PREDIS – Proceedings of the Final Conference June 2024

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Editors Pirkko Kekäläinen and Maria Oksa
VTT Technical Research Centre of Finland Ltd
Kivimiehentie 3, Espoo, Finland

pirkko.kekalainen@vtt.fi
maria.oksa@vtt.fi

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TABLE OF CONTENTS

Foreword

Maria Oksa (VTT), maria.oksa@vtt.fi

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

This Proceedings of the PREDIS workshop (Deliverable D1.5) is the fourth of a kind, after the final workshop held in June 2024 in France, and is one means to disseminate the numerous results and achievements of the project.

The four-year project PREDIS finalisation

The PREDIS project started in the midst of covid-19 pandemic purely via online means. Despite this hard challenging start, the project got gained speed after the first year's gap analysis and achieved its overall targets and over. The PREDIS project focused on to developing innovations to for metallic, liquid and solid organic radioactive waste and solutions to predisposal storage and monitoring. Besides technical achievements, also strategic implementation was made with the with predisposal community regarding formation of strategic research focus areas, compilation of the waste acceptance criteria and life cycle analysis, and as well as advancing the knowledge management programme via training, mobility, case studies and domain insight work, were very as a means of guidance. The PREDIS community with 47 partners from 17 countries, along with the 25 End User Group members, were able to make both technical achievements and also form excellent collaboration and a good atmosphere to work together, which was tangible in the Final Conference.

PREDIS Final Conference 2024

The fourth public workshop of PREDIS was organised by CEA in Avignon, France, 3.-7.6.2024 with approximately 160 registered participants. The city offered beautiful surroundings to the final event of the project. In PREDIS, the knowledge transfer, dissemination and networking have been essential parts and hence the Final Conference started with the students' session, summarizing their work and experiences in the project. On the second day, summaries from the Strategic Studies and Knowledge Management were shared with the consortium, and the technical work packages had their final technical presentations and discussions. The Final Conference then focused to on presenting the scientific and technical achievements to the end users and stakeholders, with a strong emphasis on the benefits and impact to national programmes. In the innovations in metallic treatment and conditioning, we heard presentations e.g. about decontamination processes, optimization of characterization and waste minimization techniques and advances in encapsulation of materials in magnesium phosphate cement -based matrices. On For liquid organic waste treatment and conditioning, reference formulations for real waste and direct conditioning scale-up were presented. For the solid organic waste innovations, presentations were given on thermal treatment and characterization, encapsulation, densification, physico-chemical characterization and on the economic and environmental impact of these methods. On innovations in cemented waste handling and predisposal storage, achievements in innovative instrumentation, digital twin and decision framework were presented, as well as the results from the demonstration in realistic environment.

The final workshop day, before the technical excursion to CEA facilities at Marcoule Centre, focused on the holistic outcomes and industrial impacts of the project results. The value assessments, which was were performed during the project to all technical work packages, was presented together with the case studies that are intended to be included to the IAEA Wiki. Both PREDIS partners and end users presented their views on the results and achievements on geopolymers for waste immobilisation, decontamination and supporting waste hierarchy principles, and digitalisation advancements for monitoring. The workshop was closed with two interesting panel discussions. The first panel gave overview of EU project impacts to the French Programme by representative French stakeholders. The second panel concerned the overall EU project impacts on the international community including SNETP, IAEA and Member States (DG ENER) as represented by JRC, when we also heard the very positive results of the European Commission's external review of the PREDIS project implementation.

Overall, the final conference was deemed a great success, for sharing of the technical achievements and celebrating the successes. These proceedings provide an overview of the technical achievements, while additional details can be found in other Deliverables of the project and summary outcomes available from the PREDIS web page https://predis-h2020.eu/. A more detailed summary of the Final Conference is presented in the Chapter 1.

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1 Summary of the PREDIS Final Conference June 2024

Tara Beattie (TB Environmental), tara.beattie@mcmenvironmental.co.uk

Keywords: waste, treatment, predisposal, safety, radioactive, nuclear, outcome, value assessment

Background

The PREDIS project held its final conference in Avignon, France, hosted by CEA from 3-7 June 2024. The event was attended by PREDIS partners, end users and interested stakeholders. The first two days (3-4th June) were closed sessions for consortium partners to exchange on work package results and complete planning for the completion of final PREDIS deliverables by July 2024. Thereafter two days (5th-6th June) were dedicated to open sessions with end users to disseminate and exchange on the results, achievements and impacts of PREDIS. Below is a summary of the main discussions from each of these open sessions. Wednesday focused on technical achievements while Thursday focused on industrial or end-user impacts.

Wednesday June 5th: Innovations in metallic material treatment and conditioning (WP4) - Link to WP4 Slides

The WP4 leader (Abdel Abdelouas, IMT Atlantique) opened the session by providing an overview of tasks which have focussed on new approaches to metal waste treatment which could potentially minimise waste volumes, increase recycling and offer new analytical techniques for difficult to measure radionuclides. Highlights of the work package included new formulations for magnesium phosphate cements which could reduce costs of waste treatment compared with standard cements (by replacing key components with aggregate). A great success of the work package noted was the contribution towards the provision of raw materials by end users (for example, fly ash provided by EDF) demonstrating the value in completing the work as part of an international cooperation project. Following the introduction, 5 case studies were presented to showcase the results of work completed:

- Developing and optimizing decontamination processes (T. Suzuki, IMT Atlantique)
- Optimization of characterization and waste minimization techniques (A. Savidou, NCSRD)
- Advances in encapsulation of materials in magnesium phosphate cement-based matrices (C. Cannes, IJCLab)
- A non-destructive gamma spectrometry set-up for characterization of metallic waste (D. Mavrikis, NCSRD)
- Decontamination of radioactive effluents (M. Robin, IMT Atlantique)

Outcomes from the metallic waste session

Some key takeaways from this session were as follows:

- Inorganic gels (based on the COREMIX process) have been tested successfully (advanced from TRL2 to TRL3) to decontaminate metallic waste (e.g., Ni-alloys and stainless steels) resulting in no secondary effluent (only solid waste which can be vacuumed for collection). A new gel formulation integrating magnetic particles has also been tested for remote application for difficult to access surfaces (applicable to low-level waste so no concern about activation of iron). Electrochemical gel decontamination (EASD) has been tested (advanced from TRL6 to TL7) and has proved a fast treatment (~0.5 µm/min removal for stainless steel) and can be deployed in-situ to target radiation hot spots.
- Pre-dismantling waste classification using a modelling approach combined with gamma spectrometry has been demonstrated (using neutron calculations and scaling factors methodology) leading to improved waste sorting (based on surface and volume activity determination for key radionuclides) which can be used to improve radiological characterisation on activated reactor components.

- Magnesium Phosphate Cements (MPCs) formulations have been developed using alternative fillers to fly ash, offering an alternative encapsulant for specific metal wastes that are prone to corrosion in high pH cement metrices. Production tests indicate 15% cost reduction and better curing achieved if higher moisture used. Qualification tests of the new formulations completed for corrosion and irradiation resistance with a range of encapsulated reactive metals (aluminium, carbon steel and beryllium).
- Optimisation of existing decontamination processes has been demonstration, CORD (Chemical Oxidation Reduction Decontamination) and COREMIX (Chemical Oxidation Reduction using nitric permanganate and oxalic acid MIXture). Results show volume reduction from m^3 of waste effluent into a few 100 g of residues compatible with cement/geopolymer matrices.

Wednesday June 5th: Innovations in liquid organic waste treatment and conditioning (WP5) - Link to WP5 Slides

The WP5 leader (Isabelle Giboire, CEA) led the session by providing an overview of tasks which have focussed on testing (up to TRL 6) the use of a new class of mineral binders such as Geopolymers and related Alkali-Activated Materials (AAMs). Highlights of the work package included formulations for AAMs which demonstrated a range of performance for different liquid organic wastes (for example, kerosen, liquid scintillation cocktail) using alternative binders. A success of the work package was the improved understanding developed on the importance of the water to solid ratio (e.g., porosity of conditioning matrix) when conducting leaching experiments for samples exposed to irradiation, thermal and fire hazard conditions. Following the introduction, 4 scientific presentations were made:

- Investigation of direct conditioning processes using a reference formulation for real waste Real Waste (POLIMI) and direct conditioning scale-up (A. Sears, CVRez)
- Study of conditioning matrix performances (A. Savidou, SCK + ECL)
- A non-destructive gamma spectrometry set-up for characterization of metallic waste (S. Koubeissey, ECL)
- Decontamination of radioactive effluents (G. Magugliani, POLIMI)

Outcomes from the liquid organic waste session

Some key takeaways from this session were as follows:

- Data collected from across Europe indicates that the key reference radioactive liquid organic wastes are oils, solvents and scintillation cocktails, which can be directly mixed with raw materials and additives to formulate conditioned matrices (most common are Metakaolin, Blast Furnace Slag and Fly Ash). Optimised formulations using these three options have been developed within PREDIS proving most promising for oils (now at TRL level 5/6). More optimisation is needed for solvents which can't achieve the same % waste loading, when compared to oils, and so no overall cost benefit for the approach compared to typical incineration and volume reduction. Leaching and waste release data for the formulations are also positive (with respect to long-term storage and disposal requirements) for oil mixes, but further work needed for solvents and scintillation cocktails.
- The use of geopolymers has been tested at larger scale (50 litre and 100 litre drums with 35-45 minute mixing times, TRL 6) using a liquid organic radioactive waste surrogate (various weight % waste loadings) and long-term performance data (for storage and disposability assessment) collected including: thermal performance, homogeneity (e.g., extent of uniform distribution of materials within the geopolymer matrix) and compressive strength tests.
- Application of a value assessment methodology has been successfully used to analyse the performance of alternative waste management options for liquid organic wastes compared with the typical current waste management approach (i.e., baseline scenarios). The higher waste loading achievable with geopolymers in comparison with absorption/ cementation (oils and scintillation cocktails) leads to benefits in terms of safety, materials use and cost.

Wednesday June 5th: Questions & Answers on metallics and liquid organics (WP4 + WP5)

Q1. For the liquid organic waste reference formulations, have you documented the requirements used to derive these? A. Yes

Q2. For the leach tests, you quote national leach result limits for storage conditions, but what about disposability requirements and leach data in disposal chemical conditions? A. More work is needed to underpin long-term durability.

Q3. What is the reason for cylindrical or cube test? A. No real reason, just those were the samples available.

Q4. Is there any correlation between porosity and waste loading for the geopolymer formulations? A. Yes there is a correlation between high porosity and resistance to compression.

Q5. For the geopolymer upscaling completed in 50 litre and 100 litre drums, what is the next scale-up? A. The most typical Czech repository size drum is 200 ltr so that will be tested next.

Q6. Regarding the gel that has been developed and the organic encapsultation in geopolymers, what is their status? The two gels developed (CEA and NNL), at NNL we have proved it in the lab and built and engineered a prototype and about to use it on site. The CEA one is already developed and is also close for use on reactor sites.

Wednesday June 5th: Innovations in solid organic waste treatment and conditioning (WP6) - Link to WP6 Slides

The WP6 leader (Thierry Mennecart, SCK CEN) opened the session by providing an overview of thermal treatment routes currently being considered to treat radioactive solid organic wastes: Plasma incineration, combined incineration/gasification, molten salt oxidation, wet oxidation and hot isostatic pressing. Highlights of the work package included formulations for AAMs which demonstrated a range of performance for different liquid organic wastes (for example, kerosen, liquid scintillation cocktail) using alternative binders. Key successes of the work package include demonstrated matrix reliability for thermally treated products (data from short-term leaching experiments, characterisation of condition waste form and long-term durability tests) and feasibility of encapsulation using geopolymer and cement-based materials (proof of concept from TL 2/3 to TRL 5). Following the introduction, 5 scientific presentations were made:

- Thermal treatment of the radioactive waste forms and characterisation (H. Nonnet, CEA)
- Encapsulation (CVRez)
- Densification (USFD)
- Physico-chemical characterisation of reconditioned waste form and stability testing (VTT)
- A drum full of beads / Treatment of ion exchange resins (Francesco Galluccio, Polimi)

Outcomes from the solid organic waste session

Some key takeaways from this session were as follows:

- The IRIS process (pyrolysis/calcination) can be used to treat solid organics and ion exchange resins resulting in secondary waste ash which overall provides a significant waste volume reduction.
- The use of geopolymers has been tested at larger scale (50 litre and 100 litre drums with 35–45-minute mixing times, TRL 6) using a liquid organic radioactive waste surrogate.

