viscosity was measured, which developed extremely quickly. The 7 day strength was again superior for the metakaolin samples. In order to solve the issue of flash setting. The third casting was focused on metakaolin, as they produced a superior strength. We accounted for the Na_2CO_3 in the salt into the total binder content as it is suspected to have an activating effect. Four different recipes were tested, 3 with a waste loading of 30% and a w/b ratio varying from 0.75 to 0.95, and 1 with a waste loading of 40% and a w/b ratio of 0.85. The first recipe (w/b of 0.75) still had a very fast viscosity development (12700 Pa.s at 5 minutes), but the subsequent recipes improved on this point. The recipe (w/b of 0.85, loading 40%) had the most gradual viscosity development so far. The mechanical strengths were developed very good.

CIEMAT – As part of the characterization of both the optimized matrices and the final wasteforms, CIEMAT will be using its internal qualification procedure for Barrier Materials [4]. This procedure includes the determination of parameters such as:

- Setting time (according to UNE-EN 196-3:2017)
- Mechanical resistance (compressive and flexural strength) (UNE-EN 196-1:2018).
- Dimensional stability (internal procedure PT-LCRR-22)
- Porosity
- Water immersion
- Thermal cycling

5. Results

The results will be summarized in the interim report “T6.4 - The first etapa report”.

6. Conclusions / Summary / Way forward

- CEA: Tests will going on next year from first quarter on the occasion of an intership.
- CSIC: Incorporation of surrogate wastes in geopolymers and in OPC cementitious systems.
- CVRez: Immobilization tests with salts of MSO and others residues from T6.3
- VTT: Binder comparison, Measurement of leachability of solidified low level radioactive wastes by short-term procedure, ANSI/ANS-16.1-2003
- SIIEG: Direct encapsulation with mixing slag-MK based GP. Sodium hydroxide + sodium silicate solution were used as activators and use ICP-MS, BET method in combination with SEM picture of the surface alteration will be used for the surface characterization.
- UAM: Characterization of materials in interaction with CIEMAT and IETcc (CSIC) and post-leaching characterization in interaction with CIEMAT and IETcc (CSIC), using the same structural and elemental techniques.
- CIEMAT: Optimization of the formulations defined by CSIC, maximum waste load and reconditioned waste form.
- SCK CEN: Further immobilization tests with MSO salt from CVRez.
- POLIMI: Will complete the investigation about CEC of VT and optimize the formulation of VT-based geopolymer. The fresh grout and the hardened specimen will be characterized. Furthermore, loading capacity of VT-based geopolymer towards surrogate IER residues will be assessed and the properties of the specimens will be determined.

Acknowledgements

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References

[1] Nguyen TN, Phung QT, Frederickx I, Jacques D, Dauzeres A, Elsen J, et al. Effect of precursors and water to binder ratios on the water permeability of alkali-activated mortars. The 4th International RILEM conference Microstructure Related Durability of Cementitious Composites. Delft, The Netherlands 2021. p. 10.

[2] Phung QT, Ferreira E, Seetharam S, Nguyen VT, Govaerts J, Valcke E., Understanding hydration heat of mortars containing supplementary cementitious materials with potential to immobilize heavy metal containing waste. Cement and Concrete Composites. 2021;115:103859.

[3] W. Baek, S. Ha, S. Hong, et al., Cation exchange of cesium and cation selectivity of natural zeolites: Chabazite, stilbite, and heulandite. Microporous and Mesoporous Materials, Vol. 264, p. 159-166, 2018.

[4] E. Magro., Caracterización Fisico-Química de Materiales de Barrera de Residuos Radiactivos. Procedimiento de fabriPT-LCRR-20-01. 2019.

14. Wasteform Densification

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Abstract

The task of work package 6.5 is research of wasteform treatment through densification routes, either via simple compaction or with hot isostatic pressing (HIP), utilising combined expertise from the UK, France, and Ukraine. The materials due to be treated include a range of simulant organic wastes, or materials arising from prior thermal treatment processes. A simple compaction pelletisation process is being trialled for ashes arising from incineration of organic materials at the IRIS facility in France, with some ashes also undergoing HIP thermal treatment with suitable additives (if required) to form a solidified waste product. HIP technology will also be utilised for inorganic sludges arising from Fenton wet oxidation processing of organic ion exchange resins, and for the densification treatment of geopolymeric materials containing wood ashes. These processing methods are expected to advance the technology readiness level of these technologies through demonstrating their effectivity for use with simulant wastes. These technologies may also assist underpinning other thermal treatment methods (such as wet oxidation and incineration) through the formation of solidified monolithic products post-treatment as a secondary process. Progress towards these goals are well underway, with collection, receipt and/or generation of suitable simulant materials for further processing and densification. The next 12 months are anticipated to result in extensive laboratory trials and generation of numerous densified products, in preparation for detailed characterisation and durability assessment testing.

Keywords: Densification, HIP, compaction, thermal, wasteform

1. Introduction

This work package task is aimed at the densification of materials to form solid wasteforms. Principally this includes densification via direct reconditioning (e.g. polymeric material) and conditioning of residues from thermally treated materials (wet oxidation, incineration). Densification techniques demonstrated here consist of either a simple compaction pelletisation process, hot pressing (HP), or hot isostatic pressing (HIP). These technologies have the potential to transform a wide range of suitable wastes into solidified products, due to their flexible processing parameters (heat, pressure, time) and wide range of compatible chemistries. The application of the appropriate level of pressure and/or heat to many inorganic powders will result in compaction, densification and sintering or melting, leading to the formation of a solidified monolithic product. With an increasing interest in the thermal treatment of organic wastes, which often generate inorganic residues, detailed investigations into the application of these densification technologies for a variety of wastes is critical.

This task is targeting stable densified products, through considered experimentation at various temperatures, pressure, the inclusion of additives (e.g. glass forming additives) and processing times – all to form optimum materials. Wastes targeted are generated or collected via a separate work package (Task number 6.3), which will then be ready for densification treatment within this package of work.

2. Work plan and preliminary findings

Work to be undertaken within this work package is dependent on the facilities available at each partner institution, availability of simulant wastes, and applicability to each country's priority research areas:

The French Alternative Energies and Atomic Energy Commission (CEA) is undertaking compaction pelletisation of inorganic carbon-free ashes arising from surrogate inactive waste incineration produced by the IRIS pilot (Installation de Recherche en Incinération des Solides – treating mixed plastic, cellulose and ion exchange wastes). Pelletisation will be performed on blended powdered materials (bulk mixing using a Morton blender), using a rotative press to form pellets, with additives/adjuvants if required to improve pellet properties. Previous pelletisation trials using ash and 10% bentonite as a binder have shown promise, and are helping to form the basis of this extended study [1].

The University of Sheffield (USFD) are using HIP technology (Fig 1) to treat similar IRIS ashes, along with inorganic sludges arising from Fenton wet oxidation of organic ion exchange resins. The IRIS ashes will be hot isostatic pressed as-received, or with some minor additions of glass formers if required. Preliminary trials have successfully demonstrated that direct HIP processing of IRIS ashes, without additives, yielded a densified product with waste minimisation. Detailed characterisation is scheduled to be undertaken in the near future (Fig 2). Wet oxidation sludges will likely be immobilised within a glass or glass-ceramic matrix, varying in composition depending on the waste chemistry (oxides, phosphate, and sulfate content will vary greatly depending on wet oxidation processing conditions). Furthermore, a brief scoping trial is scheduled to be undertaken targeting low temperature isostatic pressing of polymeric wastes, via a direct conditioning test.

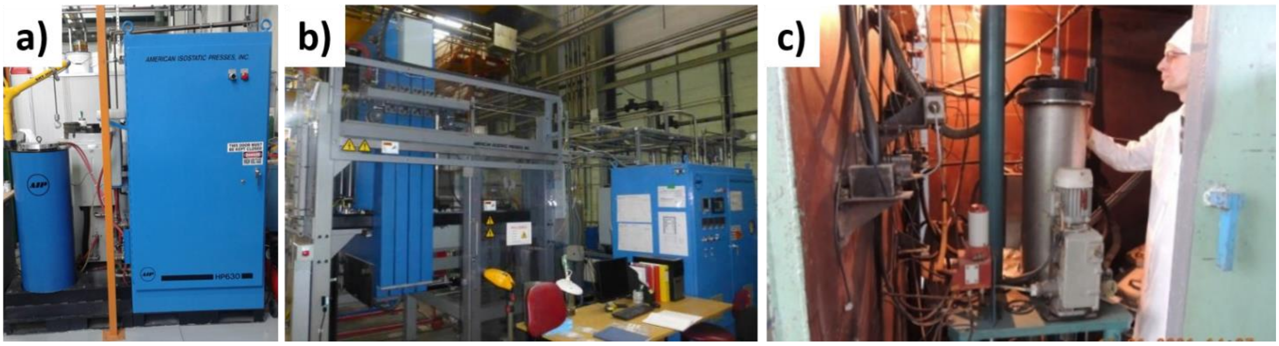

Figure 1. *HIP facilities at a) USFD, b) NNL, c) KIPT.*

Figure 2. *HIP treatment of IRIS ashes at USFD from left to right: can packing, welding, crimping, thermal treatment (1250 °C), and sectioning open the can.*

The Kharkiv Institute of Physics and Technology (KIPT) are investigating the densification of geopolymeric-ash materials, arising from incineration of non-radioactive wood (as simulant materials), using hot isostatic pressing technology (Fig 1). These ashes are encapsulated within a geopolymer cement, which is then left to cure for up to 28 days, following which, it is ground to a powder and pressed into pellets – ready for thermal treatment (Fig 3). KIPT are utilising several thermal treatment technologies ranging from conventional furnace sintering, hot pressing, and hot isostatic pressing, which will be used to form ceramic and glass-ceramic matrices.

Figure 3. *Preparation of material for treatment at KIPT: crushed geopolymer-ash material (left), alongside a pressed green body of the same material ready for thermal treatment (right).*

The National Nuclear Laboratory (NNL) will draw on their expertise of processing larger HIP products to enable scale-up trials utilising successful HIP formulations developed at USFD. Utilising simulant materials, and with a capability to process up to 8 L cans (Fig 1), this scale-up will demonstrate and underpin the applicability of this technology within an industrial setting. Successful scale-up HIP trials have previously been proven within the THERAMIN project [2], with similar wasteform characteristics observed between small and large wasteforms.

3. Way forward

This work package relies on the receipt of simulant material from other sources and work packages, with current world events having delayed the ready availability of these materials. Recently, feed-in of pre-treated materials from other work packages has begun, enabling some preliminary trials to be undertaken. Early preliminary trials have been undertaken on densification of these various simulant wastes, with promising signs. The next year of work will be focussed on ramping up production of densified simulant wasteforms, to enable these materials to undergo extensive characterisation and aqueous durability assessments.

Acknowledgements

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References

[1] M. Fournier, N. Massoni, J. F. Hollebecque, In-Can vitrification of ash. EPJ Nuclear Sci. Technol., 6, 25, 2020

[2] M. Nieminen, et al., Thermal treatment for radioactive waste minimisation. EPJ Nuclear Sci. Technol., 6, 25, 2020

[3] Hyatt, N.C., Corkhill, C.L., Stennett, M.C., Hand, R.J., Gardner, L.J., Thorpe, C.L., The HADES Facility for High Activity Decommissioning Engineering & Science: Part of the UK National Nuclear User Facility. IOP Conference Series: Materials Science and Engineering, 818 012022, 2020

15. WP6 Task 6 Physico-chemical characterisation of reconditioned waste form and stability testing

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Abstract

This task in WP6 is for the research on short and long-term stability and durability of different waste forms developed for solid organic low and intermediate level waste. The research aim give insight into conditions and phenomena like γ-radiation, chemical conditions and temperatures, which may affect to the behaviour of waste forms. To compare the results gained in this work package and draw conclusions in the end of the PREDIS project, a common reference protocol has been developed for leaching experiments. Protocol includes also characterization plan of solid and liquid samples. Next years of the project will contain executing the stability test and characterization of samples. By using reference protocol, we aim to gain comparability of the results between different waste forms, among the same waste form type from processes with a different way, and comparability between laboratories taking part into this task (CSIC, CEA, CIEMAT, POLIMI, SIIEG, SCK CEN, UAM, UH, USFD, VTT).

Keywords: Long-term stability, LILW, characterization, cemented waste, geopolymer, molten glass, HIP (hot isostatic pressing)

1. Introduction

The aim is to study the chemical and mechanical durability different waste forms produced from LILW solid organic waste (samples from task 6.4 and 6.5). The resistance and leachability of cemented waste, geopolymerized waste, molten glass coated waste and HIP waste are to be studied. The leachability study will include both the performance of the waste form matrix and the release of the bind nuclides or elements simulating their behaviour. Complementarily, most of the partners will also execute experiments based on national conditions or expected effect to take place in LILW repositories. POLIMI will also simulate the radiation effect by γ-irradiating the samples prior to stability experiments. The sensitivity to alkali silica reaction (ASR) and sulphate attack will be also assessed. Other aspects that will be studied include the effect of temperature and pH on the stability of the different types of waste form.