Wednesday June 5th: Innovations in cemented waste handling and predisposal storage (WP7) - Link to WP7 Slides

The overview presentation for WP7 was provided by Christian Köpp, BAM (absence apologies provided for WP Leader: Ernst Niederleithinger, BAM). This presented the overall WP scope to establish a state of the art of current methods and procedures (including Non-Destructive Evaluation techniques) for cemented waste management with a specific focus on monitoring and long-term storage. The tools and technologies tested in WP7 included: SciFi (gamma) radiation monitoring; SiLiF (neutron) radiation monitoring; Sensorised LoRa wireless sensor network for identification and integrity assessment of radioactive waste drums; Acoustic Emission for measuring ASR; Non-contact ultrasonic scanning; Embedded RFID Sensors; and Muon tomography. Data collected from the test measurements has been used to develop a digital twin, data platform and decision framework for predictive modelling, data handling and data visualisation.

Outcomes from the cemented waste, storage, and monitoring session

Some key takeaways from this session were as follows:

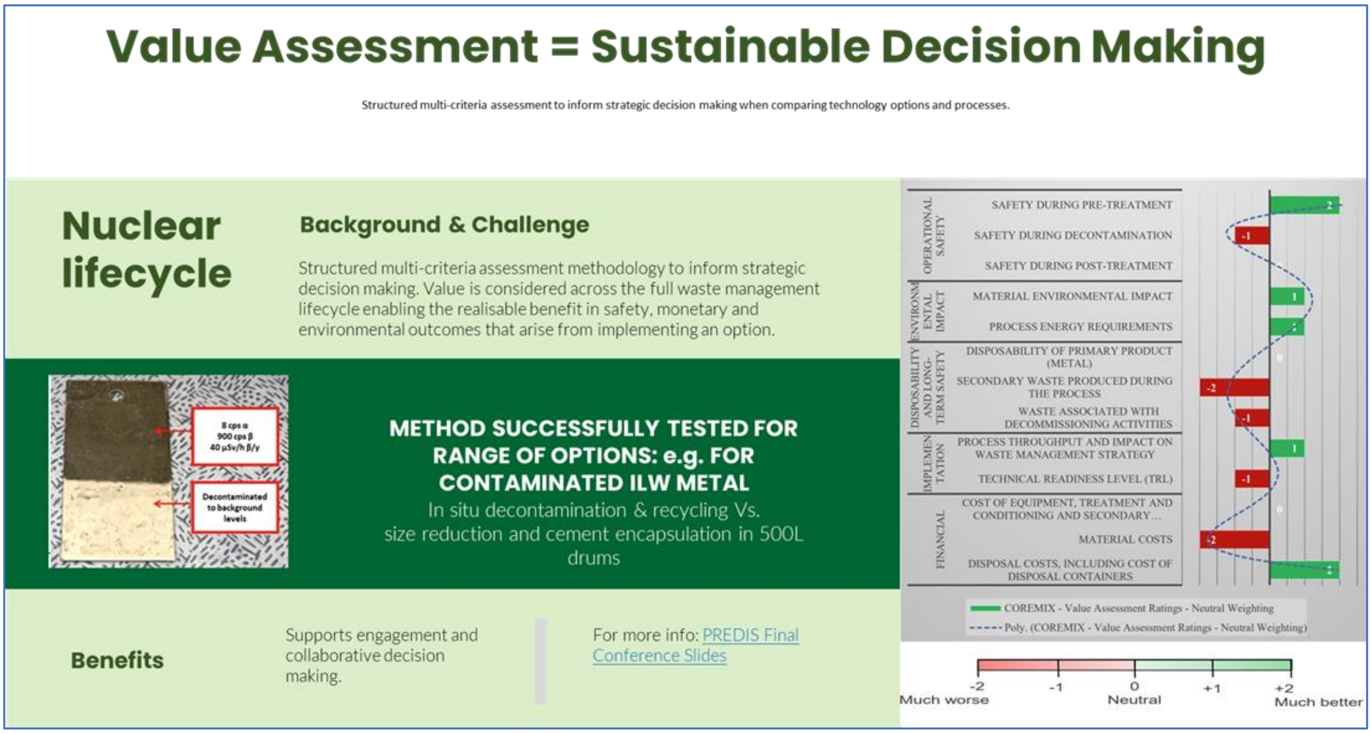
- More versatile and reliable condition monitoring technologies, which have been demonstrated on operating radioactive facilities and made available to end users.
- Improved accuracy in predicting the behaviour of waste/packages in stores through the integration of models with store and package monitoring information obtained using digital and machine learning technologies to enhance sampling, monitoring strategies and multi-method data fusion.

Thursday June 6th: Impact Workshop

This session was intended as critical to understand the benefits of the results of the technical work packages, highlighting how they have been realised and can impact the predisposal community in real terms. The session was organised into 4 topics:

- Value Assessment Process & Case Studies
- Geopolymers for Waste Immobilization (three presentations)
- Decontamination & Supporting Waste Hierarchy Principles
- Digitization Advancements, for Monitoring

Presentations were given by technical experts to show examples of how the work done increased technical readiness levels, demonstrations from concept-t to lab- to field-scale and how end users were integral to the work. A high-level impact summary is shown below for each of the topics, illustrating the main background and challenge, and the impact or level of maturity now available following the completion of works within the PREDIS project. More details for each are also available at the links above.



Value Assessment = Sustainable Decision Making

Structured multi-criteria assessment to inform strategic decision making when comparing technology options and processes.

Nuclear lifecycle

Background & Challenge

Structured multi-criteria assessment methodology to inform strategic decision making. Value is considered across the full waste management lifecycle enabling the realisable benefit in safety, monetary and environmental outcomes that arise from implementing an option.

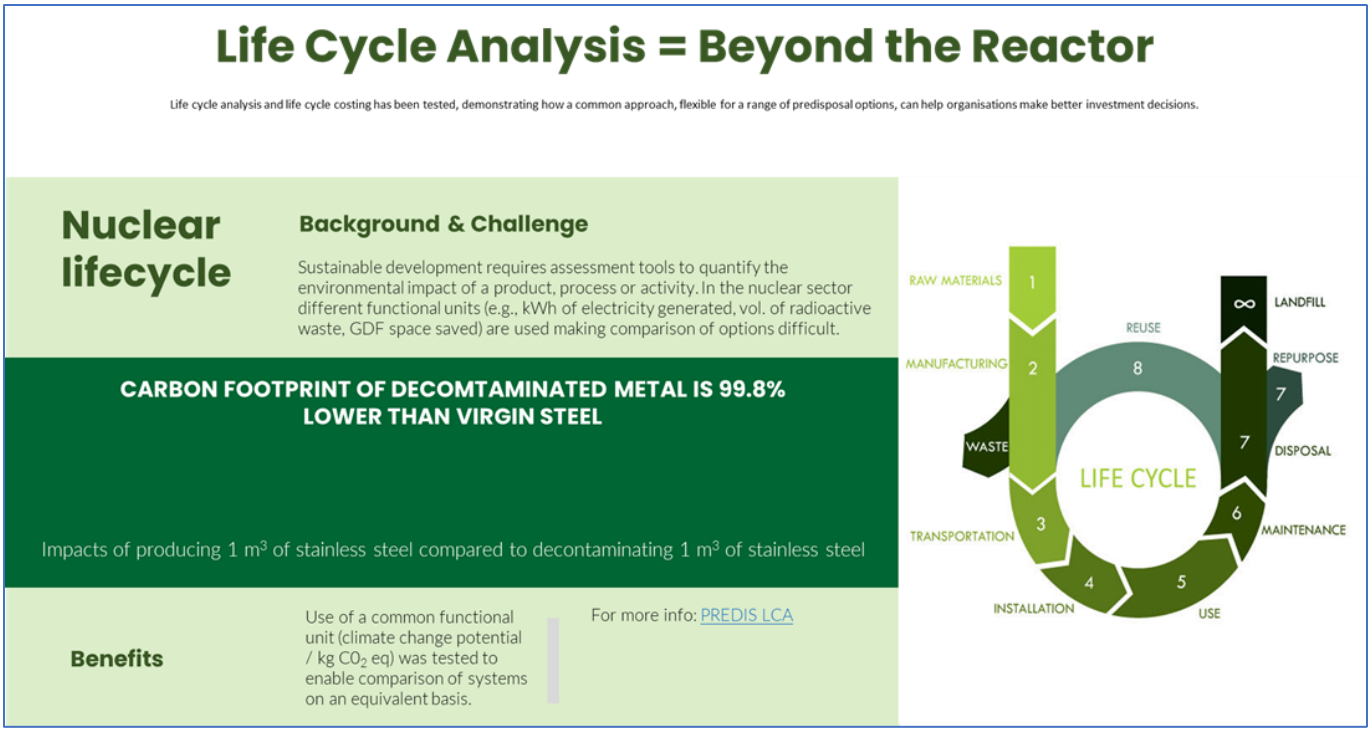
METHOD SUCCESSFULLY TESTED FOR RANGE OF OPTIONS: e.g. FOR CONTAMINATED ILW METAL

In situ decontamination & recycling Vs. size reduction and cement encapsulation in 500L drums

Benefits

Supports engagement and collaborative decision making.

For more info: PREDIS Final Conference Slides



Life Cycle Analysis = Beyond the Reactor

Life cycle analysis and life cycle costing has been tested, demonstrating how a common approach, flexible for a range of predisposal options, can help organisations make better investment decisions.

Nuclear lifecycle

Background & Challenge

Sustainable development requires assessment tools to quantify the environmental impact of a product, process or activity. In the nuclear sector different functional units (e.g., kWh of electricity generated, vol. of radioactive waste, GDF space saved) are used making comparison of options difficult.

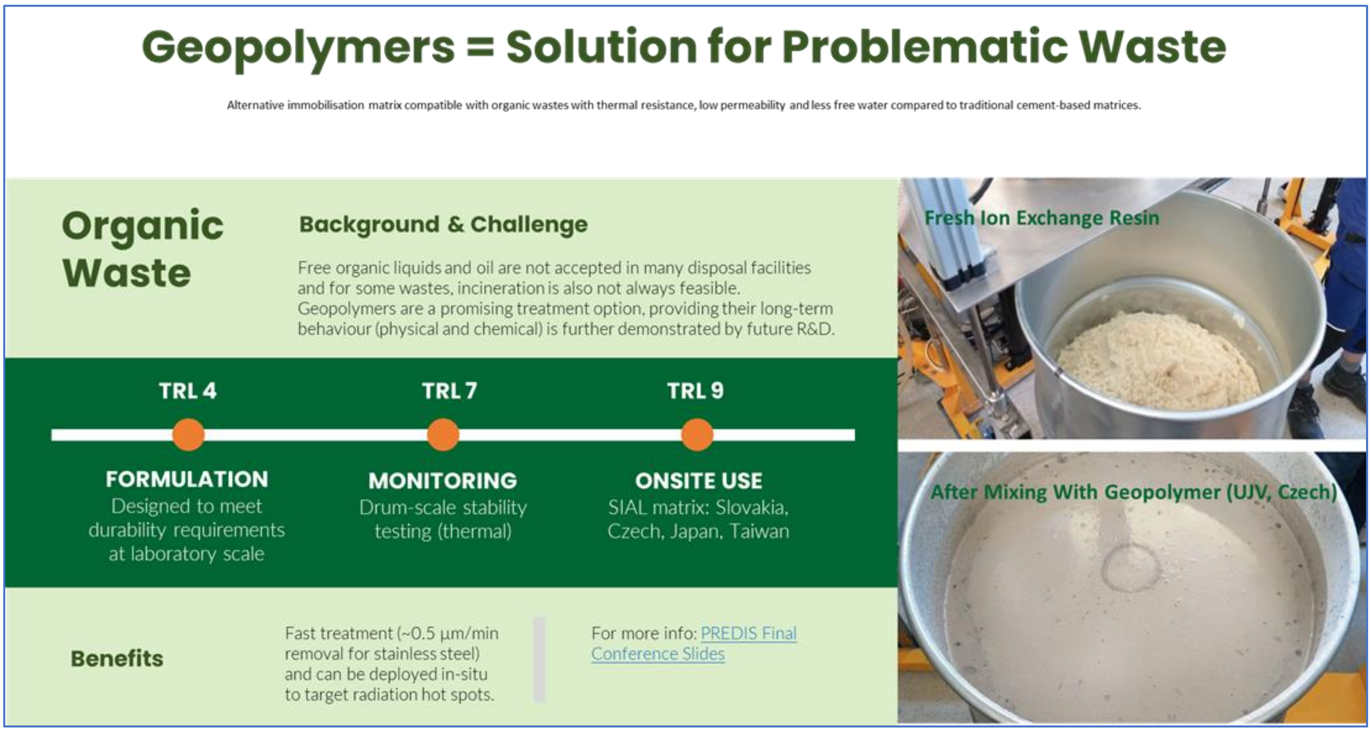
CARBON FOOTPRINT OF DECOMTAMINATED METAL IS 99.8% LOWER THAN VIRGIN STEEL

Impacts of producing 1 m^3 of stainless steel compared to decontaminating 1 m^3 of stainless steel

Benefits

Use of a common functional unit (climate change potential / kg CO_2 eq) was tested to enable comparison of systems on an equivalent basis.

For more info: PREDIS LCA



Geopolymers = Solution for Problematic Waste

Alternative immobilisation matrix compatible with organic wastes with thermal resistance, low permeability and less free water compared to traditional cement-based matrices.

Organic Waste

Background & Challenge

Free organic liquids and oil are not accepted in many disposal facilities and for some wastes, incineration is also not always feasible. Geopolymers are a promising treatment option, providing their long-term behaviour (physical and chemical) is further demonstrated by future R&D.

TRL 4
FORMULATION
Designed to meet durability requirements at laboratory scale

TRL 7
MONITORING
Drum-scale stability testing (thermal)

TRL 9
ONSITE USE
SIAL matrix: Slovakia, Czech, Japan, Taiwan

Benefits

Fast treatment (~0.5 µm/min removal for stainless steel) and can be deployed in-situ to target radiation hot spots.

For more info: PREDIS Final Conference Slides

New Gels = Less Waste: Decontaminating metal pipes

New gel formulations with good decontamination factors, consistent with the chemical decontamination, reduces waste volumes needing disposal.

Metallic Waste

Background & Challenge

Treatment and recycling of metallic wastes will serve to minimise overall environmental impacts by reducing waste volumes (and disposal facility footprints) and enhancing long-term safety by decreasing gas generation due to metal corrosion..

TRL 3

COREMIX
Proof of concept

TRL 7

EASD
Electrochemical gel decontamination at inactive commissioning

TRL 9

Vacuumable Gels
Plant Operations

Benefits

Fast treatment (~0.5 µm/min removal for stainless steel) and can be deployed in-situ to target radiation hot spots.

For more info: Link
Link

Digitization = Smart Store Monitoring

Industrial scale demonstration tests successfully conducted to validate the monitoring technologies in realistic conditions – surface laboratory/interim storage facilities around Europe.

Digital Twin

Background & Challenge

Enhanced safety, efficiency, and reliability in radioactive waste management through continuous, real-time monitoring with advanced sensors and monitoring capability to facilitate early detection of potential issues.

TRL 4

CONCEPT
Neural network models to predict chemical reactions in waste packages

TRL 5

PILOT
Digital twin toolkit and data platform

TRL 8

DEMONSTRATION
Embedded Sensors, Muon Tomography, Ultrasonic Inspection, Acoustic Monitoring

Benefits

Safer waste package monitoring capability using non-destructive, reliable and remote methods.

For more info: PREDIS Final Conference Slides

Thursday June 6th: Panel Discussion – Impacts on French Programme

This panel session was chaired by Erika Holt (PREDIS Co-Coordinator). Questions were posed to the panel members who each provided their own perspectives on how outputs of the PREDIS project could be used (individual highlights are summarised below). Panel questions included:

1) What are best practices how R&D and/or Knowledge Management activities in projects have been done together with end users or stakeholders?
2) How can the work done in projects be utilized by the wider community?
3) What type of challenges or limitations are there when utilizing results of such projects?
4) How should the research community best support governmental and industry groups to focus on the most impactful topics in projects?
5) What challenges still remain or should be the focus as we move forward with collaborative RD&D and Knowledge Management activities for the next 5 years (EURAD-2 new programme)?

Magali Saluden (CEA)

Using results: Magali acknowledged the important work of PREDIS and highlighted the next challenges to progress some of the technologies to pilot-scale research and demonstration. Numerical tools like digital twins and consideration of legacy waste are needed.
Challenges: Waste producers and regulators must work together to move in the same direction.
Future directions: There is a need to improve the representativeness of simulants which used for specific characterisation techniques. Technology Readiness Level (TRL) is still too low for many of the technologies and scale-up is needed before it could be deployed on site. In terms of innovation, Magali highlighted the progress made to up-scale geopolymer by PREDIS and that within 2 years this could be used.
Takeaway message: Holistic R&D is important and AI could be applied to better fit characterisation data.

Hélène Deniau (Veolia)

Using results: Hélène emphasized the need for site-specific R&D and pilot-scale research to ensure solutions are applicable.

Challenges: Regulations vary across countries, and sometimes changes are necessary.

Future directions: More co-processing of waste products in a single plant is needed (the example of co-processing with asbestos materials was mentioned).

Sustainability: Lessons learned from other industries should be applied to make the nuclear sector more sustainable and economical.

Takeaway message: Human resources must be ensured through KM and competence building.

Fabrice Moggia (ORANO)

R&D with End-Users: Fabrice's main interest has focused on the long-term storage of concrete and its non-destructive testing (NDT) investigation.

Challenges: The main challenge is to demonstrate that regulators can benefit from the work being done.

Future directions: Cementation in a low CO2 matrix as a future direction is key priority to support sustainable development objectives.

Takeaway message: New techniques with impressive results must be concretized.

Henri Le Monies de Sagazan (EDF)

Using results: Henri stressed the need for diversification of immobilisation methods, with a focus on low CO2 impact solutions like geopolymers. He believes PREDIS is working on the right subjects.

Challenges: Henri pointed out the need to consider the consequences of findings for transport, dose rates of workers, availability of materials, and secondary wastes.

Future directions: Co-processing, preservation of resources, and circular economy are key areas.

Takeaway message: Henri highlighted the potential for AI to revolutionize knowledge management (KM).

Virginie Wasselin (Andra)

R&D with End-Users: Virginie has collaborated in PREDIS WP7 and characterisation, participated in the SRA, and the summer school on WAC. She emphasized the need for early involvement of end-users in projects and avoiding reinventing the wheel.

Challenges: Each type of waste needs a specific solution and separate R&D. Scenarios could be developed with multi-criteria analysis and the LCA/LCC methodology demonstrated within PREDIS. Circular economy and sustainability are easily understood by the public.

Future directions: Virginie highlighted the importance of addressing other toxic elements in predisposal.

Takeaway message: Interaction between TSO, Regulator, and WMO is crucial to ensure a full lifecycle approach to options assessment (e.g., considers benefits upstream, but also the potential impacts for disposal where further long-term performance studies are required).

Thursday June 6th: Panel Discussion – Impacts on International Community

The afternoon session followed the same format as the morning panel session, including the same set of questions. A summary of panel session responses for each person is provided below which includes perspectives from questions posed by members of the audience.

Anthony Banford (SNETP Chair)

Best practices with EUG: Anthony mentions PREDIS presentations in SNETP.

Challenges in implementation: The nuclear sector is slow at implementing new things. Low TRL research is easy, but moving to higher levels becomes costly.

Solving challenges: It is a big win if PREDIS experts work in the industry on these topics in the future, as this way the knowledge is shared more broadly beyond the RD&D community.

Paul Carbol (EURAD Cooperation & KM)

Best practices with EUG: Paul mentioned KM trainings that are complementary to IAEA.

Challenges in implementation: Researchers need to socialise to share project outcomes and present results.

Solving challenges: There is a lot of data that needs to be turned into a database, and AI can be used to interpret the data. In particular each organisation should prioritised KM and open databases (where viable) to help improve access to available knowledge more broadly (e.g. old research can be indexed better). Open accessibility and socialisation of RD&D results (and other nuclear knowledge) will improve RWM.

Hans Forsström (Senior Advisor SKB International & EC Evaluator)

Utilising results worldwide: Now is the opportunity to share the results abroad, not only in publications but person to person transfer so that the knowledge is passed down.

Challenges in Implementation: It is a slow path from R&D to industry/commercial adaptation. There is a question of whether commercial entities know about the new technologies.

Solving challenges: Close collaboration is needed with WMOs, and the focus must not only be on formal adherence Waste Acceptance Criteria (WAC). Value assessment needs to include softer values.

Seif Ben Hadj Hassine (EC Programme Officer)

Best practices with EUG: Seif emphasizes cross-border research that solved problems in other member states. Knowledge preservation is vital to ensure that future entities have access to results.

Solving challenges: Waste Management Organizations (WMOs) decide what they want to implement. End-users need to be involved in planning and their feedback gathered throughout. Feedback could also be gathered after the project ends to see what has been implemented. Small inventory countries need the results the most, and big players should provide their help and “sell” their knowledge.

Vaidas Matuzas (JRC)

Utilising results worldwide: Each member state should have national R&D. There is a question of how countries that don’t have national R&D benefit from the results and how to develop KPIs at the EU Programme level to show impacts and benefit to Member States.

Solving challenges: The framework is there to help small inventory countries by getting involved with projects such as EC PREDIS.

Rebecca Robins (Radioactive Waste Team Leader, IAEA)

Best practices with EUG: Rebecca highlighted that anything done in Europe can be adopted globally. PREDIS generates valuable knowledge and information that the IAEA can share, with the value coming from captured knowledge in a wiki.

Utilising results worldwide: The big benefit is the community that has been generated.
Challenges in Implementation: Newcomers in the nuclear industry have it easier when implementing new technologies such as geopolymers.

Solving challenges: The world is changing, and radioactive waste management (RWM) needs to be done well. In the future, we will be proactive to prevent legacy waste from forming, potentially through the use of Small Modular Reactors (SMRs).

2 Strategic Implementation (WP2)

2.1 LCA and LCC: gel decontamination of stainless steel, and geopolymer encapsulation of thermally treated solid organic (Task 2.5)

Laurence Stamford, The University of Manchester, UK, laurence.stamford@manchester.ac.uk
Anthony Banford, National Nuclear Laboratory, UK
Joel Kirk, The University of Manchester, UK
Rachael Clayton, The University of Manchester, UK

Keywords: life cycle assessment; life cycle costing; sustainability; sustainable development; carbon footprint; GHG

1. Introduction

Life cycle assessment (LCA) is an environmental sustainability tool that applies the concept of life cycle thinking to assess the consequences of human activities. Thus far, LCA in the nuclear sector has focused on electricity generation, deriving estimates of environmental impacts per kWh or MJ of electricity produced, and the results have been reviewed in literature [e.g. 1, 2, 3], typically focusing on greenhouse gas emissions. Many individual LCAs of nuclear power have included a broader range of environmental impact categories — spanning issues such as carbon footprint, acidification, eutrophication, ecosystem toxicity, human toxicity, and resource depletion, among others — and have used the results to compare the impacts of nuclear systems with other power technologies [e.g. 4, 5, 6]. The insights provided by these and other LCAs have been instrumental in determining policy positions, including the inclusion of nuclear power in the EU taxonomy for sustainable activities ('green taxonomy') [7]. LCA has also been used to investigate the impacts (and mitigation of impacts) arising from potential nuclear-based energy vectors such as hydrogen and ammonia [8, 9].

However, a literature review by the authors which is due to be published imminently has shown that only one existing LCA study [10] has an explicit focus on the back-end of the nuclear fuel cycle. It evaluates the entire decommissioning process for a UK Magnox reactor and, in doing so, highlights the paucity of detailed inventory data (such as mass and energy flows) for waste treatment and decommissioning processes. Moreover, in the energy generation-focused studies mentioned above, the back-end is either greatly oversimplified, lacking specification, or missing entirely [1, 3]. Consequently, useful insights into impact reduction in the nuclear back-end are being lost.

Therefore, this paper contributes to the deepening of knowledge in this area by presenting two case studies on radioactive waste processing techniques, with selected results discussed in more depth to illustrate the outcomes and their potential implications.

2. Description of work and main findings

LCA is standardised via ISO 14040 and 14044 [11, 12], in which four key phases are identified: goal and scope definition, inventory analysis, impact assessment, and interpretation. This work aligns with these standards. The LCA modelling presented here has been conducted using Sphera LCA for Experts (GaBi) [13].

Goal and Scope Definition

The functional units (FUs) of the two case studies are defined as follows:

1. For the use of gel to decontaminate a radioactive metallic surface, the FU is the treatment of 10 m^2 of planar stainless steel surface. Stainless steel was chosen as it is regularly used in parts of a nuclear power plant that will become contaminated/irradiated over time such as areas that will come in to contact with coolant, and in radioactive material management areas such as hot cells.
2. For geopolymer encapsulation of thermally treated radioactive solid organic waste (RSOW), the FU is the pre-disposal processing of 1 kg of intermediate level RSOW surrogate. This was chosen as it

represents the encapsulation of ash from the IRIS plant [15], received as a product of thermally treated ion exchange resins and contaminated personal protective equipment.

For the gel decontamination case study, the system boundary starts at the production of reagents and equipment used to decontaminate the metallic surface and ends at the removal of the treatment gel from the target stainless steel surface once there has been sufficient contact time. It is assumed that only surface contamination is present. All upstream and downstream burdens associated with these processes are included.

For the study of geopolymer encapsulation of thermally treated radioactive solid organic waste, the system boundary includes the receipt of waste at the treatment facility to the handoff of a conditioned waste drum to a final repository. All upstream and downstream burdens associated with these processes are included. It should be noted that any such use of geopolymers would require a robust safety case and proof of leaching performance over time. This case study assumes that these requirements are met before deployment.