2. Materials

The materials to be used in task 6.6 will be received from the previous tasks of WP6, in which solid organic waste or material simulating such a waste are processed and reconditioned. These reconditioned waste forms include geopolymer, cement based materials and molten glass coated samples from task 6.4 Immobilization, and samples densified with HIP technique from task 6.5 Densification.

3. Methods

During the first 9 months of the project, the main target has been to establish reference protocol, to compare the final results of the characteristics and long- term stability of reconditioned waste form. Three different aspects of comparability were defined; 1) the comparison of different kinds or compositions of solidified waste forms; glass, glass-ceramics, geopolymers and cement based materials 2) the intercomparison between leach experimental results from different laboratories on one product 3) the intercomparison between leaching experiments on products from different processes; different waste forms and different reconditioning processes.

The steps towards the common reference protocol have included: review of existing reference protocols [1-3], feedback from the end-user group, few questionnaires among project partners, and finally two meetings to discuss the final details of reference protocol. Information sharing and collaboration with ongoing EU projects were also used to aid the e.g. the selection of water composition to be used.

In addition to reference protocol, most partners have been planning leaching experiments to research specific topic or nationally relevant leaching conditions.

4. Results

Reference protocol contains basic information to guide the execution of short term and long term experiments, including leachant composition, test type, sampling intervals, temperature, duration, target ratio for leachant to specimen surface ratio and reaction vessel type. In addition, the basic characterization techniques (minimum requirement) for liquid and solid samples were defined to compare the experimental results. The protocol is presented more detail in Table 1.

Some additional information is also given based on issues that have arisen in discussions. If possible and present in leached samples Co, Ni, I, lanthanides and main anions should be analysed also from liquid samples. Depending if methods are available for defining porosity that would beneficial. However, the gas adsorption techniques should be preferable. If partners are interested to study formation of colloids, syringe filters of 0.22 µm (PVDF) as nominal cutoff, 0.10 µm (PVDF) and 0.02 µm (Anotop) are recommended to be used at time of 1 and 2 years.

Most partners will also conduct leaching experiments based on their own or national interest.

Short term leaching studies will include following experiments by;
CEA: glass monoliths leached according ASTM Standard Test Method C
SCK CEN: Leaching of cement based waste and geopolymer waste form in alkaline solution
CSIC,UAM, CIEMAT: geopolymerized waste in national conditions; protocol based on ISO 6961:1982
VTT & HU: geopolymerized waste in nationally relevant conditions

Long term leaching studies will include following experiments by;
SCK CEN: Alkali-silica reaction (ASR) of cement-based materials
SCK CEN: 3 years dissolution of HIP samples
POLIMI: gepolymers with elevated temperatures and γ-irradiated samples
CSIC,UAM, CIEMAT: geopolymers in national conditions; protocol based on ISO 6961:1982
VTT & HU: geopolymers in national conditions

CVRez has announced that they could be able to deliver geopolymerized intercomparison samples to partners willing to take part in intercomparison test between different laboratories.

Table 1. *Defined reference protocol for short term and long-term stability testing including minimum requirements for characterization of liquid and solid.*

PREDIS Reference protocol		**Additional information**	**Comments, Recommendations and optional sampling etc.**
Leachant	"CEM I + silica fume" synthetic water (without silica)	pH ~12.7 about 18 mg/L Ca, 2800 mg/L K + minor element	
Type	**Semi-dynamic** (each step refreshing the complete volume of leaching reactant) + passive/static phase in the end of long term experiment?	Changing frequency: **1st year** 7 days, 14, 21, 28 d, and monthly there after **2nd year:** 14, 16, 18 months and 2 years	- Recommended use of **glovebox** or **N_2-purging** of the headspace of the vessels
Sampling intervals	Modified from ISO 6961-1982; Long term leaching testing of solidified radioactive waste forms	**1st year**: 7 days, 14, 21, 28 d, and monthly there after **2nd year**: 14, 16, 18 months and 2 years	-Shorter time spans (1 and 3 days) can be voluntarily sampled with small aliquot from liquid phase
Temperature	**22±2 ° C**	Some partners will use also 40, 70 or 90 °C	-Temperature monitoring recommended
Duration	At least **90 days** (or until leaching rate has become virtually constant) for short term studies AND the **2 years** for long term studies		

PREDIS Reference protocol		**Additional information**	**Comments, Recommendations and optional sampling etc.**
$\mathbf{V_{leachant}/S_{specimen}}$	Volume of the leachant / exposed **"geometric" surface area of specimen"** **RATIO** 0.10 ± 0.02m (=10 cm) between leachant volume and specimen external surface area.	Ratio means e.g 10 cm^3 of solution per 1 cm^2 of surface area. Ratio kept same, specimen geometry and size can vary	
Vessel	PP, PTFE or PFA (Polypropylene, Polytetrafluoroethylene, Perfluoroalkoxy alkane)	Glass vessels should be avoided with high-pH solution	
Basic techniques to be used as minimum characterization	**Solid specimen: Density**, XRD, (porosity with some method), SEM	Initial specimen, 90 d, 1 year, 2 years	-BET/MIP optional (gas adsorption techniques preferable)
	Leachant: pH, electrical conductivity, elemental concentrations (Ca, Na, Si, Al, Cs, Sr, Fe)	**1st year**: 7 days, 14, 21, 28 d, and monthly there after **2nd year**: 14, 16, 18 months and 2 years. **Non filtered** samples	-Co, Ni, I, Lanthanides if present in waste. -Main anions, if possible

5. Summary

The first year of the project has been focused on the development of a harmonized leaching test procedure, including the characterization of the waste forms and leaching solution before and after the tests. Partners have done plans and background research on their national level and the consortium has worked together to achieve shared reference protocol. Both nationally relevant conditions and reference protocol will be used in actual experiments. Questionnaires and online roundtable discussions with a draft protocol have been good ways to work towards common reference protocol among task partners.

Next, the preparation and stability of “CEM I + silica fume reference water recipe will be tested in collaboration of SCK CEN and VTT. The recipe and preparation procedure will be disseminated to all partners in May-June 2021. Experimental activities should start soon and preparations to made to share geopolymer intercomparison samples produced by CVRez.

Acknowledgements

All partners in task 6.6 are greatly acknowledged for their information sharing, collaboration and good discussions in the process towards shared reference protocol. Special thanks to Georg Kosakowski and Karel Lemmens for facilitating the collaboration and information sharing between EURAD-ACED and PREDIS projects. The Spanish and Belgian teams are acknowledged for their special effort of development and testing the formulation of “CEM I + silica” synthetic water. Karine Ferrand and Borja Gonzales’s work on the development of the synthetic leaching solution is greatly appreciated.

References

[1] ANSI/ANS-16.1-2019; Measurement Of The Leachability Of Solidified Low-Level Radioactive Wastes By A Short-Term Test Procedure, An American National Standard, 2019.

[2] ISO 6961:1982, Long-term leach testing of solidified radioactive waste forms.

[3] E. D. Hespe, Leach testing of immobilised radioactive waste solids. a proposal for standard method. At. Energy Rev. 9: No. 1, 195-207,1971.

16. Overview of WP7: Innovations in Cemented Waste Handling and Pre-Disposal Storage

Written by: Niederleithinger, E., Lay, V., Köpp, C., Bundesanstalt für Materialforschung- und prüfung (BAM)

Abstract

The main objective of the work performed so far in WP7 "Innovations in cemented waste handling and pre-disposal" is the compilation of information about the state of the art of current methods and procedures for cemented waste management with specific focus on monitoring/long-term storage. A variety of methods from non-destructive evaluation such as ultrasonics, RFID (radio-frequency identification) based sensors and muon tomography are crucial for characterisation of cemented packages. Based on this, the application of newly developed digital twin technology and modelling of characteristic degradation processes together with an advanced data management aims at improving the safety of all storing and handling procedures, especially with regard to people working in this area. A digital decision framework will be developed that identifies the actual condition of the waste and suggests the best possible treatment. In this context, options for post treatment of packages and potential approaches to improve package design, construction and maintenance are considered and evaluated in terms of their potential to further optimise treatment of waste and procedures of its handling and storage. The focus in WP7 is not only on the waste packages itself, but also on the storing facilities. Certain parameters concerning their condition, suitability and integrity are monitored and assessed as well.

Keywords: Non-destructive evaluation (NDE), monitoring, State-of-Knowledge, digital twin technology, modelling, data handling, quality assurance, demonstration

Description of work and main findings

1. Introduction

Grouting/cementation of radioactive waste has been deployed as a suitable treatment for the immobilisation of such waste streams for many decades and is still a routine that is widely used. Such encapsulation and waste storage operations have been done by nuclear operators across the EU, leaving significant volumes of cemented, packaged wastes for the actual and for future generations.

This situation is more or less similar for all EU member states, with waste produced by nuclear generation, fuel cycle operations, laboratory research and healthcare procedures. Innovation in this area means improving safety and cost efficiency for example by reducing intervention and repackaging. In this context it is crucial to develop a better knowledge of the characteristics of such waste prior to its final disposal and to understand the chemical, physical and thermal processes that take place over time and lead to change of characteristics and cause degradation of the waste itself and possibly the surrounding storing facilities.

While most intermediate storage operations have thus far functioned as expected, several challenges have been identified regarding external demands or unexpected material behaviour/development:

Packages must be stored in temporary storage facilities much longer than expected before being finally deposited in a permanent repository. Degradation of the waste packages has been developing faster than expected in some cases. For cemented waste, deformations have been observed for the encapsulation of reactive metals, such as Al, Mg. Deficiencies in the packaging and handling of radioactive waste have led to dangerous working conditions at some sites and have resulted in large and expensive clean-up operations. Methods for limiting direct human interaction with the waste packages and for early identification of potential problems will be essential to overcome these safety and cost barriers.

The workplan of WP7 includes both technical and informal tasks. The latter include the management within the work package (T7.1) and all activities around the dissemination of findings and results (T7.7). No explicit summaries are provided for these work packages as the workshop proceedings concentrate on the technical aspects. The starting point for the work in WP7 is the compilation of a comprehensive overview about the whole subject. The current state of the art in packaging, storage, and monitoring of cemented wastes is given in T7.2; a task that laid the ground and base for the work package. This task is still ongoing and the "state of the art report" will continuously be updated over the course of the project.

To include the very important view of the end users of all related methodologies, a WP7 workshop was held in early spring 2021. This served as an information hub to introduce the PREDIS project to the end users and, in return, ask them for their feedback and support, without which such a project would not be useful.

They were asked about specific topics/ideas/gaps that might be missing in the project or should be more focussed on. What are the biggest challenges with cemented waste treatment and where could be the greatest innovation potential for cemented waste treatment?

They were also encouraged to actively participate in the project by providing case studies, waste acceptance criteria (WAC) issues, material info, give access to test sites, provide feedback on needs (participate in gap analysis surveys),

Tasks 7.3 to 7.6 are the technical tasks of the WP7. Here, the technologies of waste characterisation, degradation monitoring, data handling and processing as well as the development of digital models (digital twins), decision making algorithms, and the adaptation and improvement of non-destructive measurement methods are worked out.

In the following, the work performed in all technical tasks is described in detail. T 7.1 (management) and T7.7 (dissemination) will not be reported here.

Tasks

See introduction above.

Task 7.2 SotA in packaging, storage, and monitoring of cemented wastes

- **SoTA report**

Written by: Stefania Uras (SOGIN) and Slimane Doudou (Galson Sciences);

Stefania Uras (SOGIN) presented the outcomes of sub-task 7.2.1 relating to compilation of the state-of-the-art (SoTA) in packaging, storage, and monitoring of cemented waste packages. The scope of the SoTA report was to record the current packaging and storage system, current monitoring and data collection systems, store management procedures, and use of digital twins for continual system assessment. The SoTA report provides a starting point for performing the gap analysis and enables a comparison between the current state of knowledge and the state that will be reached at the end of the PREDIS project. The original plan was to employ a combination of site visits to storage facilities, distribution of questionnaires to store operators, and use of available publications to collect data for the SoTA report. However, owing to COVID restrictions, site visits were not possible. Completed questionnaires were received from 11 organisations across Europe. The responses were compiled into the SoTA report which was submitted to the EC at the end of February (Deliverable 7.1). Preliminary results from the limited number of questionnaire responses received so far were presented and noted that further information from End Users and project partners is welcome and the SoTA report will be updated to include any additional material received.

- **Reference package and factors affecting package evolution and degradation**

Written by: Darren Potter and Alex Potts; National Nuclear Laboratory, United Kingdom; email: darren.potter@uknnl.com

2. Summary and Way Forward

At the All Partner Workshop, NNL presented the draft consolidation of its finding for establishing a reference package and factors affecting the evolution and degradation of packages for WP.7 task 7.2.2.

This reference package uses an UK RWM standard single skinned 500l drum containing a BFS:OPC grout and a homogeneous/heterogenous waste content. This example is to be scaled accordingly to the 200l EN drum standard for our reference package scenario.