Inventory Analysis

The technical data required to specify the foreground systems were collected iteratively with PREDIS project partners using a data collection template and collation in Excel files. The template was relatively generic to maximise flexibility, and the data received from partners varied from lab-scale data with many missing data points to detailed inventory based on upscaled systems. Interpretation and adaptation by the authors was enabled by the collection of indicative values, ranges, and explanatory comments in the template, followed by iterative meetings online and in person.

In all cases, background data were sourced from the ecoinvent database v3.9 [16], as it is the most widely used and accepted life cycle inventory database, particularly for Europe-focused systems. We note that many other similar databases exist, such as the U.S. LCI Database managed by NREL [17], which may be more suitable in some cases.

Gel decontamination is based on data provided by CEA [18] including masses and ratios for the gel ingredients, as well as information on the type of equipment used to apply and remove the gel from the target surface. An exemplar 10 m^2 contaminated stainless steel surface was used as a basis for decontamination.

Geopolymer encapsulation of thermally treated radioactive solid organic waste (RSOW) surrogate is based on data provided by Politecnico di Milano [19]. The inventory information provided was based on a 20% waste loading of a bespoke zeolitic volcanic tuff based geopolymer. The waste, tuff and respective activation materials are mixed in-situ within a standard waste drum.

Due to data confidentiality, full detail of each inventory dataset is not presented here, but rather the approach of data collection and iteration with partners is emphasised to arrive at mutually agreed representative datasets.

Results (Impact Assessment and Interpretation)

This work adopts the ReCiPe impact assessment methodology [14], providing information on all included impact categories. Alongside Environmental Footprint, ReCiPe is often seen as the state-of-the-art and there is some evidence to suggest that ReCiPe is the most widely used method [15].

Gel Decontamination

For the treatment of 10 m^2 of radioactive stainless steel surface using a decontaminating gel, the model was separated into four sub-processes: treatment (including gel production), application (including sprayer production), removal (including vacuum cleaner production) and energy used by equipment.

FIG. 1 shows all 18 midpoint impact categories arising from the ReCiPe 2016 methodology. Impacts are dominated by the production of the decontamination gel and vacuum cleaners that are used to remove the gel from the treated surface: these processes account for an average of 41% (range 12-90%) and 58% (range 10-88%), respectively, across the impact categories. Cerium nitrate in the gel is the main contributor due to the upstream impacts arising from mining and processing of bastnaesite ore involving multiple stages, each using heat and chemical reagents. The vacuum cleaner impact arises from their short lifespan and therefore the quantity of cleaners necessary: once full, the vacuum cleaner drum must be safely disposed of, which involves compaction and encapsulation. Consequently, the main areas for potential improvements are gel reformulation and minimisation of usage, followed by identifying ways to reuse the vacuum cleaners or some of their components. These potential changes must of course be undertaken bearing in mind any resultant effects on waste acceptance criteria.

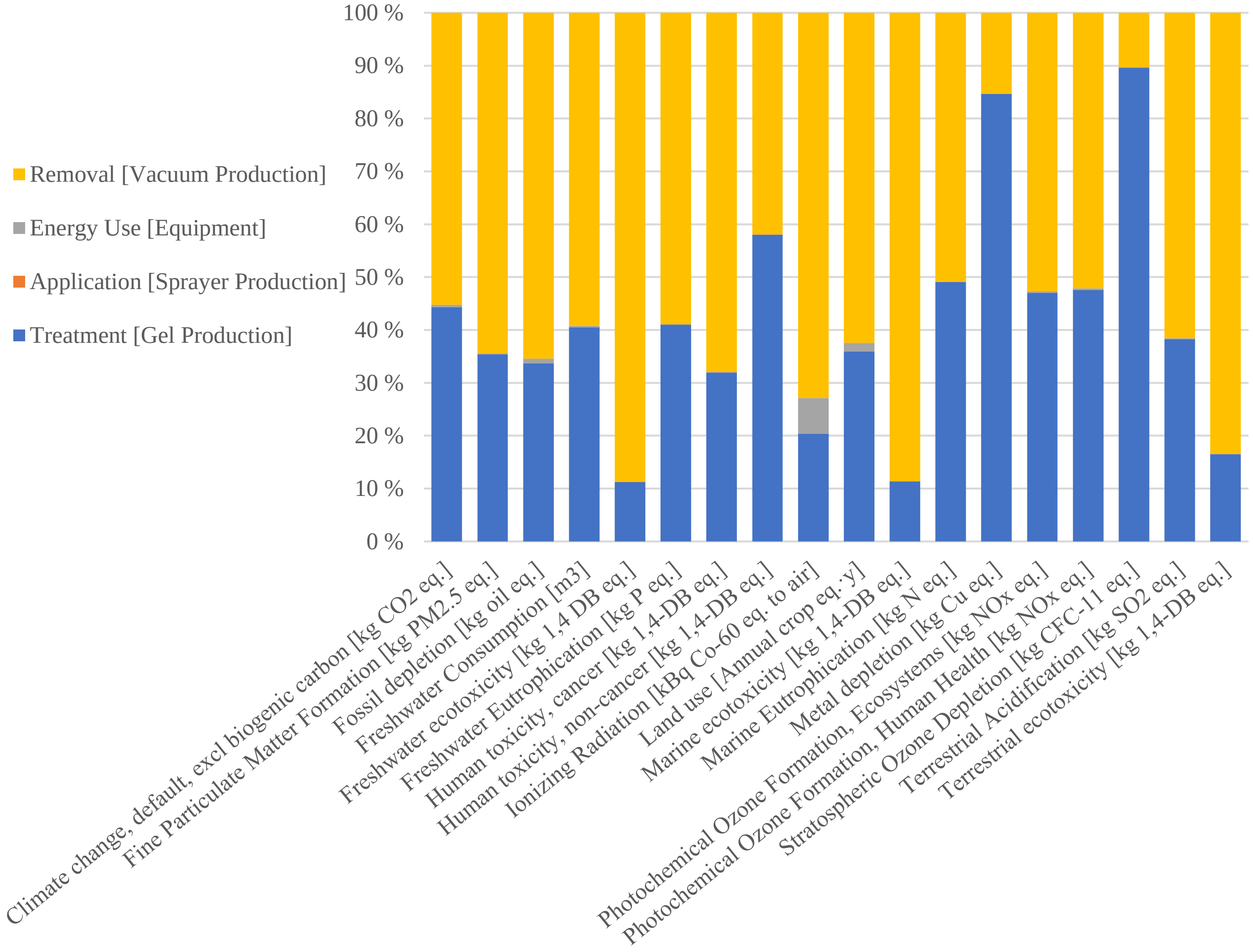


Figure 1. Impacts of treating 10 m2 of contaminated stainless steel with decontamination gel.

Once treated, the stainless steel could potentially be recycled rather than being disposed of in a radioactive waste store. FIG. 2 illustrates that the carbon footprint of decontaminated stainless steel is 99.8% lower than that of virgin stainless steel, even before savings in GDF space are accounted for. It should be noted that this case assumes only surface contamination was present on the steel: any subsurface contamination or activation could substantially reduce the benefits implied by FIG. 2.

Forthcoming work has quantified the impacts of recycling via induction furnace to produce free-release metal, demonstrating that very large impact savings persist (versus direct disposal) despite furnace operation.

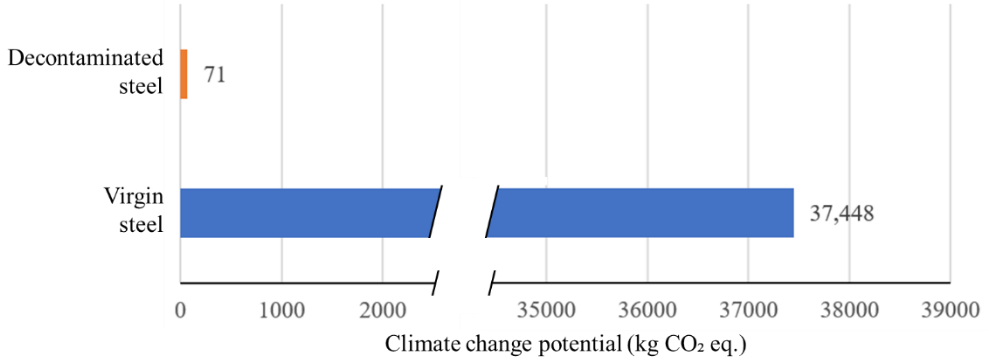


Figure 2. Impacts of producing 1 m^3 of stainless steel compared to decontaminating 1 m^3 of stainless steel.

Geopolymer Encapsulation

Results from the geopolymer encapsulation case study are shown in FIG. 3 which compares a base case treatment technique for radioactive solid organic waste — encapsulation in cement — with a geopolymer alternative. As geopolymer encapsulation is still under development, uncertainties remain around waste loading in different circumstances. A baseline assumption of 20% was used for the direct comparison to cement, as this matches the typical loading for cementitious matrices. However, preliminary data suggest that higher loadings may be possible with geopolymers, therefore additional models were developed to investigate increased waste loading (30% and 40%).

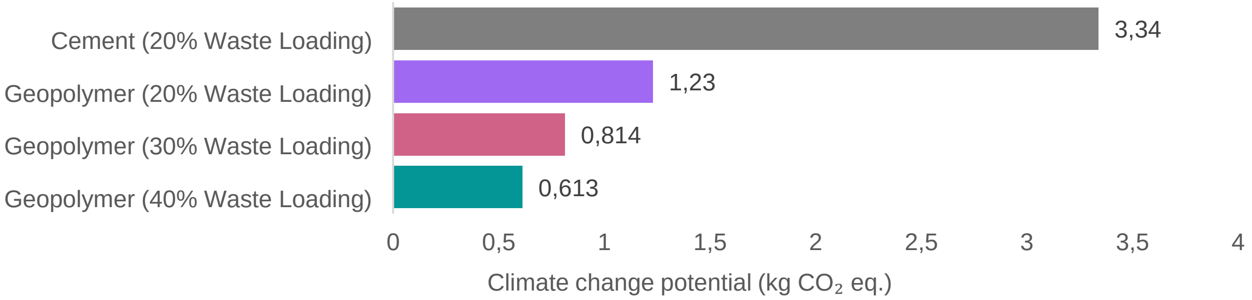


Figure 3. Life cycle environmental impacts of thermally treated RSOW encapsulation via geopolymers and cement at different loadings.

A clear distinction can be made between the climate change potential of utilising novel geopolymer technologies in comparison to typical Portland cements at the same waste loading factor. A clear corelation can also be drawn between the increase of waste loading factor and decrease in climate change potential. Similar trends were also identified for the other 17 impact categories in the ReCiPe 2016 LCIA methodology.

Hence, it can be inferred that a shift towards utilising geopolymer matrices is likely to reduce carbon footprint by at least ~63% for similar waste loading factors, validating the environmental driver for further research into geopolymer treatment processes. However, the cost of implementation at scale requires further investigation and is the subject of future work by the authors.

Conclusions can also be drawn surrounding the increase in waste loading. Higher loading increases the energy consumption during waste processing activities, but the results demonstrate that those impacts are outweighed by the benefits of reduced use of materials for encapsulation. Therefore, research and development of these advanced matrices should focus on assessing the feasibility of increased waste loading. At larger scales of RSOW processing, improved waste loading would also reduce the final number of drums allocated to a final repository which would have consequential reductions in environmental impact and cost, but quantification of these issues is outside the scope of this study.

These recommendations could have relevance to the waste acceptance criteria (WAC) set out by WMOs, which could even potentially be adjusted to include environmental conditions in parallel with a robust safety case.

3. Conclusions and way forward

This paper has outlined the approach taken in the PREDIS project to incorporate life cycle thinking into the development of radioactive waste treatment technologies, illustrated by two case studies addressing gel-based decontamination of metallic waste and geopolymer encapsulation of organic solids. Key elements include the appraisal of multiple impact assessment categories – 18 in this case – to provide a broad understanding of the environmental profile of the developing technologies, as well as the use of hotspot analysis to identify future focal points for R&D, alongside benchmarking against base case treatment techniques to establish potential benefits and/or drawbacks of new approaches.

The two case studies presented have identified the following:

- Gel manufacture and vacuum cleaner production have broad, multi-criteria dominance over the environmental impacts of metal decontamination, with energy consumption and application playing almost negligible roles. Therefore, future efforts should identify alternative oxidants in gel formulation and explore opportunities to minimise or reuse vacuum cleaners or their components.
- The impact of gel decontamination of planar stainless steel surfaces has a carbon footprint three orders of magnitude lower than the production of virgin metal, suggesting substantial climate benefits to this approach over the base case of direct disposal (provided only surface decontamination was present on the contaminated steel).
- Geopolymer encapsulation of thermally treated solid organic wastes outperforms conventional cementation at similar waste loadings, by >60%, while higher waste loadings increase this advantage despite the concomitant increase in energy consumption. The latter is true even without considering downstream benefits resulting from repository space savings, which would amplify these benefits.
- Costs and optimisation of waste loadings should be the focus of future geopolymer encapsulation research to maximise sustainability.

Given the large volume of radioactive waste in need of treatment/disposal (5.2 million m^3 across the EU by 2030), the insights gained from LCA during process development could enable far-reaching future benefits. This requires close collaboration with technical partners to ensure the validity of input data and suitability of improvement suggestions, as has been practised in the PREDIS project.

Acknowledgements

The authors acknowledge with gratitude the funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098. The contribution to this paper of numerous PREDIS project partners is also gratefully acknowledged, including Galson Sciences Ltd for their work on inventory data collection, Andrea Santi (Politecnico di Milano) on geopolymer encapsulation, and Alban Gossard (CEA) on gel decontamination.

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3 KNOWLEDGE MANAGEMENT (WP3)

Paul Carbol, JRC, Belgium, Alba Valls, Amphos 21, Spain, alba.valls@amphos21.com, Jiri Faltejsek, UJV Rez, Czech Republic, Maria Abada, Amphos 21, Spain

Keywords: Knowledge management, mobility programme, training programme, State-of-Knowledge, student group

1. Introduction

The objectives of WP3 in PREDIS is to develop and transfer knowledge and competence across EU Member States national programmes and to preserve knowledge transfer to coming generations in the field of predisposal of radioactive waste.

Through the production of State-of-Knowledge (SoK) documents such as the domain insight (DI) documents knowledge has been preserved in an easily transferrable manner. By organizing training courses and webinars, WP3 has been contributing to building competences. Students, young professionals and project partners have had the opportunity to acquire tacit knowledge by attending courses, visiting partner organisations and infrastructures or attending conferences through the help of the PREDIS mobility programme. Furthermore, dissemination of the work performed in WP3 has been presented on several occasions at international conferences as well as through project deliverables and milestones. A number of actions (student group meetings, PhD-work presentations and posters) initiated by WP3 has continuously facilitated networking within the student group, e.g. at student meetings as well as with experts during annual meetings.

WP3 lead gave a 45-minutes presentation at the final PREDIS conference to inform partners and participants on the progress made during the last year and to summarise the outcome of all four years KM work. The presentation can be downloaded from the PREDIS web site. A short summary of the presented KM progress is given below.

2. Description of work and main findings

WP3 is the project's knowledge management hub with the responsibility to manage all types of knowledge management (KM) activities; focus on overall KM goal, creating courses, producing SoK documents, mobility measures, creating a functional student group, all actions taken in consideration of projects partners' needs, already existing KM initiatives, the budget and participants feedback after each KM activity. The overall coordination of these activities is in Task 1 KM programme.

One part of the Knowledge management program was to encourage creation of a PREDIS student group and to disseminate the development and progress of PREDIS KM activities. The student group was created at the start of the project and throughout the four years a total of 51 students have been part of the PREDIS project where some students have taken part in more than one WP. More than 50% of the students have been PhD students and the rest were MSc students and PostDocs, a picture of a part of the student group is shown in Figure 1.

Figure 1. Picture of student group at PREDIS Final conference, Avignon, June 2024.

Regarding dissemination, WP3 has presented its work at 11 conferences in Europe, North America and Asia. In correlation to these conferences 11 oral presentations have been given, three posters have been presented and 7 papers published. The alignment and cooperation between EURAD and PREDIS is presented in the common paper [1].

SoK work included organizing and overseeing authoring as well as reviewing of twelve DI documents for each topic to feed Theme 2 of the EURAD roadmap, see Figure 2. All 12 DIs are planned to be finished by the end of the project.

All twelve Domain Insights (DIs) are planned to be finalised by the end of the project. Figure 3 shows the status of DIs production at the time of the PREDIS final conference. All DI authors have announced that it will be possible to finalise their contribution before end of PREDIS. The PREDIS review of the DIs is also planned to be made in time. An quality check for cross referencing between the PREDIS documents and alignment/referencing to other EURAD Roadmap/DI topics is planned, before the DIs are sent for EURAD internal review, insertion into EURAD Wiki, given a DOI number, published on EURAD web site and IAEA/INIS.

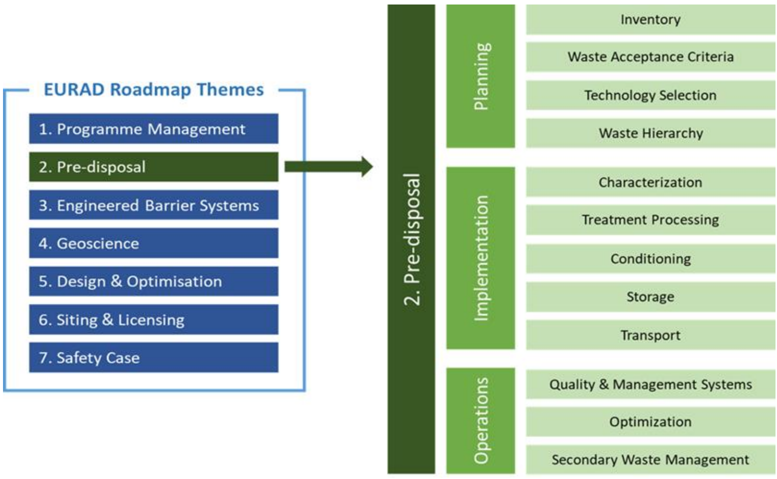


Figure 2. PREDIS roadmap.

Organizing trainings courses was one of the main activities in WP3 (Task 3). A total of 8 training courses were organized during the course of PREDIS and a summary is shown in Figure 3. The course topics, formats and durations were chosen by identifying existing courses as well as survey answers on wants and needs from the PREDIS community. There were different types of participants to these courses. The majority were PREDIS partners, students and EUGs. EURAD partners, students and EUGs as well as externals to both projects were able to attend the courses. The general feedback received on the training programme was very positive (in general, a score of 4.5-4.7 out of 5 = excellent) where the most appreciated part usually was the on-site visits and a point of improvement was better communications before training courses.

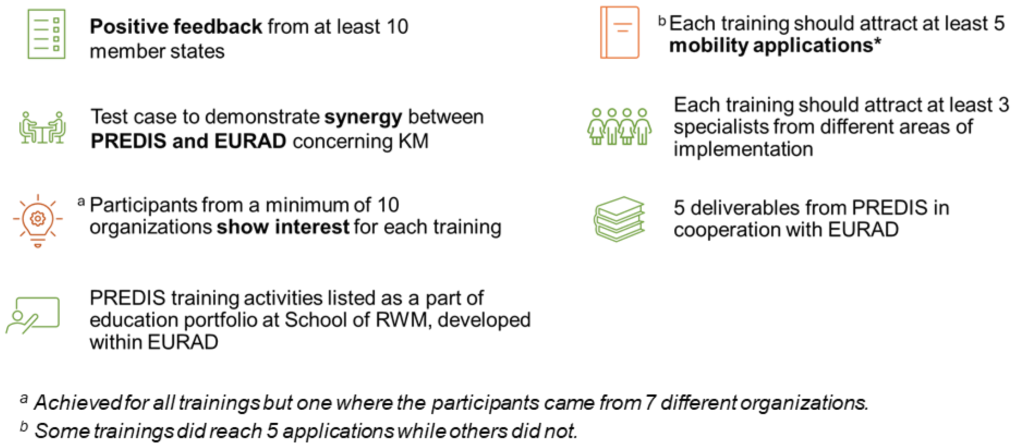
Figure 3. Summary of PREDIS training courses organized throughout PREDIS.

Apart from training courses, webinars were also organised to disseminate knowledge and share progress of research in PREDIS R&D work packages with PREDIS partners, predisposal community, as well as the broader radioactive waste management community. A total of 19 webinars were organised by PREDIS; 11 of them were held in 2021, 4 in 2022, 3 in 2023 and one in 2024. The average number of participants/viewers was 110, with more to come as the webinars were recorded and the recordings are available on PREDIS website.

Another important activity of the KM WP is the mobility programme. It facilitates knowledge transfer and networking through student workshops, internships, trainings and conferences. A total of 65 mobilities have been accepted during the PREDIS project where 34 of them have been used to attend student workshops, 13 to attend trainings and 9 to attend internships and 9 to attend conferences.

3. Conclusions

A comparison of the key performance indicators (KPI) fixed in the PREDIS proposal, and the work carried out by WP3, shows that WP3 has met all KPIs, see Figure 4. The KPIs not fully completed can be explained by a) some trainings had less than 10 training places and b) some WPs used internal budgets to attend trainings courses.



Positive feedback from at least 10 member states

Test case to demonstrate **synergy** between **PREDIS and EURAD** concerning KM

[a] Participants from a minimum of 10 organizations **show interest** for each training

PREDIS training activities listed as a part of education portfolio at School of RWM, developed within EURAD

[b] Each training should attract at least 5 **mobility applications***

Each training should attract at least 3 specialists from different areas of implementation

5 deliverables from PREDIS in cooperation with EURAD

[a] *Achieved for all trainings but one where the participants came from 7 different organizations.*

[b] *Some trainings did reach 5 applications while others did not.*

Figure 4. KPIs, marked in green = achieved and marked in orange = not fully achieved.

Acknowledgements

WP3 lead would like to acknowledge the support and help received from various actors throughout the project. Thanks for the great support by Erika Holt and Maria Oksa, coordinators of the PREDIS project. The WP leaders for active involvement in KM WP contributed to a successful KM programme. Without the support from the partners inside the KM WP the KM programme would have not worked out. Many thanks to Jess McWilliams (Manchester University) for keeping together and leading the PREDIS student group. Finally, special thanks to Lara Duro and Venda Havlova for their work done as WP lead and co-lead and to Niels Belmans and Alexandru Tatomir for support from EURAD.

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4 Scientific progress in Innovations in metallic treatment and conditioning (WP4)

PREDIS project is developing technologies for treatment and conditioning of radioactive waste such as metallic waste as well as radioactive organic waste whether liquid (RLOW) or solid (RSOW). The WP4 focus is on steel and Ni-alloys radioactive metallic waste, which are major components in nuclear installations. These metallic wastes are often surface-contaminated in the form of corrosion layers of a few tens of micrometers retaining radionuclides including but not limited to activation corrosion products (Co-60, Ni-63, Fe-55) and fission products such as Cs-137.

4.1 Defining Europe-wide Needs and Opportunities for Management of Metallic Waste Streams (Task 4.3.)

Delhia Alby, Jenny Kent, Tim Harrison (Galson Sciences Ltd, UK), da@galson-sciences.co.uk

Keywords: metal melting, metal decontamination, secondary waste, value assessment, inventory

1. Introduction

Task 4.3 is focused on understanding needs and opportunities for managing metallic radioactive waste.

Decommissioning of the current fleet of European civil nuclear power plants is expected to generate thousands of tonnes of radioactive metallic waste. Therefore, we need to develop more effective decontamination and remediation processes for metallic wastes, as well as optimising routes for recycling and reuse.

This document summarises work completed during the four years of the project and presented in the Deliverable 4.2 (Synthesis Report on Management of Metallic Waste Streams) and describes:

- The technologies presented in the report
- The methodology of Value Assessment and some conclusions

2. Description of work and main findings

WP4 is investigating the treatment metallic waste with existing or new technologies. The final version of Deliverable 4.2 was sent to the external reviewers in June 2024 [1]. The outline is the following:

- The inventory of metallic waste prepared with the partners
- A methodology and evaluation of secondary waste produced by decontamination technologies.
- The potential for innovative application of non-nuclear metal melting technologies.
- A strategic analysis of the economic and environmental impacts of decontamination and metal melting, using Value Assessment.

The following technologies were described in datasheets in the report:

- Physical decontamination processes:
    - Jet washing.
    - Laser decontamination.
    - Sandblasting.
    - Dry ice blasting.
- Chemical decontamination processes:
    - Chemical bath.
    - Electrochemical decontamination.
    - CORD (Chemical Oxidation Reduction Decontamination).

  - COREMIX-HP (a chemical decontamination technique similar to CORD being optimised within the PREDIS project by IMTA ; Chemical Oxidation REduction using nitric permanganate and oxalic acid MIXture followed by Hydrogen Peroxide treatment).
  - MEDOC (Metal Decontamination by Oxidation with Cerium).
  - Decontamination gels (EASD (Electrolytically Assisted Surface Decontamination) gels and Aspigel).
  - Decontamination foams.
- Metal melting processes:
  - Induction Melting (including vacuum inducting melting).
  - Electric and Plasma Arc Melting.
  - Immersion Melting – for low melting point metals.
  - PIVIC (combined plasma torch with cold-crucible induction melting).

Three of the decontamination technologies developed in PREDIS WP4 were then assessed in Value Assessment and compared to a baseline which was size reduction, packaging and cementation. The technologies selected for the assessment were COREMIX-HP, Aspigel and EASD gels (these are termed variant scenarios). Value Assessment is a comparative approach which focuses on differentiators between the baseline and the variant scenarios. This assessment is qualitative or semi-quantitative depending on data availability and uncertainties. Table 1 describes the baseline and the variant scenarios considered.