To date, no end user requests for package type for the mock-up tests have been received and so the State of the Art (SOTA) Report [1], Table 9, was extended by NNL and was used to identify characteristics of waste packages that are common for end users across EU states. On this basis the most common description of a package was found to be: EN Standard 200l drums, single skin, stainless steel, and with an OPC based grout matrix.

The draft parameters for a reference package were presented at the All Partner Workshop and will be finialised in the August 2021 deliverable.

Common degradation mechanisms highlighted include: Expansion creating stack stability issues, package identifier degradation, reactive metals, radiolysis, off-gassing, residual stresses leading to expansion which causes cement cracking and package deformation, chloride corrosion, microbial and chemical processes.

Generally, packages are single skinned however there are some instances where double skinned packages with an annulus grout are used. Our partners, UJV, have agreed that both a single and double skinned package can be manufactured, if selected, for the mock-up tests in Sub-task 7.6. A suitable cement formula has already been identified for this package annulus. A final proposal will be presented to WP7 Task Leaders at the beginning of July for discussion so that a decision on the reference package can be made at the July WP7 Task Leader Project Meeting.

Our reference package deliverable will look to identify a concrete package type in order to cover other package types. However, a mock-up of a concrete package is not foreseen.

References

[1] S Uras, State of the Art in packaging, storage, and monitoring of cemented wastes. Deliverable 7.1: 2021-04-14 version 1.1. Accessible via: https://predis-h2020.eu/wp-content/uploads/2021/05/PREDIS_WP7_D7.1_V1_SOTA_2021_04_14.pdf (Access confirmed: 14/06/21)

Task 7.3 Integrity testing and monitoring techniques

T7.3 has not yet fully started. It will do so, when a) in T7.2 a final decision has been made which waste package type(s) will be used in WP7 and specifically in T7.6 and b) T.7.4 has identified the parameters which are needed to update the digital twin models. For the time being, the work in T7.3 has been limited to identifying the most promising techniques which would be needed to fulfil the needs identified by end users, compiled in the state of the art report produced in T 7.1

However, work hast started to adapt several measurement and monitoring techniques to the requirements of PREDIS. Work plans and eventually first results are described here.

- **Muon tomography**

Muon tomography has the potential to “x-ray” legacy waste packages without actually using X-rays but particle produced naturally by cosmic radiation. An experimental setup is available at INFN which will be used first to check whether certain features (metallic parts, voids) can be detected inside a package. The results will be verified later by a blind test using one of the PREDIS WP7 mock-ups.

The first experimental activity of the muon tomography is the detection of metallic bodies of different shapes, dimensions, and elemental composition, embedded in a concrete volume. The concrete volume is a cube of side 60-70 cm. To have more flexibility in placing the various metallic bodies within the concrete volume, we propose to compose the cube using small commercial concrete bricks (dimension 10.5 x 21 x 8 cm^3, density ~ 2.25 g/cm^3). We will produce some special bricks (Figure 5) cointaining the metallic bodies, with the same dimension as the previous ones. Table 1 summarises a preliminary list of the materials we are planning to incorporate in the concrete, which includes also an “empty” brick (item nr.11) to simulate the presence of an air bubble.

Table 1. *List of items which will be used in the first muon tomography experiments.*

Item nr.	Material	Shape	Dimension	Note
1	Iron/steel	Slab	5x5x10 cm^3	
2	Iron/steel	Cylinder	Ø=4cm, L=15cm	
3	Iron/steel	Slab	2x6x17 cm^3	
4	Iron/steel	Isosceles triangle slab	Base=5cm, Height=15cm, Thickness=2cm	
5	Iron/steel	Cube	4x4x4 cm^3	

Item nr.	Material	Shape	Dimension	Note
6	Iron/steel	Screw M20 Exagonal head with nut	L=6cm	
7	Iron/steel	Cylinder	Ø=3cm, L=16cm	to be placed in diagonal from top to bottom
8	Iron/steel	Slab	2.5x2.5x8.4 cm^3	for comparison with item 9
9	Pb	Slab	2.5x2.5x8.4 cm^3	for comparison with item 8
10	W	Slab	100x38.6mm^2, thickness varying from 7.5 to 15.0mm	
11	air	Empty box, faces made by Aluminium	empty box with same dimension of concrete bricks (10.5x21x8 cm^3)	

Figure 5. *Concrete bricks which will be used in the first muon tomography experiments.*

- **Ultrasonics**

As a second technique providing insight in to existing packages (for quality assurance or investigation of legacy packages), ultrasonic technique are planned to be used. These activities have been put on hold until the mock-up package types have been finally decided. If a type with outer steel casing is chosen, ultrasonic methods might be of limited use and the (very limited) budget allocated for these activities might be reallocated for additional WP7 work triggered by the end user questionnaire replies.

- **Low cost gamma and neutron detectors, readout electronics**

The low-cost gamma ray and neutron detection technologies available at INFN, namely SciFi and SiLiF, are being evaluated with respect to their possible implementation in the PREDIS framework of the cemented waste as highlighted in Figure 6. Their radiation detection features look nicely compatible with a medium-long term radiological monitoring scenario. Taking advantage of the possibility of data collection on an extended time span, such a monitoring looks capable of detecting small radioactivity asymmetries arising from a radwaste package whose concrete matrix is cracked. This is also supported by preliminary FLUKA simulations of a cracked concrete cylinder encased in a 1cm thick steel drum, as shown in Figure 7. The dedicated compact electronics supporting the detectors are designed with wired and/or wireless data connection capabilities.

Figure 6. *A possible arrangement of SciFi and SiLiF detectors around a radwaste package.*

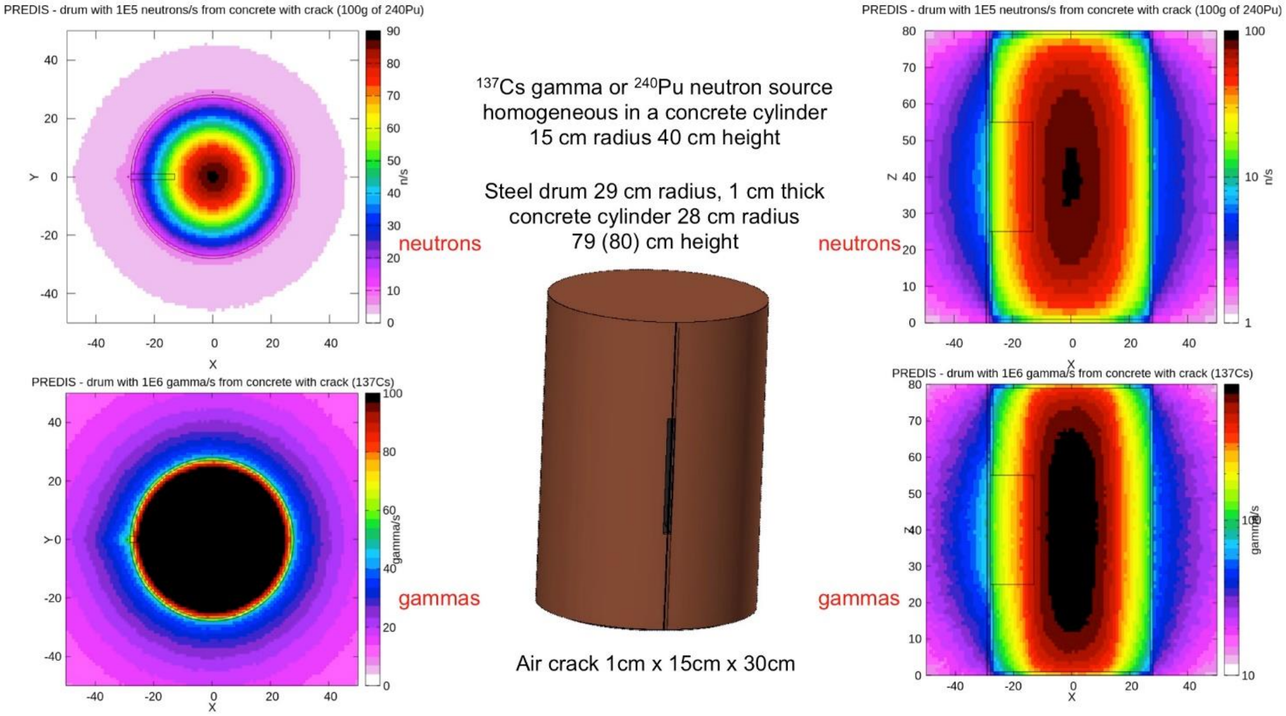

Figure 7. *FLUKA simulation of a concrete cylinder with a crack, encased in a steel drum. Gamma and neutron emission were simulated, and an increase of the radioactivity near the crack is observed.*

INFN is presently studying, within the framework of the PREDIS project, a new general purpose read-out electronics which can be used with different kinds of radiation monitoring detectors and in different scenarios: inside and outside a radioactive waste stockage site, during the radioactive waste transportation and for a more general environmental radiation monitoring. The main requirements for these electronics are the low cost, the low power consumption, an easy remote set-up and control and a high modularity. Moreover, other important features are the possibility to read-out sensors for environmental parameters (temperature, pressure, humidity, wind intensity and direction,...), the use of wired and wireless connections for remote control and data transmission, the local data buffering, the internet Cloud data collection and the geolocalization (GPS). The utilization of a FPGA CmodA7 device (for the detector output data management, data analysis, histogramming, comparison with alarm thresholds, ...) and of an ESP32 Micro Controller Unit (for the management of all other devices and of the communications with Wi-Fi and Bluetooth Wireless connections) should ensure the high degree of modularity and configurability required and a sufficient low cost of the components. Long-life rechargeable batteries could be used as power supply for the electronics, and a small photovoltaic panel could recharge them, with solar or artificial light. A low power consumption can be obtained by leaving the electronics always in «sleeping mode». Wake-up of the system happens periodically in an automatic way, with duration and frequency user definable, but a forced awakening of the system should be always possible through a device remaining awake but with a very low power consumption. In Figure 8 the interconnection among several modules and the external world is shown: the remote control of the modules and the data transmission is obtained via a Wi-Fi/Ethernet Router. In this example, the wake-up system, uses a Bluetooth device. Other possible wake-up systems using infrared or ultrasound signals are presently under study.

The Bluetooth device is used for the forced awakening of the system.

Figure 8. *Possible interconnection scheme for the detector read-out electronic boards and the external world, making use of a Wi-Fi/Ethernet Router and of a Bluetooth wake-up device.*

- **RFID sensors (internally)**

For new waste packages, internal radiofrequency identification (RFID) sensors could deliver data on the hardening process (short term monitoring) and condition (long term monitoring). The prototypes currently developed and tested by BAM have temperature, humidity and (optional) corrosion sensors integrated into a 3D-printed casing (Figure 9). The setup has been successfully tested in a concrete specimen, where the values delivered were compared to those of conventional cabled sensors (Figure 10). Additional sensing capabilities (e. g. pressure to detect swelling in an early phase) will be added later.

As a steel casing will block the communication between classical RFID sensors and the respective readout device, a new communication methodology e. g. based on piezoelectric ceramic materials such as PZTs (lead zirconate titanate) will be developed by VTT.

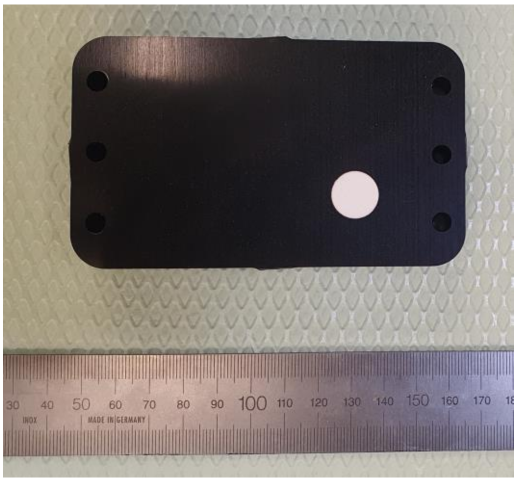

Figure 9. *BAM prototype for RFID sensor to be embedded in concrete.*

Figure 10. *Test setup (before concreting) with RFID sensor and cabled sensors for comparison.*

- **RFID sensors (externally)**

The UNIPI group is in the process of defining the design specifications for the development of sensorized RFIDs. These will provide both identification of waste-drums for chain of custody purposes, and radiation monitoring for structural integrity assurance. Use will be made of innovative semi-passive RFID tags equipped with high-sensitivity, low battery-drain gamma and beta radiation sensors. For a timely achievement of the deliverables, our group mainly utilizes off-the-shelf components and focuses on systems engineering for an innovative use of the chosen technologies.

In particular, we have already identified low-cost radiation sensors and semi-passive RFID tags & antennas operating with a supply voltage (and output pulse level) of ~ 3 V and a low current of ~ 20 µA, thus allowing a low battery drain and an expected battery life of well over one year. The radiation detector responds to gamma rays from 0.1 to 2 MeV and can operate in a dose rate range of 0.1 µGy/h to 100 mGy/h with a sensitivity of ~ 300 cts per µGy.

The semi-passive RFID tags provide sampling intervals from 5 seconds to 18 hours, either fixed or adaptive (i.e. based on radiation dose rate) and currently store up to 4,096 samples (16 bit depth) in their internal memory. The sensorized RFIDs can be interrogated remotely at distances of up to ~ 5 m with antennas/readers mounted on self-moving robots or overhead rail-mounted sliding trolleys.

The interrogation approach will be based on an analogue of the Anger logic implemented in medical gamma cameras and will be able to detect variations in the emission rates, also accounting for cross-talk and shielding between the drums.

Finally, an irradiation facility is also being developed by UNIPI, featuring a mixed radionuclide environment and expected dose rates of ~ 5 Gy/day in a shielded setting. The facility will allow the safe delivery of hundreds of grays for radiation hardness studies and it will be available to collaborating interested parties.

Task 7.4 Digital Twin

A Digital Twin/Tool for waste package evolution

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1. Short summary

The use of Digital Twin technology is a new hot topic in the industry and research. A Digital Twin can be seen as a digital representation of the physical object that can be used to monitor and predict its evolution as a function of time. While many Digital Twins are related to monitoring and modelling changes that happen over short time intervals (seconds, minutes for bridges, engines, cars etc.) a Digital Twin designed to represent the evolution of radioactive waste packages during interim storage is concerned with modelling changes that happen on scales of tens of years due to the very slow processes involved. A PREDIS Digital Twin would contain a selection of independent and/or coupled processes which can simulate the waste package evolution as a function of time.

As input, the Digital Twin will require main waste package properties such as its chemical composition, physical dimensions, and storage conditions.

Based on these input values, the Digital Twin will then select the appropriate evolution submodel(s) and use these models that calculate parameters that indicate integrity evolution of the waste package as a function of time (e.g. pressure and or volume changes)

Keywords: Digital Twin; digital tool; waste package degradation; chemical evolution; surrogate models; machine learning.

About task 7.4:

The Digital Twin technology is becoming a topic of interest in different industrial and research fields due to its capabilities of combining monitoring and modelling in a digital space. This allows the users to make inferences about the system's behavior as it happens and/or make predictions on the system's evolution with time. A Digital Twin can be seen as a combination of state-of-art process models that represent an approximation / abstraction of the physical entity in the digital space [1,2]. These models provide digital information on the state of the system at present or its evolution with time using a set of input data such as: monitoring data, the systems evolution history, model specific parameters (i.e., physico-chemical properties). In the context of the PREDIS project the aim is to build a proof-of-concept Digital Twin that can be used in waste predisposal applications. This will be based on machine-learning algorithms which will be trained with the output from state-of-the-art geochemical, and geo-mechanical models for predicting waste package evolution as a function of time, monitoring and geochemical characterization of real waste packages during interim storage. The Digital Twin technology covers a wide range of applications, and its implementation can vary highly depending on the system the considered, its breakdown into sub models and the evolution time frame of interest. In the following paragraphs we provide a short overview of our interpretation of a Digital Twin, what would be the purpose of a PREDIS Digital Twin, what could be the main input and output parameters, and how detailed the integrated models of the geochemical process should be. Finally, some ideas in the technical implementation are given.

A PREDIS Digital Twin

Madni et al. [3] give the following Digital Twin definition: "A Digital Twin is a virtual instance of a physical system (twin) that is continually updated with the latter's performance, maintenance, and health status data throughout the physical system's life cycle". Such a Digital Twin is aimed for systems where changes happen on the scale of minutes, seconds, hours. Readings form sensors are permanently used for improving/refining the models in the Digital Twin. The physical object could be a car, a building, a bridge, or a jet engine connected to sensors that collect data feeding the digital model. The user can observe how the physical object is behaving in real time in the real world.

When considering waste packages and the changes that happen during predisposal, these changes are related to chemical processes that happen very slowly over time scales of tens of years. For example, the degradation of organic matter (10^{-3}-10^{-5} mol/a), corrosion of metals (10^{-5}-10^{-8} mol/a for aluminum and steel), mineral dissolution/precipitation (10^{-14}-10^{-16} (mol/m^2 s), quartz dissolution; 10^{-7}-10^{-11} (mol/m^2 s), calcite precipitation), and ion diffusion in cement (10^{-12} m^2/s; gas diffusion 10^{-7} m^2/s) take several years to proceed in a significant amount [4]. Due to the very slow kinetics of these processes, the evolution of radioactive waste packages during interim storage has to be modelled in time scales of tens of years. A definition of a Digital Twin better suited for application to the predisposal of waste packages is one adapted from Bankhead et al. [5]: A digital Twin is a **framework capable of predicting** the most important variables of a physical asset, built from **several components** (or submodels) integrated into a single **powerful tool** that enables the end user to **predict the outcome of scenarios**, predict the values of outputs as a function of the inputs.

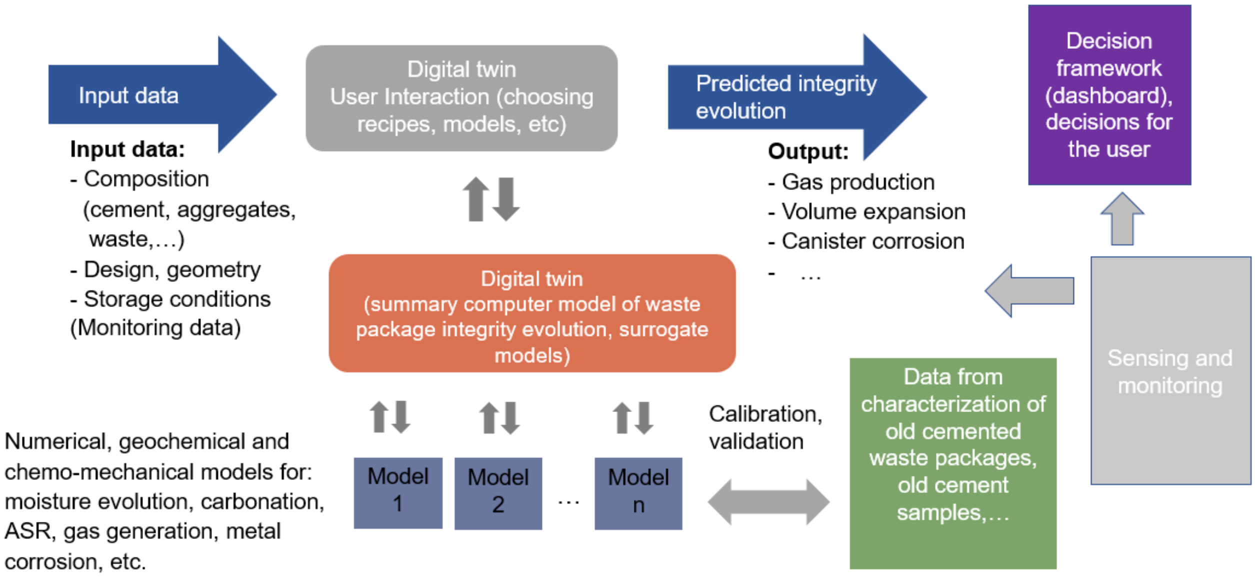

Figure 1. *A schematic overview of the Digital Twin (work in progress).*

We envisage a PREDIS Digital Twin (**Figure 1)** as a user-friendly and accessible tool specifically designed for assessing / predicting different waste package evolution scenarios. The tool should take into account a selection of independent and/or coupled processes (usually a few main processes are generally responsible for most changes) related to the evolution of mineralogical and mechanical properties. Full thermal-hydrological-mechanical-chemical (THMC) coupling is not foreseen. It uses fast machine-learning generated surrogate models that are trained on separate, detailed time-consuming numerical models. The user should be able to compute the chemical and physical behavior of cemented waste packages during interim storage for given waste package properties (input) to retrieve parameters (output) relevant for its integrity evolution as a function of time. Based on available data on waste packages (composition and properties) a set of reference waste types, predefined compositions, and materials will be available for the users to create their desired waste package "recipe" (matrix, waste type, material amount and volume) and run the available evolution models for a given time interval. This will allow to test different compositions of upcoming/ future waste packages (e.g., suitable aggregates, new phosphate rich cements) with the goal of predicting and avoiding potential problems. But also, to test different "what if scenarios" on legacy waste packages for which limited data are available. For example, to replace missing waste package data with predefined default data provided in the Digital Twin, combine it with the available information and see if there could be any waste package "recipe" that would result in exceeding waste acceptance parameters (e.g., use of different aggregates that could promote chemical reactions leading to a large volume change).

By running the models on different input parameters (based on waste packages composition data), a dataset of waste package evolution scenarios can be generated. These datasets could be used to train surrogate models such as neural networks for fast and efficient prediction of the evolution of future wastes without the need to run the full, time consuming, degradation models. In addition, having the possibility to efficiently run degradation models thousands of times allows for the use of different statistical models such as Monte-Carlo (MC) based uncertainty propagation (UP), and Global Sensitivity Analysis (GSA) [6]. These methods provide information on the probability that output properties exceed a threshold based on sampling the input parameter distribution (MC-UP) and rank input parameters based on their influence on the model output (GSA).

Input and output parameters

As input, the PREDIS Digital Twin will require data on the chemical and physical composition of the waste packages, their design, and their physical dimensions. Furthermore, data on the relevant storage conditions (e.g. temperature and humidity) will be used as input. Currently, this description is relatively generic.

To define this set of input parameters more precisely it is important to consider both the type of information about waste packages that is currently available, or can easily be measured, as well as the type of information that is required by the chemical evolution process models.

Because it is to be expected that the set of required input parameters will change over time, as new models will be added or new measurements become available, the Digital Twin structure is designed to accommodate such changes relatively easily.

This also facilitates the implementation of a prototype version of the Digital Twin, that can easily be adapted and extended.

Model integration

As the evolution of waste packages is most likely governed by a combination of chemical and physical - mechanical processes, it is logical that the Digital Twin has to contain a combination of chemical interaction and chemo-mechanical process models.

Examples of chemical processes are cement hydration, carbonation, moisture evolution, alkali silica reactions (ASR) sulphate attack, gas generation, metal corrosion, etc.

As reactants and reaction products of many of these reactions have different volumes, these reactions often induce volume changes, which as a result can affect physical – mechanical properties and integrity (stress, stretching, cracking, gas pressure build up etc.).

The occurrence and rate of such chemical reactions is determined by local (mm scale) chemical conditions within the waste package, which is a challenge as waste packages are usually relatively heterogeneous (Figure 2) and local chemical conditions may be very different from the average chemical composition.

There are, however, different ways to approach this and technical methods to implement and integrate. One approach would be to model a complete single waste package using a detailed reactive transport model discretized at mm scale, that is combined with a mechanical module to describe physical behaviour based on local chemical conditions. The drawbacks of this approach would be that not only calculations would take a very long time, but also that a large set of input data would be required that is currently not available in practice for any waste package.

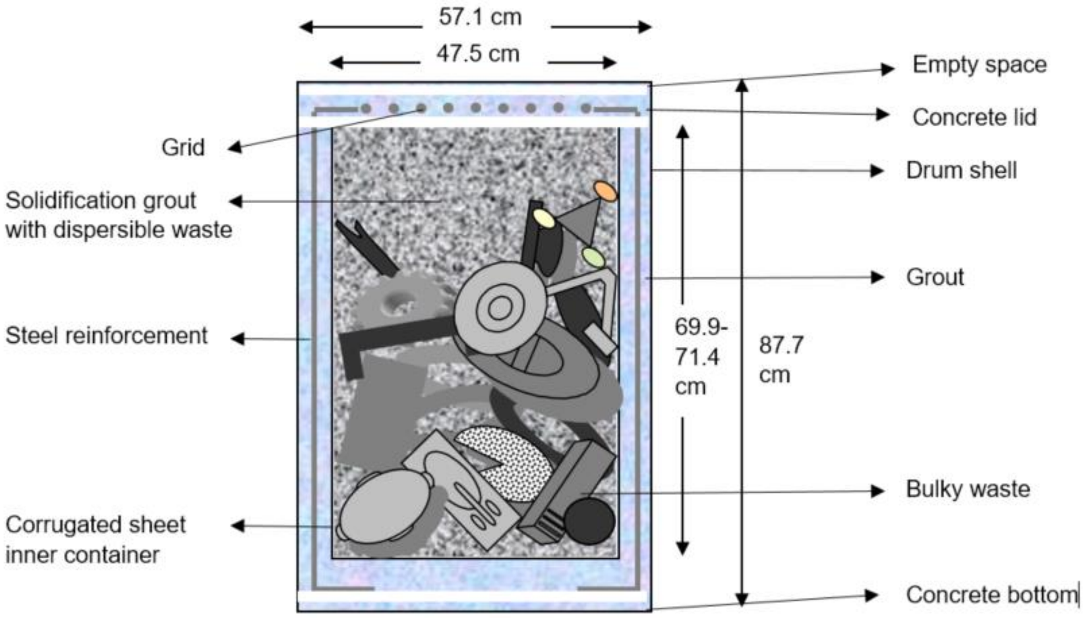

Figure 2. *Schematic diagram of a cemented waste package: Cement solidified dispersive and bulky waste in a 200 l steel drum. (Wällisch, A. 2020. Paul Scherrer Institut, Villigen, Switzerland. Pers. Comm.)*

The other end of the scale of complexity would be to treat the complete waste package as a homogeneous well-mixed cell, in which the main degradation processes are represented with a small set of reaction equations. The advantage of this approach would be that calculations are much faster and that much fewer input data would be required. A problem would be that this method would probably not be able to capture the main driving forces for chemical evolution in heterogeneous systems as these are determined by local chemical conditions.