Table 1. Technologies considered for Value Assessment compared to the baseline scenario.

Waste type / example	Scenario ID	Treatment technology	Scenario origin and research organisation	Treatment output
Bulk, complex geometries, e.g. steam generator	4.1.1	COREMIX-HP	LCA (Life Cycle Assessment)/LCC (Life Cycle Costing), D4.1 IMT Atlantique	Full decontamination – cleared for recycling.
	4.1.2	COREMIX-HP	LCA/LCC, D4.1 IMT Atlantique	VLLW (Very-Low-Level Waste) metal Packaging in ISO containers for disposal at a near-surface facility (not cemented).
	4.1.B	Size reduction, packaging and cementation.	LCA/LCC	500L cemented drums Disposal at a GDF (Geological Disposal Facility)
Planar metals, e.g. hot cell walls	4.2.1	Decontamination gels (CEA)	LCA/LCC CEA	VLLW metal Packaging in ISO containers for disposal at a near-surface facility (not cemented). CEA byproduct is ILW/LLW – placed in small container in canister with other solid wastes.
	4.2.2	Electrolytically Assisted Surface Decontamination (EASD) gels (NNL).	LCA/LCC NNL	VLLW metal Packaging in ISO containers for disposal at a near-surface facility (not cemented) NNL gel byproduct is ILW/LLW – grouted product.
	4.2.B	Size reduction, packaging and cementation	LCA/LCC	500L cemented drums Disposal at a GDF

An example of the result of an assessment is presented in Figure 1 where the different categories and attributes are detailed as well as the different ratings.

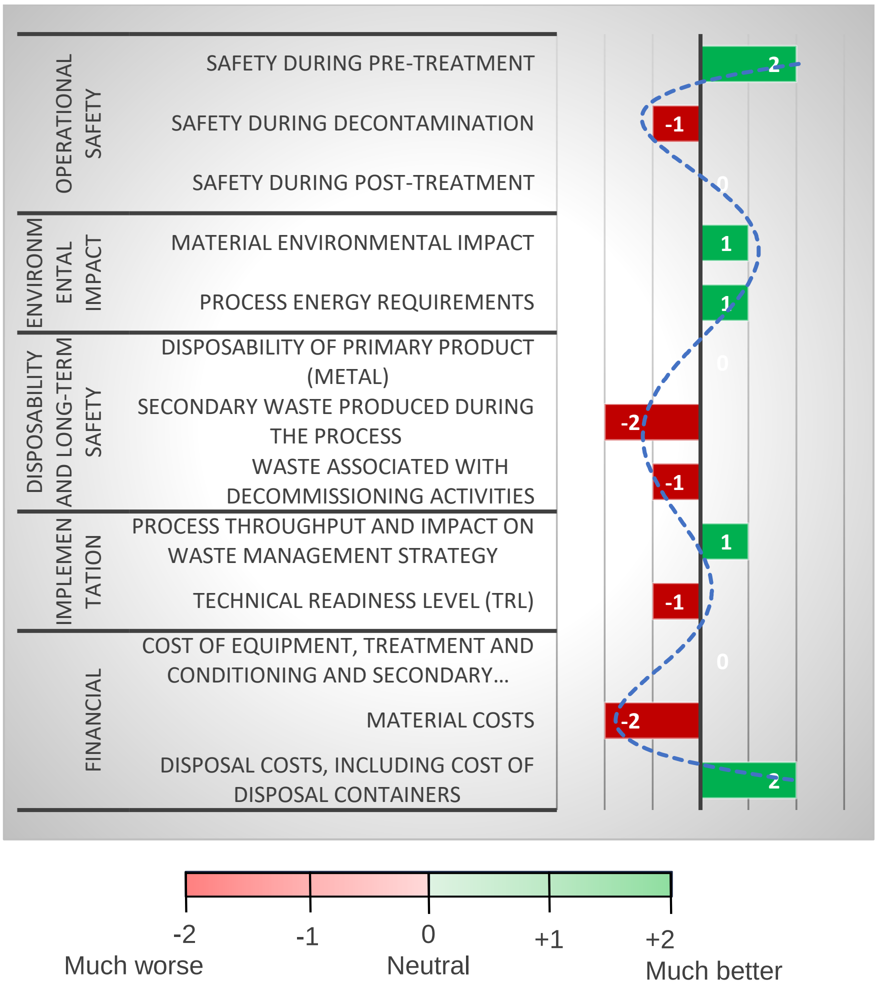

Figure 1. Example of a Value Assessment result.

The conclusions were unequivocal. Both COREMIX-HP and gel decontamination were found to lead to significant cost savings, driven by waste volume reduction, and metal recycling, made possible in some instances by surface decontamination. Both avenues present neutral to improved environmental outcomes when compared against the current option, which is size reduction and disposal as ILW. Secondary waste management (e.g. spent ion exchange resins generated by the COREMIX process) and disposal were identified as areas requiring further research and development, although no unsurmountable issues were identified.

3. Conclusions

Deliverable 4.2 [1] was sent to external reviewers in June 2024 and will be published by the end of the project.

Some of the waste streams identified in the inventory do not currently have a management route; the approaches developed in PREDIS WP4 can demonstrably offer solutions to treat and condition these waste streams, whilst reducing waste volumes and costs compared with conventional approaches. A forward work programme to address uncertainties associated with the disposability of some of the secondary wastes is proposed under EURAD-2.

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4.2 Development and optimisation of decontamination processes (Task 4.4)

Task 4.4 “Development and optimisation of decontamination processes” is focused on understanding optimization techniques for the decontamination of metallic radioactive waste. Decommissioning of the current fleet of European civil nuclear power plants is expected to generate very large quantities of radioactive metallic waste. Therefore, there is a need to improve the decontamination processes for metallic wastes, and the associated secondary effluents with a goal to be able to recycle the metals in order to promote the concept of circular economy through LCA routes, whilst accounting for the Waste Acceptance Criteria (WAC).

The presentation summarised work completed to date, including:

- Decontamination strategy to be used as a guideline.
- Characterization of surrogate samples used for testing of decontamination techniques.
- Identification of decontamination techniques selected for testing and the parameters which can affect efficiencies.
- Demonstrated the efficacies of different conditions, which show promise in decontamination of such metals.
- Demonstrated the associated treatment techniques for the secondary liquid effluents generated.

4.2.1 Metallic waste surrogates preparation

Thomas Carey, Anne Callow and Jessica Hopkin (NNL, UK); thomas.carey@uknnl.com

1. Introduction

WP4 stakeholders are developing innovative decontamination technologies for the treatment and conditioning of metallic wastes where no or inadequate solutions are currently available. Common technical challenges exist in the development of these innovations, particularly centred around the technology’s deployment, decontamination performance and secondary waste treatment. All these technical challenges need to be overcome if future offerings or services are to be made commercially available for the civil nuclear decommissioning market.

2. Description of work and main findings

Contamination of metallic surfaces can occur via range of different mechanisms and is dependent on the specific environment within a nuclear plant (e.g. temperature, pressure, pH, metal type etc.). Although there is often an ambition to assess decontamination techniques on ‘real’ plant components, factors such as radiological hazards, limited accessibility, high bureaucracy and cost can often be prohibitive. Therefore, the preparation of artificial coupons that replicate common metallic waste challenges was required as part of the WP4 scope of work. Artificial sample coupons are useful for 2 main reasons: i) to act as a benchmark for the assessment of decontamination techniques and ii) to further scientific understanding of the contamination mechanisms.

NNL utilised their knowledge of UK’s reprocessing plants to prepare artificial coupons which reflected the contaminated and highly corroded metallic surfaces expected in plant infrastructure. These contaminated surfaces are highly complex and are currently not well understood by the industry. Knowledge of these contaminated surfaces is required to enable effective decommissioning strategy and safety case preparation.

Detailed characterisation of the prepared coupons was conducted using a suite of techniques including Energy-dispersive X-Ray Spectroscopy, Focused Ion Beam - Secondary Ion Mass Spectrometry, and Atom Probe Tomography. [2] Successful characterisation provided an estimation of the contaminated layer on the corroded surface. Data showed contamination had not penetrate into the bulk metal matrix beyond the nickel-enriched / oxygen saturated metal beneath the metal-oxide interface. An iron-rich outer oxide was identified of which had the following contaminating elements associated in low concentration: Zr, Nd, Gd, Ru, Pa, Cs, Ru and Sm. A deeper underlying Cr-rich layer was also identified with additional contaminating elements: Nd, Zr, Rb, Gd, Cs, Ru and Pd. The measured depth of contamination within the metal was extremely thin (nanometre scale), however when this data was extrapolated to the scale of plant infrastructure, ILW classification can be expected.

The artificial coupons (discussed above) were prepared and shared with WP4 collaborators (Subatech and CEA, France and UJV, Czech Republic). In parallel, SORC (Hungary) have shared artificial coupons which replicated the contaminated surfaces expected in the steam generators of PWR nuclear power plants. WP4 stakeholders demonstrated their decontamination innovations (as follows) on these common coupons to allow direct comparison of techniques:

IMT Atlantique, France – COREMIX (chemical technique for tank/pipe cleaning)

CEA, France – COREMIX gel (sprayable gel for large surfaces treatment, e.g. walls)

NNL, UK – EASD gel (an electrochemical technique for radioactive hotspot treatment)

UJV, Czechia.– Ionic liquids (a non-aqueous electrochemical technique)

NNL stakeholders worked in partnership to characterise the decontaminated samples and secondary waste generated, utilising the equipment (e.g., XRF, SEM/EDX) across several facilities. This effort greatly benefited from the PREDIS mobility funding that enabled stakeholders to visit each-others facilities and gain a better understanding of capabilities.

In addition, Subatech and NNL performed collaborative studies on optimising the treatment secondary waste arising from the COREMIX chemical decontamination technique, as detailed elsewhere. [3]

3. Way forward

WP4 collaborators have published their findings and are looking forward to building on the share relationships and capabilities formed during PREDIS. [4] [5].

Acknowledgements

NNL would like to thank all stakeholder involved in WP4, in addition to Sellafield Ltd for their support.

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4.2.2 Decontamination of metallic waste using chemical solutions

Mathurin Robin, Tomo Suzuki-Muresan, Abdessalam Abdelouas, Marcel Mokili, (IMT Atlantique, France)

contact: robin@subatech.in2p3.fr

Keywords: decontamination, CORD process, radioactive metals, effluent treatment, radioactive waste, precipitation

1. Introduction

During the maintenance and decommissioning of nuclear power plants, metallic materials with complex geometries are usually chemically decontaminated. The COREMIX process, a derivative of the CORD process, falls into this category. However, this type of treatment generates large volumes of radioactive effluent that must be decontaminated prior to any conditioning stage. Under normal circumstances, the use of ion exchange resins is recommended to treat these type of effluents. However, they are highly concentrated in metals, which means that a large amount of resin must be used. In order to reduce the amount of resin required and consequently the associated treatment costs, a pre-treatment step involving metal hydroxide precipitation has been developed previously. Details of this precipitation protocol and the associated results are presented in the Period 2 Technical Report (M13-M30) and Deliverable D4.5.

The precipitation of metals in the COREMIX effluents is carried out by adding a precipitating reagent (NaOH or KOH) until precise pH values (8.5 and 12) are reached, allowing the selective elimination of metallic cations as hydroxides. Optimisation tests (pH, stirring time, reagents, etc.) were carried out in order to develop a fast, effective and versatile protocol, capable of eliminating a large number of different metals and radionuclides. All these results were used as a basis for the work carried out during period 3 (M31-M48), which is described in this report.

2. Description of work and main findings

Validation on radioactive sample

As the hydroxide precipitation protocol works on surrogate effluents, it was decided to validate it on radioactive samples, in order to estimate its decontamination factor. For this purpose, liquid effluents (R1 and R2) from the decontamination of Nickel 600 alloys by the COREMIX process were used. Radiological characterisation of the effluents was performed before and at the end of the protocol for all radionuclides analysed by liquid scintillation and gamma spectrometry. Details of the activities are given in Table 1.

Table 1. Radiological characterisation of the radionuclides present in the radioactive effluent R1 and their decontamination factor at the end of the protocol

	Activity before precipitation $(Bq.L^{-1})$	Activity after précipitation $(Bq.L^{-1})$	Décontamination factor (FD)
^{54}Mn	73 ± 29	<0,7*	>60
^{55}Fe	5 200 ± 1 200	28 ± 8	190 ± 100
^{60}Co	15 300 ± 1 100	4,8 ± 0,7	3 200 ± 700
^{63}Ni	7 300 ± 1 800	<0,8*	>6 900
^{99}Tc	124 ± 44	<0,3*	>270
^{125}Sb	94 ± 38	<1,8*	>32
Total	**28 100 ± 4 200**	**36 ± 9**	**780 ± 310**

* Activities below the detection limit of measuring instruments

After the hydroxide precipitation protocol, the decontamination factor is at least 60 for ^{54}Mn, 6900 for ^{63}Ni, 270 for ^{99}Tc and 32 for ^{125}Sb (as their activities are very low, the detection limit of the measuring equipment has been taken into account for the DF). For radionuclides still in solution after the precipitation protocol, ^{55}Fe is decontaminated by a factor of 190 ± 100, while ^{60}Co is decontaminated by a factor of 3200 ± 700. Finally, the total decontamination factor (including all radionuclides) of the radioactive effluent R1 is 780 ± 310. The same protocol was done for the radioactive effluent R2, whose decontamination factor was estimated to be 2640 ± 480. These tests have shown that the hydroxide precipitation protocol is very effective on radioactive effluents with high metal concentrations.

Using information on AmberLite IRN97 H (Dupont Water Solutions) ion exchange resin, it is possible to estimate the amount of resin saved by using the hydroxide precipitation protocol on effluent R1. This strong nuclear grade cationic ion exchange resin is one of the resins that can be used to decontaminate effluents from the COREMIX process. Taking into account its characteristics and an initial effluent volume of 300 mL, the theoretical mass of resin required to decontaminate the R1 effluent would be 29.8 g.L^{-1} without the precipitation protocol. This is reduced to 7.7 mg.L^{-1} with the developed protocol. This represents a 99.97% reduction in the amount of resin required. This value was calculated taking into account all metals and radionuclides in the effluent, excluding dissolved salts. Considering that all potassium can also be retained by this resin, the percentage reduction in resin volume drops to 2.5%.

Phosphate precipitation

In order to make the decontamination protocol for radioactive effluents as versatile as possible, another form of precipitate was investigated, namely phosphates. These complexes have the advantage of being easy to use and efficient for many transition and heavy metals. Firstly, a study of precipitation pH was carried out by modelling using PHREEQC software. The influence of effluent pH on the solubility of metal phosphate complexes was observed in Figure 1.

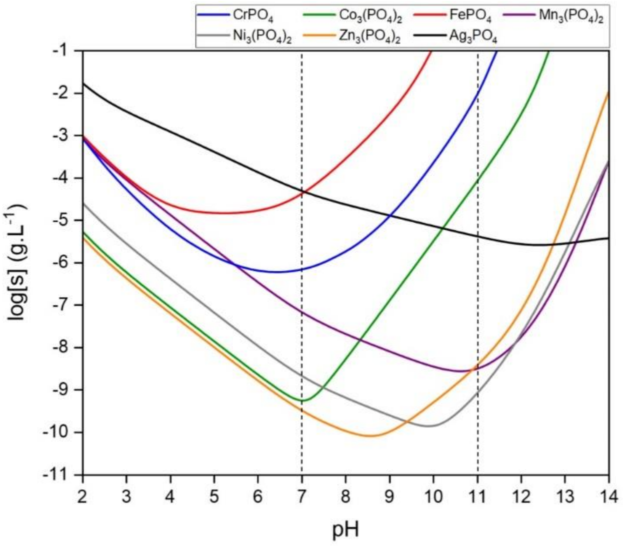

Figure 1. Solubility modelling of various metal phosphates as a function of pH

The results show that some metals precipitate preferentially at neutral or even acidic pH values, such as Fe at pH 5, Cr at pH 6 and Co at pH 7. The other cations require more alkaline conditions to be able to precipitate efficiently, this is the case for Zn (pH 8.5), Ni (pH 10), Mn (pH 11) and Ag (pH 12). These theoretical values allowed the identification of two optimal precipitation pH values for the quantitative precipitation of metallic phosphates. The first value was set at 7 for the removal of Fe, Cr, Co and Zn, while the second value, at pH 11, is mainly used for the precipitation of Mn and Ag. As the solubility of Ni is equivalent at both pH values, it is likely to be present in both precipitates. These pH values were tested on synthetic samples created from metal salts dissolved in ultrapure water. The pH of the synthetic solution was adjusted by progressive addition of Na_3PO_4 and aliquots were analysed by ICP-MS at pH 7 and 11. The precipitation efficiencies are shown in Table 2.

Table 2. Phosphate precipitation results on a synthetic sample after precipitation at pH 7 and 11

Element	*% precipitated pH 7*	*% precipitated pH 11*
^{52}Cr	99 ± 8	100 ± 8
^{55}Mn	60 ± 7	100 ± 8
^{56}Fe	100 ± 12	100 ± 12
^{59}Co	68 ± 9	100 ± 10
^{60}Ni	58 ± 8	99 ± 9
^{66}Zn	97 ± 11	99 ± 11
^{140}Ce	100 ± 8	100 ± 8

The ICP-MS measurements show that Cr, Fe, Zn and Ce precipitate predominantly at pH 7 with an efficiency of 99 ± 8%, 100 ± 12%, 97 ± 11% and 100 ± 8% respectively. However, Mn, Co and Ni precipitate at this pH only to the extent of 60.7%, 68.9% and 58.8% respectively. On the other hand, they are completely removed from the effluent at pH 11 with a removal efficiency of 99 ± 8%, 100 ± 10% and 99 ± 9% respectively. The phosphate precipitation protocol applied to the synthetic sample reduced the metal concentration from 51.1 $mg.L^{-1}$ to 0.2 $mg.L^{-1}$ (99.6% reduction). The experimental results are in agreement with the theoretical results, except for cobalt, which seems to have precipitated at a higher pH, close to that expected for the precipitation of cobalt hydroxide. In addition, phosphate complexes do not appear to dissolve between pH 7 and 11. For this reason, the following tests were carried out at pH 11 only. Avoiding the intermediate step at pH 7 saves time and reduces the number of different precipitates to be conditioned later.

In order to identify the composition of the secondary solid waste produced during the precipitation stages, a characterisation of the phosphate sludge was carried out using XRD and FTIR. The results of these characterisation tests are shown in Figure 2.

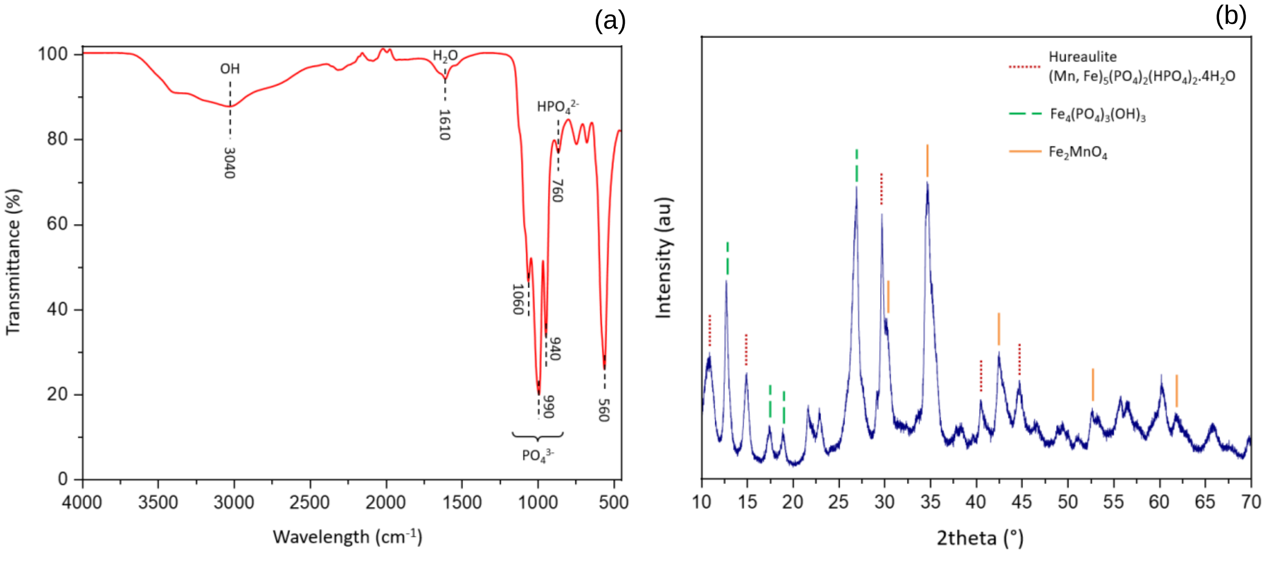

Figure 2. Characterisation test by (a) FTIR (b) XRD on phosphate precipitate generated at pH 11

The IR spectrum studied in the range 500 - 4000 cm^{-1} shows peaks of vibrations related to the presence of water molecules (1610 cm^{-1}) and hydrogen bonds O-H (3040 cm^{-1}). In addition, representative peaks of phosphates are also present in the spectrum. The absorption bands at 560, 940, 990 and 1060 cm^{-1} are characteristic of the stretching vibrations of the PO_4^{3-} anions. Another form of phosphate ion is also observed at 760 cm^{-1}, this low intensity peak is defined in the literature as hydrogen phosphate ion HPO_4^{2-}.

The diffractogram of the phosphate precipitate then shows many peaks characteristic of several metal complexes. The first compound is hydrated hureaulite, composed of Fe, Mn, HPO_4^{2-} and PO_4^{3-} ions, as observed by FTIR. However, substitutions between iron and manganese atoms may occur in this compound. The treated effluent contains a significant concentration of iron, so the hureaulite compound was defined by $(Mn,Fe)_5(PO_4)_2(HPO_4)_2(H_2O)_4$. Iron and manganese are also the main components of the other two complexes observed in the diffractogram. Indeed, manganese iron oxide Fe_2MnO_4 and iron phosphate hydroxide $Fe_4(PO_4)_3(OH)_3$ can be identified by several characteristic peaks. These characterisation tests showed that the phosphate precipitate obtained contained a mixture of several species of phosphates and oxides rather than a single compound.

Effluent treatment by electrocoagulation

As outlined in section 3.2.1, hydroxide precipitation is highly effective for decontaminating radioactive effluents, but produces dissolved salts that can be a problem for the resin purification steps. To overcome this problem, it is possible to precipitate metals by electrochemistry. This technique does not require the addition of reagents but does require two iron electrodes. Under the effect of a current, the anode oxidises and dissolves in the solution as metal cations (M^{n+}), while the cathode reduces water to form hydroxide ions (OH^-) and dihydrogen gas (H_2). The OH^- ions then react with the metal cations to precipitate insoluble metal hydroxides ($M(OH)_n$), which then form sludge by flocculation/coagulation. One of the main parameters that can affect the precipitation efficiency is the current applied between the electrodes. In order to test different current values and select the most suitable one, tests were carried out on three different synthetic solutions containing different metals for current values of 0.5, 1.5 and 2.5 A. Metal concentrations were measured over time by ICP-MS and are shown in Figure 3.

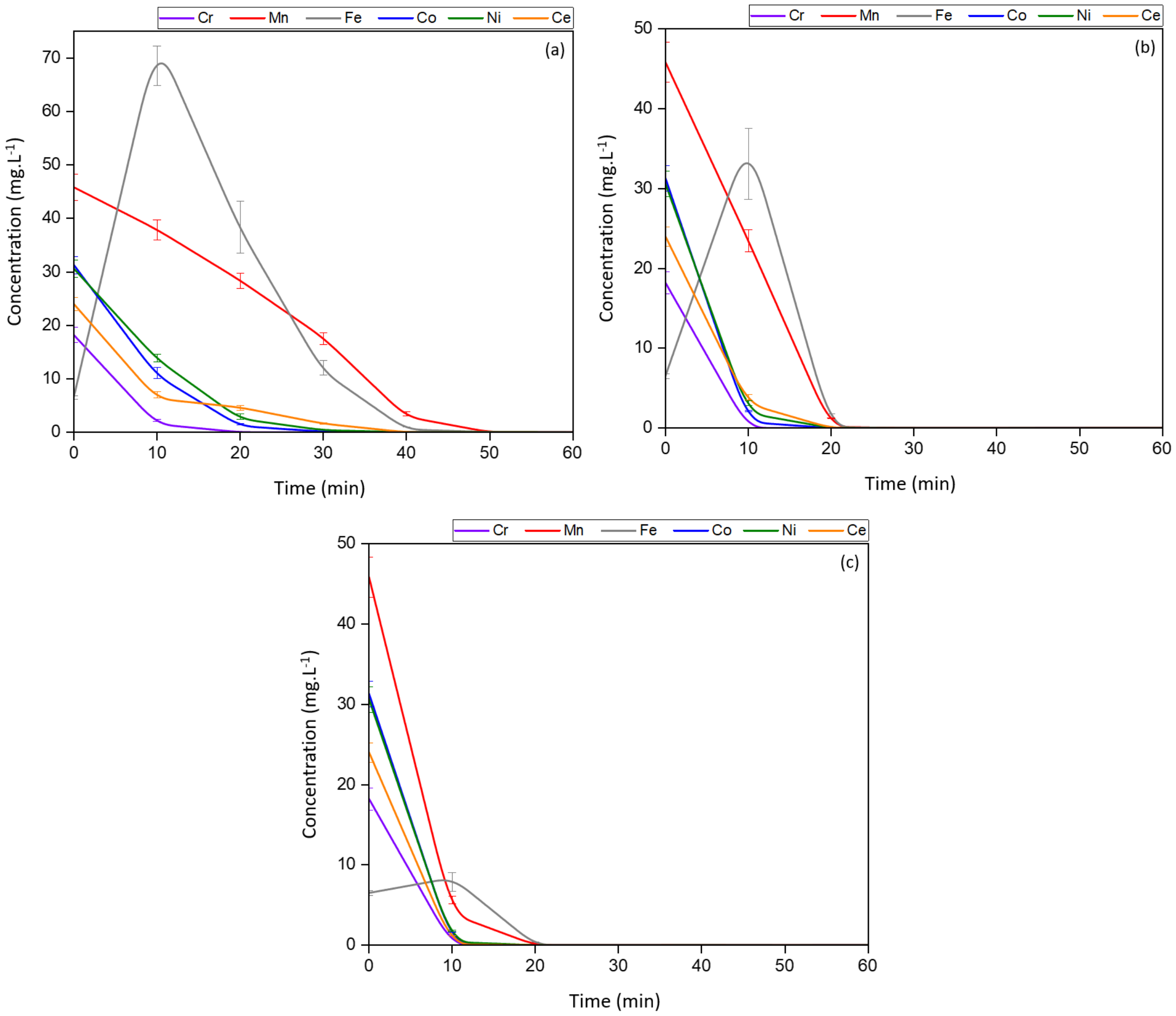

Figure 3. Evolution of metal concentration as a function of time for different electric currents (a) 0.5 A (b) 1.5 A (c) 2.5 A