For the PREDIS Digital Twin, we therefore aim to follow an approach between these extremes, in which we define a waste package in terms of building blocks selected from certain categories (e.g., cement, metallic iron, metallic aluminium, bituminous, PVC, to be decided) each with their own degradation process model.

Instead of linking actual detailed physico-chemical degradation process model codes into the Digital Twin, we aim to use machine learning surrogate models for this purpose instead. Training of individual surrogate models can take place off-line using data generated with detailed models that may take long times to run.

Technical implementation

The Digital Twin can be implemented using the Python programming language as a glue for different methods and codes. Python offers a suite of libraries for data processing, statistical analysis, visualisation, and machine learning. Codes that are written in C++ can be used in python with the addition of a C++ - python API for the main functionality using the pybind11 library. Data from other codes that are closed source or available in other programming languages can be exchanged with the Digital Twin using simple input/output ascii/text files in CSV (comma separated value) format that can be easily converted to other formats and can in principle to be uploaded in an actual database (for large amount of data).

The development environment will be Jupyter notebook / Lab. This is a web-based, collaborative interactive development environment that works in the browser. One can easily create simple demonstrative web apps that can be shared between developers and users with no or minimum requirements for installing dependencies.

2. Conclusions

Constructing a Digital Twin describing the evolution of cemented waste packages is a challenge because of their heterogeneity, the slow and complex evolution process, and computing intensive detailed model simulations.

Our aim is therefore to design and implement an easily extendable modular Digital Twin that uses fast machine learning generated surrogate models that are trained on separate detailed numerical models.

In this way the PREDIS Digital Twin can be easily extended to cover additional evolution mechanisms and can be used to simulate complex evolution scenarios.

Acknowledgements

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References

[1] P. Aho, An Open Source Digital Twin Framework, (2019).

[2] T. Zhang, Y. Li, J. Cai, Q. Meng, S. Sun, C. Li, A Digital Twin for Unconventional Reservoirs: A Multiscale Modeling and Algorithm to Investigate Complex Mechanisms, Geofluids. 2020 (2020). https://doi.org/10.1155/2020/8876153.

[3] A. Madni, C. Madni, S. Lucero, Leveraging Digital Twin Technology in Model-Based Systems Engineering, Systems. 7 (2019) 7. https://doi.org/10.3390/systems7010007.

[4] E. Wieland, G. Kosakowski, B. Lothenbach, D.A. Kulik, Geochemical modelling of the effect of waste degradation processes on the long-term performance of waste forms, Appl. Geochemistry. 115 (2020) 104539. https://doi.org/10.1016/j.apgeochem.2020.104539.

[5] M. Bankhead, K. Fritsch, J. MacDonald-Taylor, D. Trivedi, G. Ecclestone, W.J. O'Brien, Digital twin of nuclear waste management facilities, 8Th Int. Work. Reliab. Eng. Comput. "Computing With Confidence." (2018).

6] E. Laloy, D. Jacques, Emulation of CPU-demanding reactive transport models: a comparison of Gaussian processes, polynomial chaos expansion, and deep neural networks, Comput. Geosci. 23 (2019) 1193–1215. https://doi.org/10.1007/s10596-019-09875-y.

17. An integrated approach to assess the alkali silica reaction of cemented wastes

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Abstract

This paper summarizes the overall strategy to assess the alkali silica reaction (ASR) in the context of cemented wastes. This encompasses deployment of laboratory ASR tests and industrial scale drum tests at both reference and accelerated conditions, both of which provide data for future deployment of multiphysics based model for ASR, supplemented by computationally efficient meta model. In particular, this paper discusses preliminary laboratory ASR tests that are conducted to examine the efficacy of various instruments such under penalizing conditions, for example, the performance of pH sensors, strain gauges, thermocouples, pressure transducers, etc. So far expansion test results have become available, which shows a relative expansion under accelerated conditions, which results in a slight decrease in compressive and flexural strength of samples using reactive aggregate. For the corresponding tests, piezo sensor results are currently being examined, which offers a glimpse of crack formation.

Keywords: ASR; Cemented wastes; accelerated test; Non-destructive testing; modelling, digital twin

1. Introduction

The predisposal waste management is to produce waste packages suitable for storage, transportation and final disposal. For decades, the nuclear industry has used cement-based materials (CBM) to immobilize low- and intermediate-level short-lived and long-lived radioactive waste [1, 2]. Compared to other solidification techniques, cementation is relatively simple and inexpensive. Moreover, CBM shows many advantages including a good self-shielding, and a high alkalinity allowing them to precipitate some radionuclides. One could expect that this practice would result in a stable waste form and being well compatible with the final disposal site. There are, however, many examples that show that this is not always the case. Specific issues have been addressed, such as the gel-formation attributed to ASR in the concrete operational waste of the nuclear power plant of Doel, Belgium [3]. The cement–waste interaction disturbs the equilibrium between the pore solution of the cementitious materials and the solid phases of the cement matrix, which results in dissolution and/or precipitation of minerals. The degradation is a function of many factors including the constituent materials, its location (e.g. coastal, inland or underground for waste disposal), climatic conditions (e.g. temperature and moisture), and the presence of external agents (e.g. sulfates and chemicals). The most common chemical degradation processes include chloride ingress, sulphate attack, alkali-silica reactions, carbonation and Ca-leaching.

ASR is a deleterious reaction between the silica from aggregates and alkalis in pore solution or portlandite (CH) in the presence of water to form ASR gel (e.g., calcium potassium silicate hydrate, calcium sodium silicate hydrate) [4]. The amount of ASR gel varies depending on the reaction temperature, type and proportions of the reacting materials, gel composition, gradation of aggregates, and other factors, among them silica content and the internal structure of aggregate are the most important. Swelling of this gel leads to stress development and potentially cracking of concrete. It has long been known that irradiation affects concrete properties. Nuclear irradiation can significantly increase the reactivity of silica-rich aggregates.

Within the WP7 of PREDIS project, SCK CEN, Magics Instruments and Belgoprocess propose an integrated approach to address the ASR of cementitious materials used for waste encapsulation. This approach includes comprehensive laboratory and drum scale experiments, which assesses the ASR at various accelerated levels. Furthermore, a modelling framework is proposed in which a combination of continuum scale thermo-hydro-chemo-mechanical model and a meta model will be used to simulate ASR expansion.

2. Description of work

In this reported period of the project, the joint SCK CEN, Magics Instruments and Belgoprocess has focussed on developing an integrated approach to assess the ASR issue. Laboratory scale ASR experiments have been successfully implemented with the aim of testing instrumentation technology during ASR progress such as pH sensors, thermocouple, piezo sensors, strain gauges, UPV, pressure transducers, acoustic emission, etc.

3. Materials

In order to keep the system simple but still realistic, we propose to perform the experiments on mortar without the waste at this stage. In this way, we will reduce the complexity of the modelling work. The combination of ASR and cement-waste interaction would introduce a new challenge for the proposed model in which we intend to use the existing chemo-mechanical constitutive laws for ASR without much change. Table 1 shows the compositions of 3 recipes, which are expected to give different expansion degrees due to ASR. These recipes are proposed but with slightly modified compositions suggested in ASTM standard 1260 [5] (due to the finer sand used). The recipe SIB used Sibelco M32 sand, which has been tested at Belgoprocess and classified as non-reactive sand. The recipe RIV used river sand, which is expected to be more reactive. Furthermore, the recipe LI also used river sand, but with the addition of $LiNO_3$ to mitigate the ASR. The molar ratio of Li to cement alkalis (Na + K) is 0.74 [6, 7].

Table 1. *Mix compositions for ASR tests.*

Mix	Cement, kg/m^3	Water, kg/m^3	Sand, kg/m^3	$LiNO_3$, kg/m^3	Note
LI	635.47	298.67	1270.93	3.36	Li + reactive sand
RIV	635.47	298.67	1270.93	0	Reactive sand
SIB	635.47	298.67	1270.93	0	Non-reactive sand

4. Methods

The diagram presented in Figure 1 shows an integrated approach including both experimental and modelling work to assess the ASR from lab to drum scale. The new approach is proposed in order to obtain a successful digital twin validation. This approach allows to provide sufficient inputs for modelling and digital twin. Lab scale experiment is for calibration of the model, while drum scale experiment is for blind prediction.

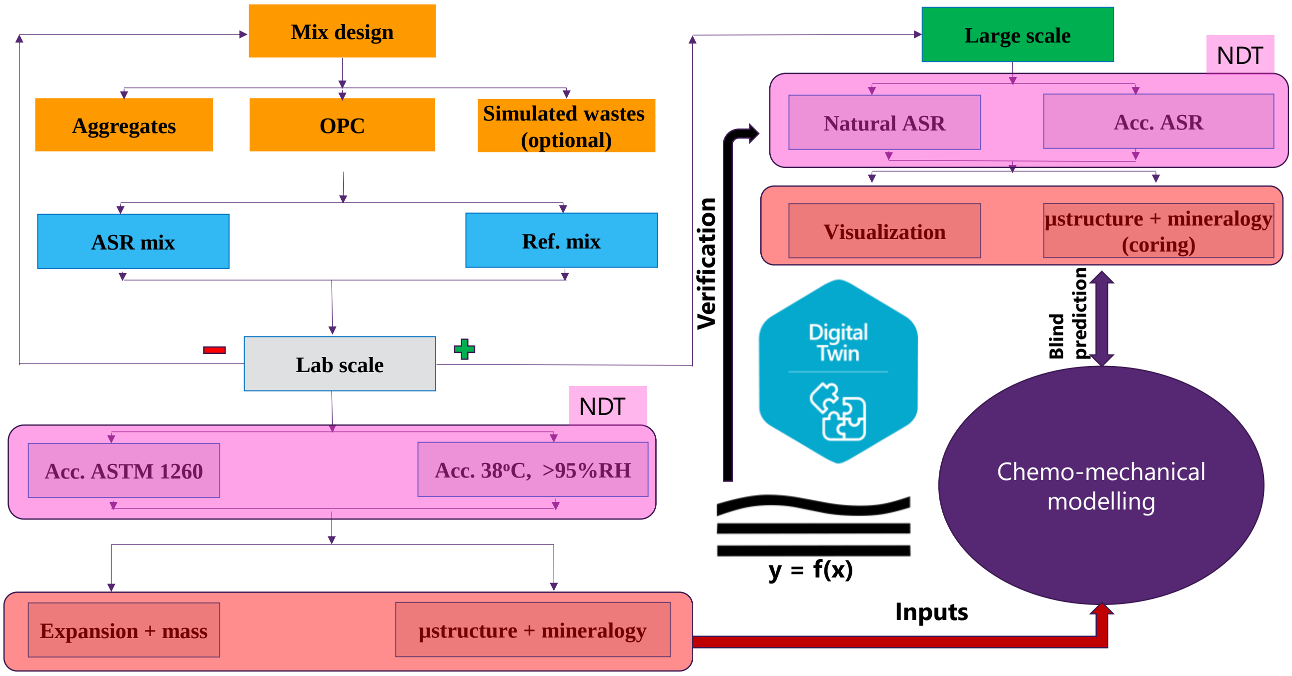

Figure 1. *An integrated approach to assess the ASR from lab to drum scale.*

Experimental

Lab scale tests

Accelerated ASR tests are performed according to the standard ASTM C 1260 [5]. The mixtures are prepared and three specimens are moulded in 25 x 25 x 285 mm^3 moulds. The pH sensors and thermocouples are embedding during casting. Two metal gauges are included at the bottom and top side of the bar in order to allow the length measurements. The mold is placed in the curing cabinet, at 20 °C and R.H. > 95%, immediately after their filling. After 24 hours, the specimens are removed from the molds and an initial length and mass measurement is done. The piezo sensors and strain gauges are embedded on one of the specimen surfaces as shown in Figure 2. The specimens are then saturated under water for 24 hours in an oven at 80 ± 2°C (**Figure 3**). A zero length measurement is taken of each specimen immediately after 24-hour saturation. The specimens are then placed again in a container at 80 °C in 1 N NaOH solution for accelerated ASR test. The test is run for 28 days and the length and mass of the specimens are measured again at the end of the test.

In order to evaluate the change of flexural and compressive strengths of the material due to ASR, standard prisms of 40 x 40 x 160 mm^3 are also cast. These samples are subjected to the same testing conditions as described above. Furthermore, the reference prisms are just immersed in water (without NaOH) at 80ºC. After 28 days experiments, both reference and accelerated prisms will be submitted to mechanical strength tests.

In addition, moderate test conditions close to realistic service conditions are also applied. The test conditions are modified from ASTM standard 1293, which is used to evaluate the potential expansion due to any form of alkali-silica reactivity [8]. After 28 days curing at 20ºC, the samples are placed inside a reactor at 38°C and relative humidity higher than 95% for 1 year. Note that in this case, NaOH is added to the mix to obtain a Na_2O equivalence of 1.25% by mass of the cement. Length and weight measurements are measured monthly on all samples, including the reference sample. After 360 days, the mechanical strengths of all samples are determined. During the experiments, the strength is estimated by the ultrasonic pulse velocity (UPV) method. The UPV measurement can be done during the length and weight measurements.

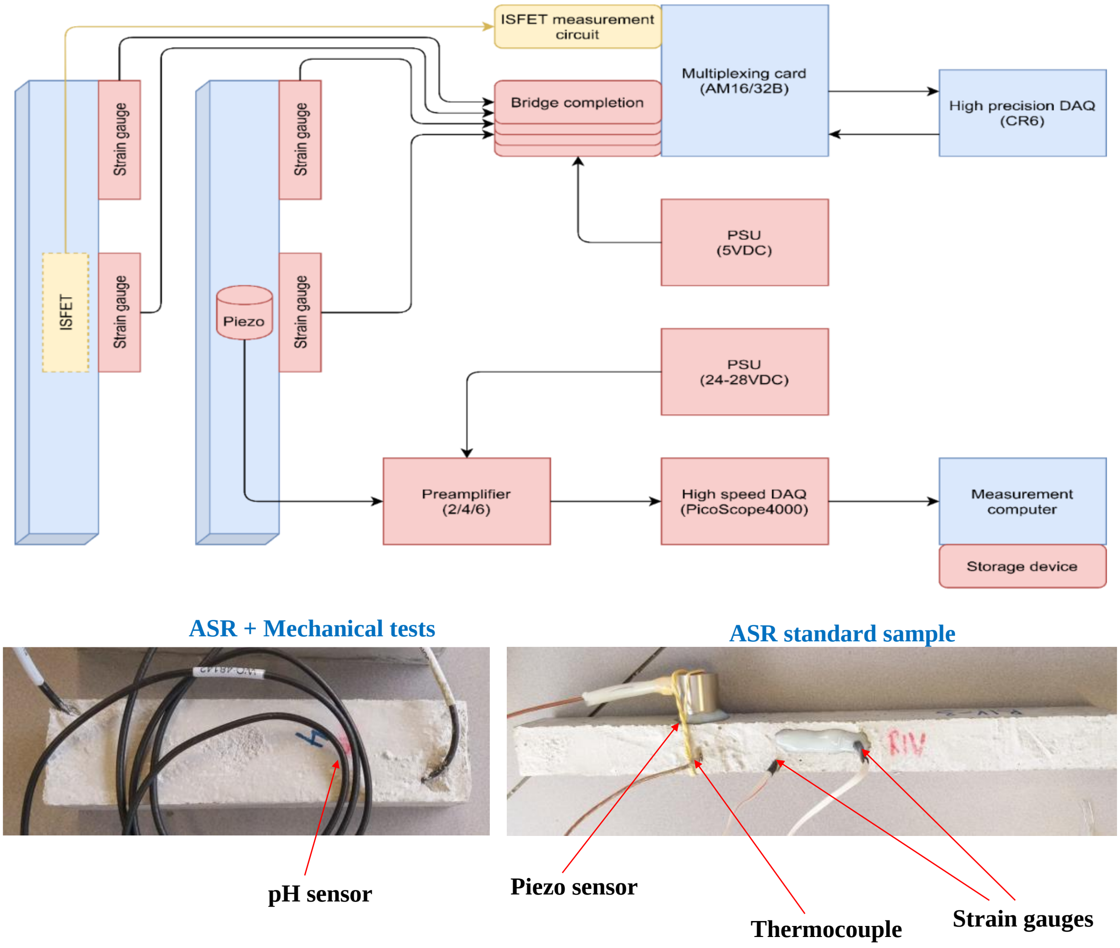

Figure 2. *A diagram of sensor installation and data acquisition (top) and examples of sensors embedded on long and short prisms (bottom).*

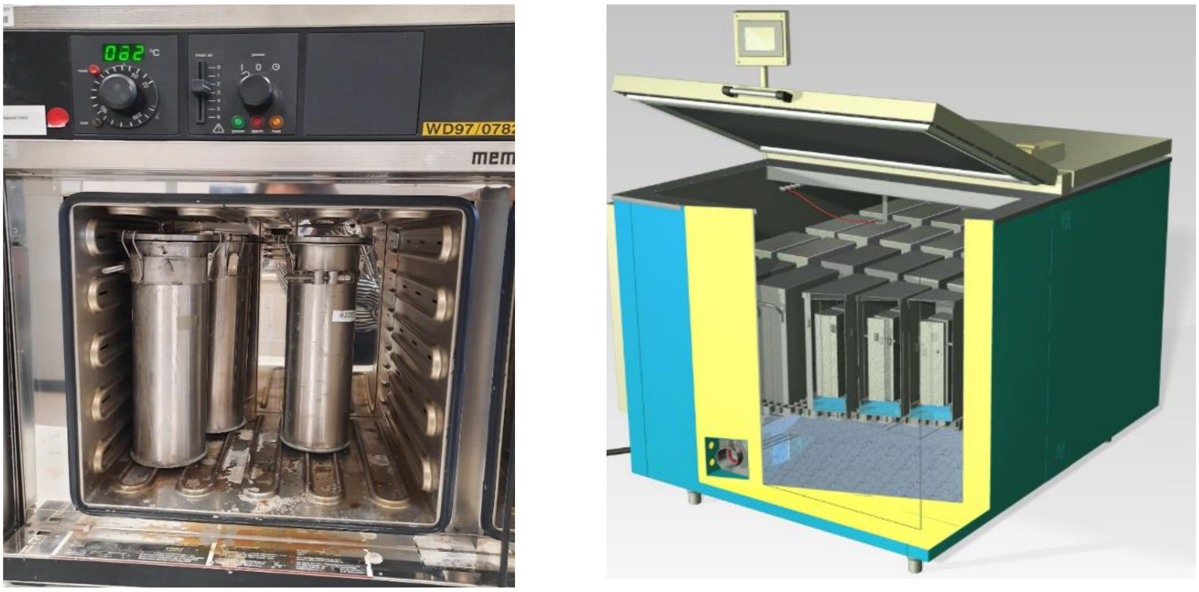

Figure 3. Accelerated ASR test at 80ºC in 1 N NaOH solution (left) and at 38ºC, RH > 95% (right)

Drum scale tests

We intend to cast four drums of 220 l, which is relevant for Belgium storage conditions. Furthermore, drums with smaller sizes of 10 and 30 l will also be designed to test ASR and provide more data to calibrate the model and to study the size effect. Two 220 l drums are tested under accelerated ASR at temperature of 38oC and RH > 95%, in which 1 drum is added with LiNO3 to mitigate the expansion. The other two 220 l drums are tested under reference conditions with temperature of 20oC and RH ~ 50% (close to storage conditions). The same testing conditions are applied for smaller drums of 10 l and 30 l. The ASR tests will last for 2 years.

A number of monitoring techniques will be used including acoustic emission and strain gauges to measure the expansion; pH sensors and thermocouples; pressure transducer to measure internal stress; and UPV to monitor the strengths. The design of the drum and location to install the sensors are still under development.

Microstructural and mineralogical characterization

A variety of techniques will be used to quantify the formation of ASR gel and its consequences on the changes in microstructure and phases in degraded samples. Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectrometry (SEM/SEM-EDX) [9, 10] is used to characterize the change in microstructure and crack formation as well as the formation of ASR gel. Quantitative X-ray Diffraction (XRD/QXRD) [11, 12] and Thermogravimetric Analysis (TGA) [13, 14] are used to quantify the mineralogical and bound water changes. Furthermore, Mercury Intrusion Porosimetry (MIP) [15, 16], and N2-adsorption [17, 18] are used to determine pore size distribution and accessible porosity. The sub-samples will be taken from both lab and drum scale samples for both accelerated and control conditions.

5. Modelling

Literature studies are ongoing to select a suitable thermo-hydro-chemo-mechanical model to simulate ASR tests. To make computationally-demanding tasks such as sensitivity analysis, uncertainty propagation and inversion (model calibration) tractable, machine learning approaches will be used to build a meta model (or surrogate model) of the complex physics-based model [19]. The underlying idea is to devote the available computational budget to the construction of a computationally cheap meta model and then use it to perform the otherwise impracticable analyses.

Regarding the NDT signal analysis, the goal of the task is to confidently verify a correlation between the data of the piezoelectric sensor and the strain gauge. In a first approach, an acoustic event (see **Figure**), potentially related to ASR, will be detected by means of a threshold on the amplitude. Given the set of detected events, several features will be extracted, e.g., the total amount of events within a timespan, event duration, rise time and energy. From these features statistical analysis will be performed on the correlation with the data obtained from the strain gauge. This approach is similar to the work presented in [20, 21] which showed a correlation between acoustic emission obtained by the piezoelectric sensor and other measurements related to ASR.

However, the aforementioned method of detecting these events might be susceptible to erroneous event detections when deployed in a non-lab environment. To circumvent this issue, in a next phase of the project, a data-driven approach could be pursued. In a first step an anomaly detection model is deployed that, given data from a non-reactive state of the cement is available, can be used to detect deviating segments such as ASR events or other artifacts (e.g. barrel movement). Once these events are obtained similar analysis can be performed as described earlier. As these artifacts influences the correlation in a negative manner, expert labelling by SCK CEN could be used to improve our model in a data-driven manner, similar to the work performed in [22].

Preliminary results at lab scale

The lab scale testing campaign is still under the optimization phase where the sensor embedding methods need to be adjusted to make sure that all the sensors can work properly under severe conditions with temperature up to 80ºC and high alkali environment. The preliminary results showed that most of the sensors work well under such conditions. However, few strain gauges only work well in the first few days of testing, and then fail due to loss of contact between the strain gauges and the samples. The modified embedding procedure has been implemented to provide improved contact.

Figure4 shows the expansion of samples under accelerated conditions at a temperature of 80ºC and high alkalis solution of 1 N NaOH obtained from strain gauges signals. The results show that the expansion is increasing over time and reaches 0.07% after one week of ASR test. The addition of $LiNO_3$ significantly reduces the expansion by more than 50%. Monitoring of tests are still ongoing.

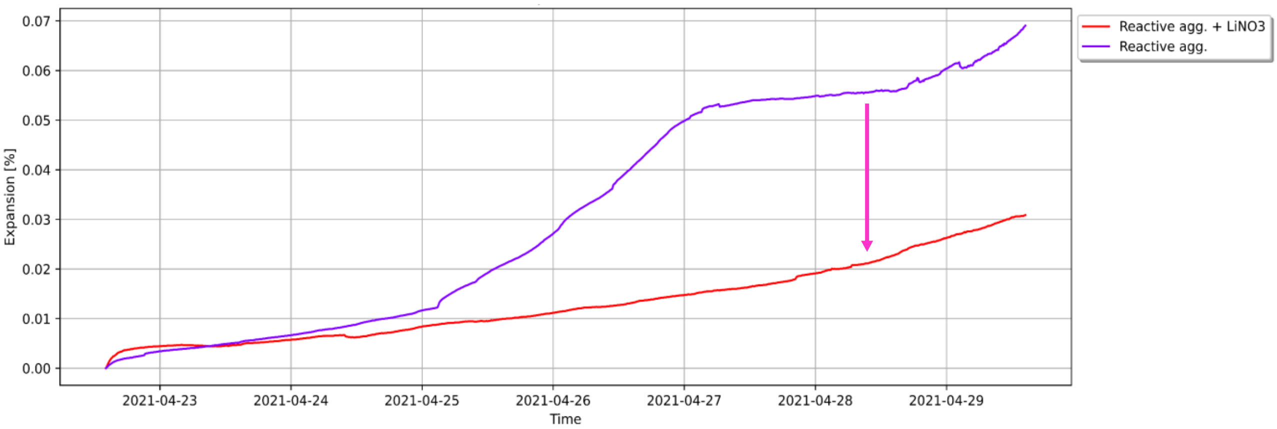

Figure 4. *Expansion of samples with reactive aggregate under accelerated ASR at T = 80ºC and in 1 N NaOH solution.*

Figure 5 shows an example of piezo sensor signal obtained on a sample with $LiNO_3$ after 10 minutes of ASR test. A spike or burst of spikes only happens a few times per minute or a few times per hour depending on the ASR expansion rate. For now, only the zoomed in snapshot of such spikes is shown as it is impossible to see anything useful when looking at a zoomed out version. Every spike appeared is expected to link to the formation of cracks in the samples. The number of cracks occurred in a specified time is linearly related to the amount of expansion of the sample. Further analysis to correlate the piezo signal with the strain gauge data is still ongoing.

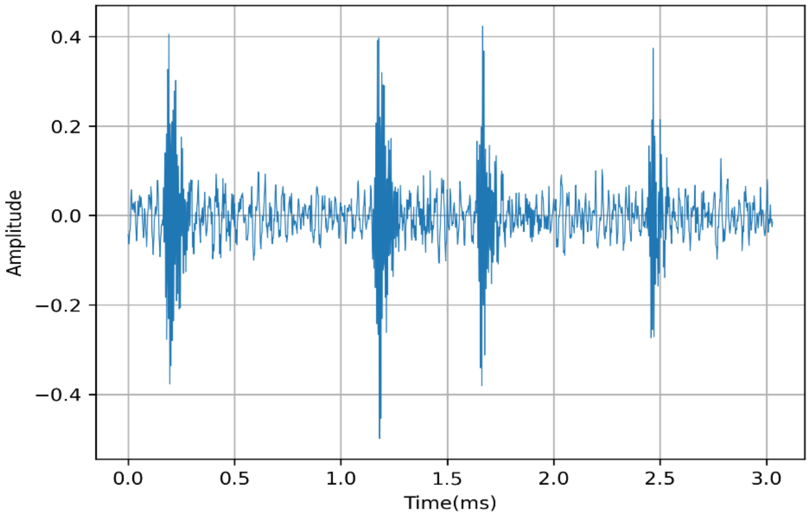

Figure 5. *Snapshot of Piezo signal obtained after 10 minutes of ASR test.*

Figure 6 shows the changes in compressive and flexural strength of the samples under accelerated ASR and under water saturated conditions at 80ºC after 3 weeks of testing. As expected, both flexural and compressive strengths of samples using reactive sand are slightly decreased due to ASR. The ASR expansion could induce the formation of microcracks in the samples, which normally decrease the strengths of the material, however, the extent of strength loss is strongly depended on the crack density and geometry. In this study, the expansion is very little. Therefore, we only observed a light decrease in the strengths. Note that the addition of LiNO3 helps to reduce the expansion, however, it does not help to reduce the extent of strength loss due to ASR. The ASR testing conditions seem not to induce any loss in strength compared to reference conditions, even with a slight increase in both flexural and compressive strength. However, the deference may well be within the deviation of measurements.

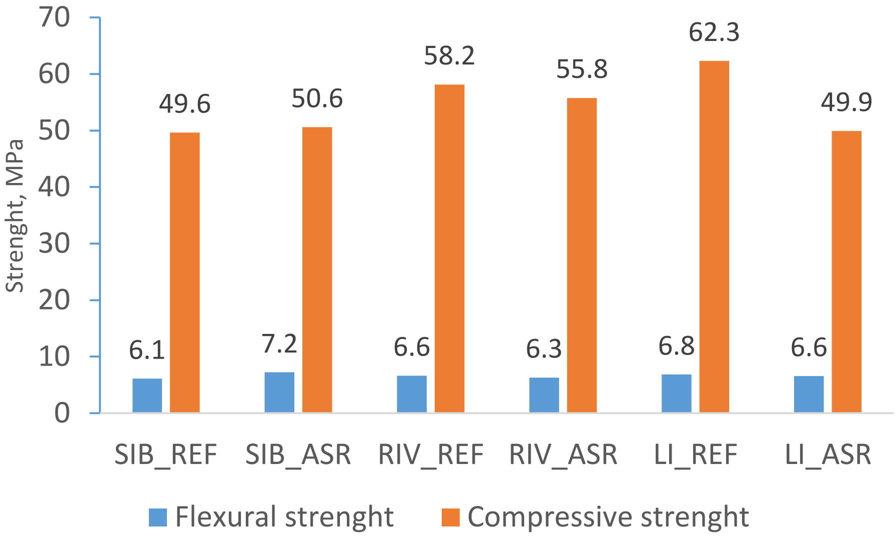

Figure 6. *Changes in mechanical properties of samples subjected to accelerated ASR and under reference conditions (saturated in water at 80ºC) after 3 weeks of testing.*

6. Summary and concluding remarks

This paper presents the overall strategy to assess the alkali silica reaction (ASR) in the context of cemented wastes, which is the joint effort of three institutions: SCK CEN, Magics Instruments, and Belgoprocess. In this approach, the laboratory ASR tests and industrial scale drum tests at both reference and accelerated conditions are proposed, which provide data for future deployment of multiphysics based model for ASR, supplemented by computationally efficient meta model.

The preliminary test results of the first phase within this approach have become available, which shows that with an optimized installation procedure, the investigated non-destructive techniques (e.g. pH sensors, strain gauges, thermocouples, etc.) function well under severe test conditions. The strain gauges are able to capture the expansion of the sample during accelerated ASR tests. The expansion of samples with reactive aggregates slightly reduces the compressive and flexural strength, but not the case for samples with non-reactive aggregates. The addition of $LiNO_3$ can reduce the expansion by 50% but does not help to prevent the loss in mechanical properties. The piezo sensors are able to detect crack formation, however, further analysis is needed to correlate the piezo signal with the data obtained from strain gauges.

Acknowledgements

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References

1. Phung, Q., et al., Long-term performance of cementitious materials used in nuclear waste disposal-a case study at SCK CEN. LIFE-CYCLE ANALYSIS AND ASSESSMENT IN CIVIL ENGINEERING: TOWARDS AN INTEGRATED VISION, 2019: p. 619-627.

2. Phung, Q.T., N. Maes, and D. Jacques, Current concerns on durability of concrete used in nuclear power plants and radioactive waste repositories, in Proceedings of the 4th Congrès International de Géotechnique - Ouvrages -Structures, Lecture Notes in Civil Engineering 8, H.-H. Tran-Nguyen, et al., Editors. 2018, Springer Nature Singapore: Singapore. p. 1108-1121.

3. Federal Agency for Nuclear Control (FANC), B., Sixth Meeting of the Contracting Parties to the Convention on Nuclear Safety. 2013.

4. Rajabipour, F., et al., Alkali–silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps. Cement and Concrete Research, 2015. 76(0): p. 130-146.

5. ASTM, C., Standard test method for potential alkali reactivity of aggregates (mortar-bar method). 2007.

6. Ekolu, S., G. Rakgosi, and D. Hooton, Long-term mitigating effect of lithium nitrate on delayed ettringite formation and ASR in concrete – Microscopic analysis. Materials Characterization, 2017. 133: p. 165-175.

7. Venkatanarayanan, H.K. and P.R. Rangaraju, Effectiveness of Lithium Nitrate in Mitigating Alkali-Silica Reaction in the Presence of Fly Ashes of Varying Chemical Compositions. Journal of Materials in Civil Engineering, 2014. 26(7).

8. ASTM, Standard test method for determination of length change of concrete due to alkali-silica reaction. 2008, ASTM International.

9. Georget, F., W. Wilson, and K.L. Scrivener, edxia: Microstructure characterisation from quantified SEM-EDS hypermaps. Cement and Concrete Research, 2021. 141.

10. Durdziński, P.T., et al., A new quantification method based on SEM-EDS to assess fly ash composition and study the reaction of its individual components in hydrating cement paste. Cement and Concrete Research, 2015. 73(0): p. 111-122.

11. Snellings, R., A. Salze, and K.L. Scrivener, Use of X-ray diffraction to quantify amorphous supplementary cementitious materials in anhydrous and hydrated blended cements. Cement and Concrete Research, 2014. 64(0): p. 89-98.

12. Phung, Q.T., et al., Investigation of the changes in microstructure and transport properties of leached cement pastes accounting for mix composition. Cement and Concrete Research, 2015. 79: p. 217-234.

13. Morandeau, A., M. Thiéry, and P. Dangla, Investigation of the carbonation mechanism of CH and C-S-H in terms of kinetics, microstructure changes and moisture properties. Cement and Concrete Research, 2014. 56(0): p. 153-170.

14. Phung, Q.T., N. Maes, and S. Seetharam, Pitfalls in the use and interpretation of TGA and MIP techniques for Ca-leached cementitious materials. Materials & Design, 2019. 182: p. 108041.

15. Phung, Q.T., Effects of Carbonation and Calcium Leaching on Microstructure and Transport Properties of Cement Pastes, in Department of Structural Engineering. 2015, Ghent University: Belgium. p. 249.

16. Yuan, S., X. Liu, and O. Buzzi, Technical aspects of mercury intrusion porosimetry for clays. Environmental Geotechnics, 2018: p. 1-9.

17. Bertier, P., et al., On the use and abuse of N 2 physisorption for the characterization of the pore structure of shales. Clay Clay Miner, 2015.

18. Odler, I., The BET-specific surface area of hydrated Portland cement and related materials. Cement and Concrete Research, 2003. 33(12): p. 2049-2056.

19. Laloy, E. and D. Jacques, Emulation of CPU-demanding reactive transport models: a comparison of Gaussian processes, polynomial chaos expansion, and deep neural networks. Computational Geosciences, 2019. 23(5): p. 1193-1215.

20. Świt, G. and J. Zapała-Sławeta, Application of acoustic emission to monitoring the course of the alkali-silica reaction. Bulletin of the Polish Academy of Sciences: Technical Sciences, 2020: p. 169-178.

21. Abdelrahman, M., et al., Classification of alkali–silica reaction damage using acoustic emission: A proof-of-concept study. Construction and Building Materials, 2015. 95: p. 406-413.

22. Soltangharaei, V., et al., Damage mechanism evaluation of large-scale concrete structures affected by alkali-silica reaction using acoustic emission. Applied Sciences, 2018. 8(11): p. 2148.

Task 7.5 Data handling, processing and fusion

While there had been not much scheduled progress for T7.5 before the May Workshop good discussion rose from the current situation of T7.5. T7.5 started on time with the data discussion. T7.3 provided sample data to give comprehension of the requirements for the data storage and used protocols for the data management. The data contained samples from fibre optics measurements, ground penetrating radar measurements, temperature and relative humidity measurements and ultrasonic testing measurements. Moreover, the idea was to get more info on the data quality and possibilities the data offers.

One of the concerns regarding the T7.5 was the amount and the size of data, which is related to the sampling frequency. For this type of project the changes affecting the storage are relatively slow, thus moderately low sampling frequency should keep the data amount manageable. For instance the traditional time series data such as temperature and relative humidity do not take large amount of storage space. Conversely, inspection data such as ultrasound and ground penetrating radar measurement produce considerable data chunks, but are infrequent to time series data. Thus, the required storage space for this research project is estimated around 2TB of storage.

Another discussion topic was the data structure. Due to the nature of the data, containing numerical data, such as temperature and relative humidity and inspection data containing the whole inspection area, storing the data is not a straightforward process, especially for machine-readable format. In addition, the file format for the inspection files varies and may cause data loss or mishandling when opening the file format outside intended software. Therefore, at least some of the data may need to be pre-processed by the acquisition party on the edge, before uploading to the database. Moreover, the importance of metadata along the data itself was discussed. Trough the metadata, it should be made clear about the technique the data was acquired as well as other important factors affecting the data handling. Mainly, this relates the data being FAIR. FAIR data stands for Finable, Accessible, Interoperable, and Reusable.

It can be estimated, that the actual sensor data and inspection data would not exceed over 2TB of storage, thus the raw format can also be stored easily within the platform. While the raw data might be left redundant after the data transformation, it is often a precaution to store the raw format as well, if it is financially feasible. The preliminary data storage schematic can be seen in **Figure** . The idea in the figure is to store all the available data in a data lake, from which it can be converted to a more machine-readable format and stored into the data warehouse. The data warehouse would store data usable for decision making and other tasks planned for data handling in T7.5. Some cases such as temperature and humidity data may not need any transformation before storage to the data warehouse, thus these kind of data can skip the data lake phase completely. The infrastructure of this data lake and data warehouse is still under discussion, however Microsoft Azure, or Amazon Web Services (AWS) and open source platform XAMPP were suggested as options in the workshop.

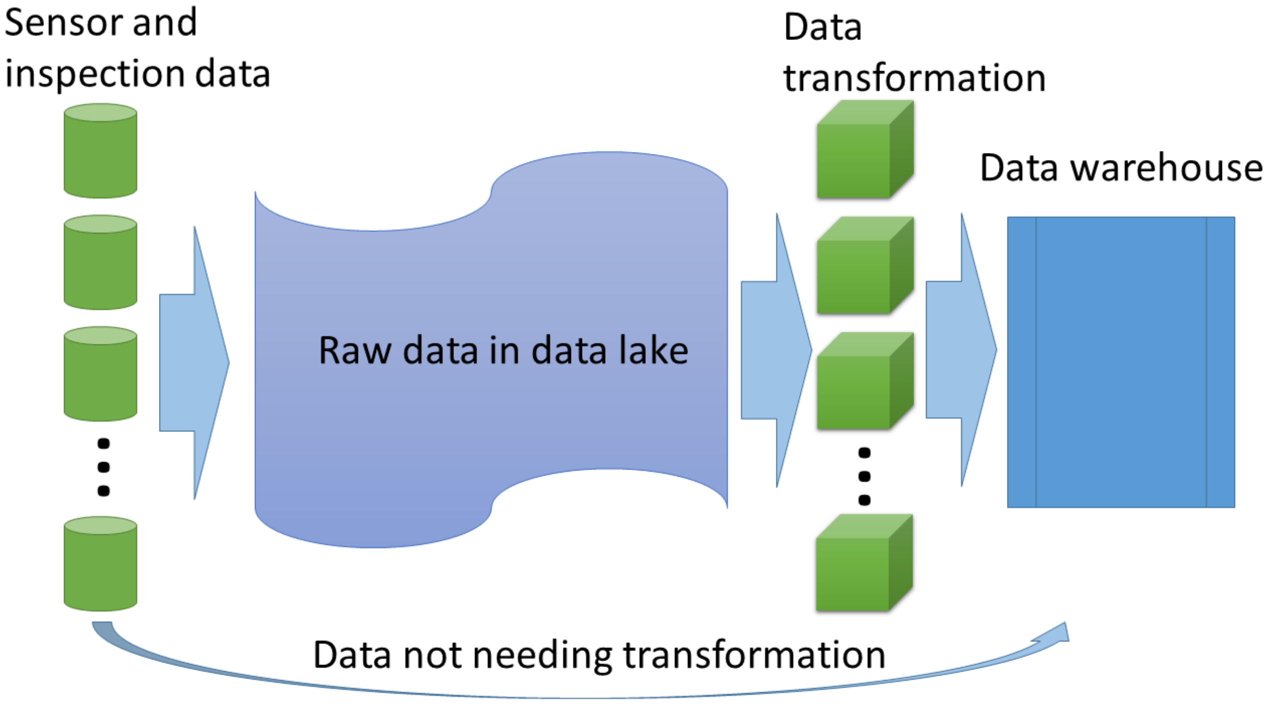


Figure 1. *Preliminary data storage schematic.*

Once the data has been transformed into machine-readable format, the main tasks, mainly machine learning aspects and decision making can commence in T7.5. However, the initial target from the data is yet undetermined. The prediction and decision making target needs to be determined with collaboration between the task groups T7.3 and T7.4.

18. Task 7.6 Implementation of monitoring - digitalisation techniques

Demonstration work

Written by: Sabah BEN LAGHA , Coralie CHAPUZET, Eric BREUIL, ORANO, France,

1. Short summary

WP7/task 6 consists of the preparation of the demonstration work which will be carried out at the end of the PREDIS project. However, the preparation work for this task 6 began quite early at the beginning of the project. Thus, Orano, which is both task 6 leader and contributor, initiated the construction of a tool allowing to compare technologies developed in WP7 to control cemented waste packages. This tool is a comparison table based on a list of criteria that will be rated and weighted. The criteria considered to compare are quite diverse technologies and include among others: Technical performance, Safety/security, Cost and planning (including procurement, fabrication, exploitation and dismantling), Operability (including exploitation, availability, maintenance). During the May 2021 workshop, the table was well structured and has been shared with all of the WP7 contributors allowing to integrate different comments. Some adjustments are planned by the end of the 3rd quarter and it will therefore be addressed to the various developers to complete the document by the end of the year 2021 / beginning of 2022.

Keywords: Demonstration work/ technologies comparison/ comparison tool

About task 7.6:

In the frame of task 6, the demonstration and implementation of monitoring technologies is performed.

It consists of several main tasks:

- First, to develop/design a waste package prototype for performing large-scale trials through gathering and analyzing results and outputs from Tasks 7.2 to 7.5 (task 7.6.1).
- Second, to evaluate the technologies and developed system from an end-user perspective (tasks 7.6.1/7.6.2) and then to perform a series of full-scale trials in a realistic testing environment on the selected technology (task 7.6.2)
- Third, to define potential mitigation actions and design improvements (task 7.6.3).

In order to evaluate the technologies and system developed from an end-user perspective, a comparison table is being developed. It takes into account several parameters such as availability, their technical performances, TRL level and the safety requirements needed for their implementation.

Each technology studied in the frame of the PREDIS project will be assessed with this table.

2. Methods

The table of comparison is based on a methodology used by Orano to compare the technologies, concepts and design options during the engineering design process. It is based on a quantitative assessment which will be used for the selection of technologies, concepts, and design options.

Four main criteria are taken into account in the table:

- Technical performance
- Safety/security
- Cost and planning (including procurement, fabrication, exploitation and dismantling)
- Operability (including exploitation, availability, maintenance)

Each main criterion is subdivided into different sub criteria which have to be defined precisely depending of the technologies, concepts or design options to be assessed. The definition of the sub criteria is the most important part of the work. The sub criteria must not be redundant. The number of sub criteria per main criterion can vary.

The weights of the main criteria are equal. The weights of the sub criteria have to be defined.

The assessment of the sub criteria is usually done using an excel file resulting in a global assessment.

For R&D, it is possible to add information about the maturity and the risk but it is not included in the global assessment.

Description of work and main findings

The comparison table is divided in three parts.

A first part focuses on gathering information on the data collected by the technology to compare it to the end-user's need.

The aim of this part is to gather information about the data/parameters that can be followed by the technology and the type of packages for which it can be implemented. This information is important in order to regroup several technologies together and to be able to select technology for testing according to the key degradation phenomena stated.

The interoperability of the technologies together is also a key factor.

A second part focuses on the performance of the technologies in terms of technical performances, cost, safety/security, easiness of operation for end-users (operability and amount of maintenance needed), and induced wastes generated. Each sub criteria will be weight differently.

Technical performances of the technology contain among other the possibility to use the technology for old packages already produced by the end-users, the measurement uncertainties and the easiness to have information on the ageing indicator.

Costs required for procurement, manufacturing, operating of the system and additional development cost are assessed.

Safety/security for operators depends on how the technology has to be implemented and how data retrieval is performed.

Operability for the end user facility takes into account among other the easiness of calibration of the technology, the impact on the interim storage facility or on the conditioning process and the operator qualification.

The amount and level of induced waste generated is also considered.

Other additional data on the technology maturity in form of the technical readiness level (TRL) and scalability are gathered from the technology developers.

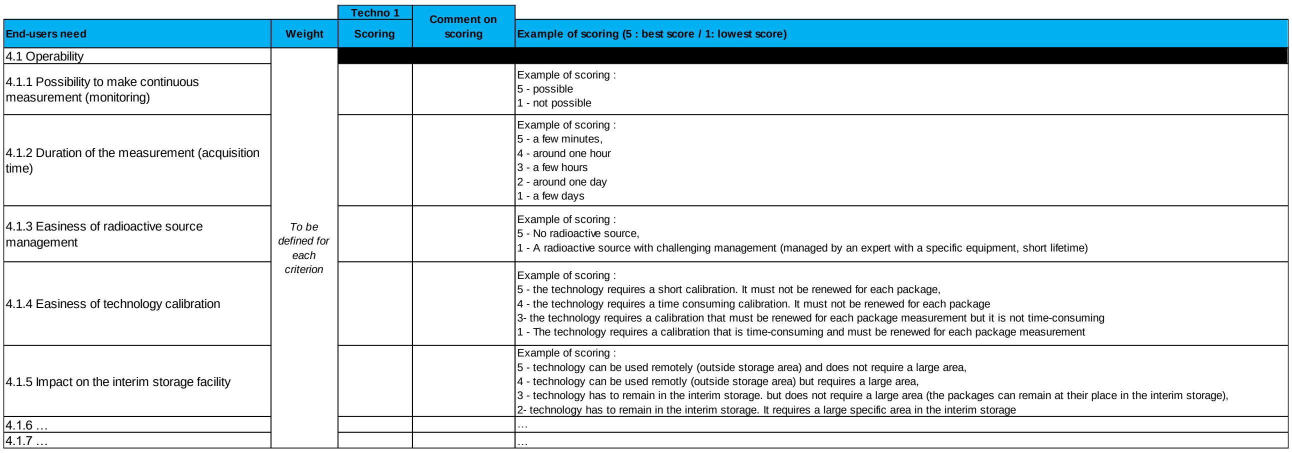
Last, the table should be completed by end-user to assess the impact of the technology on the interim storage facility (in terms of additional safety studies required for the technology implementation), the impact on long-term behaviour of the package and on decommissioning.

This table is currently being developed and must be further discussed with tasks 7.4 and 7.5. The weight of each sub criteria has still to be defined and the scoring of each sub criteria has to be fine-tuned.

3. Results

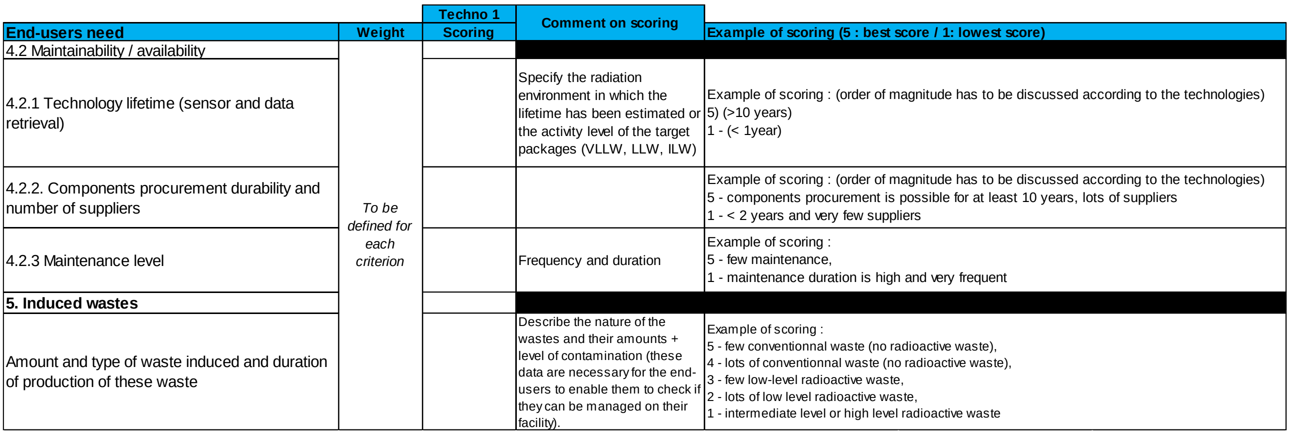
The draft of the comparison table of May 2021 is linked in the PREDIS WP7 Team folder {1].

Extracts are presented in the figures below.



End-users need	Weight	Techno 1 Scoring	Comment on scoring	Example of scoring (5 : best score / 1: lowest score)
4.1 Operability	*To be defined for each criterion*			
4.1.1 Possibility to make continuous measurement (monitoring)				Example of scoring : 5 - possible 1 - not possible
4.1.2 Duration of the measurement (acquisition time)				Example of scoring : 5 - a few minutes, 4 - around one hour 3 - a few hours 2 - around one day 1 - a few days
4.1.3 Easiness of radioactive source management				Example of scoring : 5 - No radioactive source, 1 - A radioactive source with challenging management (managed by an expert with a specific equipment, short lifetime)
4.1.4 Easiness of technology calibration				Example of scoring : 5 - the technology requires a short calibration. It must not be renewed for each package, 4 - the technology requires a time consuming calibration. It must not be renewed for each package 3- the technology requires a calibration that must be renewed for each package measurement but it is not time-consuming 1 - The technology requires a calibration that is time-consuming and must be renewed for each package measurement
4.1.5 Impact on the interim storage facility				Example of scoring : 5 - technology can be used remotely (outside storage area) and does not require a large area, 4 - technology can be used remotly (outside storage area) but requires a large area, 3 - technology has to remain in the interim storage. but does not require a large area (the packages can remain at their place in the interim storage), 2- technology has to remain in the interim storage. It requires a large specific area in the interim storage
4.1.6 …				…
4.1.7 …				…

Figure 1. *Example of draft table for operability criteria.*



End-users need	Weight	Techno 1 Scoring	Comment on scoring	Example of scoring (5 : best score / 1: lowest score)
4.2 Maintainability / availability	*To be defined for each criterion*			
4.2.1 Technology lifetime (sensor and data retrieval)			Specify the radiation environment in which the lifetime has been estimated or the activity level of the target packages (VLLW, LLW, ILW)	Example of scoring : (order of magnitude has to be discussed according to the technologies) 5) (>10 years) 1 - (< 1year)
4.2.2. Components procurement durability and number of suppliers				Example of scoring : (order of magnitude has to be discussed according to the technologies) 5 - components procurement is possible for at least 10 years, lots of suppliers 1 - < 2 years and very few suppliers
4.2.3 Maintenance level			Frequency and duration	Example of scoring : 5 - few maintenance, 1 - maintenance duration is high and very frequent
5. Induced wastes				
Amount and type of waste induced and duration of production of these waste			Describe the nature of the wastes and their amounts + level of contamination (these data are necessary for the end-users to enable them to check if they can be managed on their facility).	Example of scoring : 5 - few conventionnal waste (no radioactive waste), 4 - lots of conventionnal waste (no radioactive waste), 3 - few low-level radioactive waste, 2 - lots of low level radioactive waste, 1 - intermediate level or high level radioactive waste

Figure 2. *Example of draft table for maintainability, availability and induced wastes criterion.*

4. Conclusions

The table developed in task 7.6 is a useful tool in order to prepare demonstration work. Works done so far will be consolidated in the coming months. the next steps consist of sharing the content and integrating criteria related to digital twin and data management. Also, this table will be tested with a MICADO technologies in order to see if all the criteria mentioned fit with WP7 developed technologies. The final objective is to distribute this table to developers in the 4th quarter of 2021 and to have a completed table by the end of 2021 / beginning of 2022.