The first graph (a), relating to a current of 0.5 A, shows a gradual decrease in metal concentration. In fact, all the metal cations analysed are completely precipitated after 40 minutes (Cr, Fe, Ni, Ce, Co) or 50 minutes (Mn). On the other hand, the iron concentration increases rapidly during the first ten minutes of the experiment due to the oxidation of the iron anode, which produces Fe^{2+}. During the first 10 minutes, the amount of iron produced is greater than the amount of iron precipitated, which is why this peak is observed. This concentration peak then decreases just as much as the pH of the solution increases, reversing the production/precipitation ratio. When the current is increased to 1.5 A and 2.5 A, as shown in Figures 4b and 3c, the same pattern occurs after 10 minutes. However, this increase is lower than at 0.5 A. In addition, the precipitation of metals appears to be faster, as their concentrations fall below 100 $\mu g.L^{-1}$ after 10 and 20 minutes, reducing the handling time by a factor of 2 or more. These results show that the value of the current has a direct effect on the precipitation efficiency over time. The higher the current between the electrodes, the faster the metals are precipitated.

To validate the electrocoagulation precipitation protocol, it was tested on a multi-element effluent containing fifteen different elements. This test was used to evaluate the precipitation efficiency of this process on several elements from different families. Aliquots were taken every 30 minutes to monitor the evolution of their concentrations over time. In addition, this surrogate effluent has a larger volume than previous solutions, which allowed a first scale-up of the decontamination process (1.5 L instead of 300 mL). The results of this scale-up are shown in Figure 4.

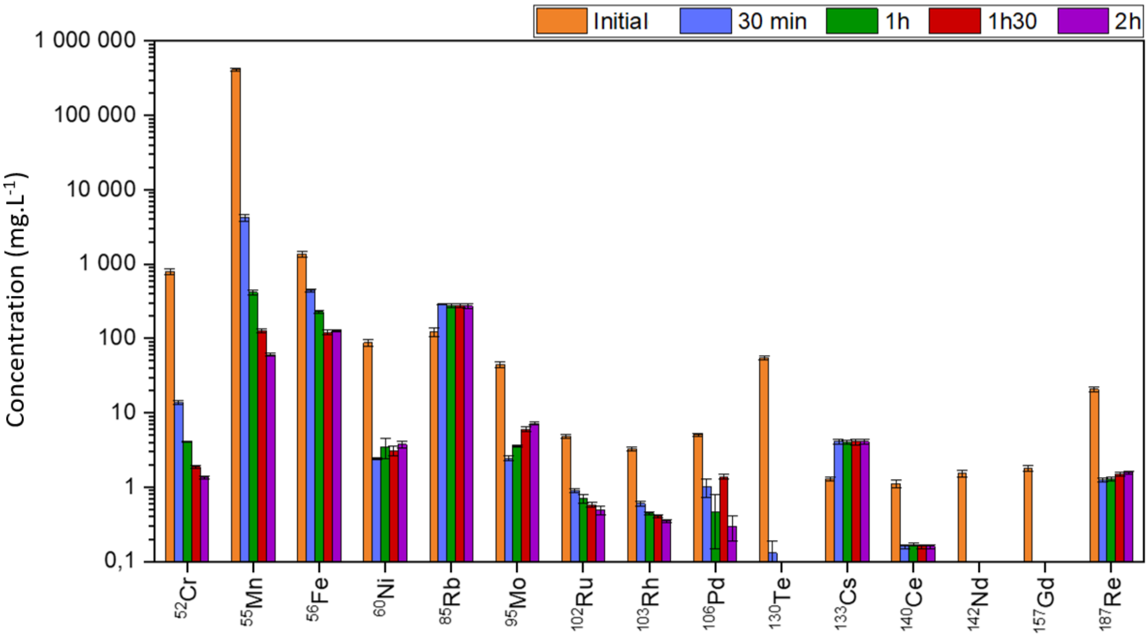

Figure 4. Evolution of metal concentration in a multi-element effluent as a function of electrocoagulation time

This electrochemical precipitation process was efficient for a large proportion of the metals in solution, with precipitation efficiencies of up to 100% for some transition metals and lanthanides. For some elements, the treatment time also plays a role in the precipitation efficiency. This is particularly the case for Cr, Mn and Fe, whose concentrations decrease with time and reach their minimum values after 2 h. This phenomenon is less visible for Ni, Ru, Rh and Pd, with little variation between 30 min and 2 h. At the end of the treatment, the precipitation efficiencies of the metals analysed vary between 84% (Mo) and 100% (Nd, Gd), which makes the electrocoagulation precipitation protocol very effective and versatile. Only Rb and Cs did not precipitate during the protocol. In addition, this test shows that a larger volume of effluent to be treated does not have a major effect on the electrocoagulation process.

The mass of resin required to purify the multi-element effluent was calculated with and without the electrocoagulation process. Considering only the metals present in the solution, 29.5 g of resin per litre of effluent would be required to completely purify the effluent without electrocoagulation, compared to only 25.4 $mg.L^{-1}$ when the process is used, representing a 99.9% reduction in resin mass. As electrocoagulation does not require the use of reagents and salts, it is a viable and cost-effective option for the decontamination of radioactive effluents generated by the COREMIX process.

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4.2.3 Decontamination of metallic samples using a gel technology avoiding secondary liquid waste

Alban Gossard, Fabien Frances (CEA, France), Aditya Rivinkar, Richard Katona (SORC, Hungary)

alban.gossard@cea.fr

Keywords: magnetic gel, decontamination, stainless steel

1. Introduction

Metallic wastes are critical materials to decontaminate. They are produced in very large volumes and have different nuclear energy industry origins, such as the contamination of the primary circuit components within power stations, processing vessels at reprocessing plants or even hot cell walls and floors.

“Vacuumable” gels can be utilised to chemically decontaminate metallic waste components and have the advantage of producing secondary solid waste, only. This proceeding describes the development of new vacuumable gel formulations and implementation processes performed within the PREDIS project, which had the overall aim to increase their range of application.

New gel formulations, inspired form the COREMIX (Chemical Oxidation REduction using nitric permanganate and oxalic acid MIXture) process, were initially developed and their decontamination capability demonstrated and compared to a commercial product, Aspigel 100E from the FEVDI Company. Although the COREMIX-based gels were found to be less efficient, they offer an alternative in situations where the commercial product cannot be used (e.g. due to waste acceptance compatibility etc.) or for soft surface decontamination operations.

New processes were then developed for the decontamination on small objects with complex geometries (such as pipes, valves or pump) or limited access surfaces. Particularly, “magnetic gels” were formulated to be applied using magnet. Indeed, by adding ferromagnetic particles in their formulations, the gels can be spread by attraction with a magnet, allowing their deposition on surfaces non-accessible by spraying.

2. Description of work and main findings

Coupling electrochemistry and mass loss to better understand the gel decontamination mechanism

Electrochemical characterization and mass loss measurements have been coupled to highlight the Aspigel decontamination efficiency on SS 1.4571 samples (Figure 1). Thus, a corrosion rate comprised between 2.5 and 4 mm/year has been determined in a case of an “infinite” contact between the gel and the substrate, i. e. if the gel never dries. However, as soon as the first cracks appear during drying, the surface of contact between the gel and the SS substrate decreases, particularly in the case of a vertical surface because dried part of the gel may fall by gravity. Consequently, some inhomogeneities may be induced but, despite that, the dissolution of few tens of microns already occurred during the first hour (before drying), which is enough to decontaminate the metallic surface on this thickness. Note that this phenomenon is certainly less marked on a horizontal surface but will nevertheless occur at some time or another.

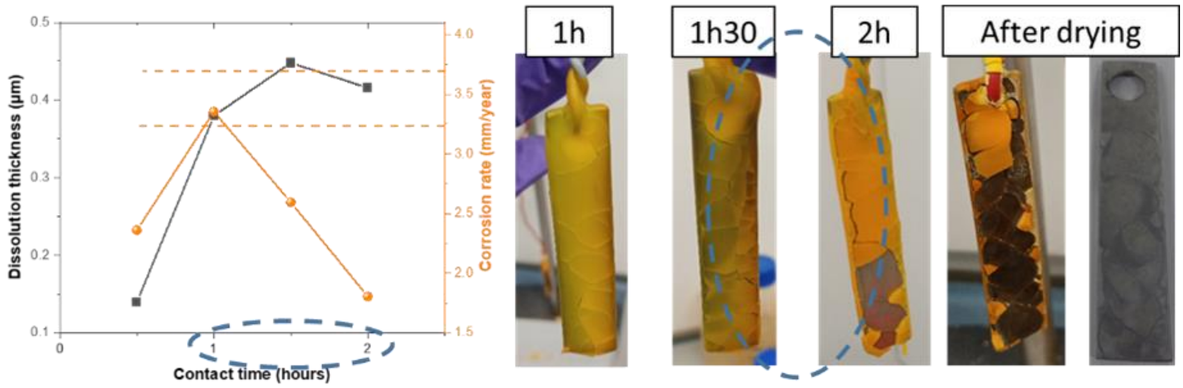

Figure 1. Evolution of the dissolution thickness of the SS after gel application as well as the calculated corrosion rate as a function of the Aspigel100E – SS 1.4571 contact time and associated pictures.

New vacuumable gel formulations based on the COREMIX process

A new two-step decontamination gel process has been developed based on the COREMIX process. An initial gel, containing 15 mmol.L^{-1} of $KMnO_4$ and 3 mmol.L^{-1} of HNO_3 with 9 %wt of silica NPs as a viscosing agent, was used to oxidize an enriched Cr layer. After drying, a second gel, containing 18.5 mmol.L^{-1} of oxalic acid and 9 %wt of silica NPs as a viscosing agent, was applied to dissolve iron phases. This new process was shown to be efficient to decontaminate slightly or moderately oxidized SS surfaces (Figure 2), but they were still less effective than the commercial Aspigel 100E containing nitric acid and Ce(IV). However, these new gels may be utilised as an alternative to Aspigel 100E, notably in situation where Ce(IV) cannot be used (e.g. not compatible with available secondary waste routes) or if soft decontamination operations are required, i.e. only very slight surface removal required to not deeply corrode the surface.

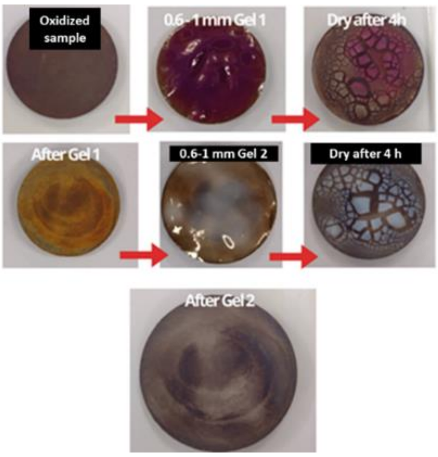

Figure 2. Pictures of a decontamination operation of a moderately oxidized SS sample using the COREMIX-based gels

Application of decontamination gels on hardly accessible surfaces: presentation of a new application process using a magnet

A new gel decontamination process was developed specifically for the decontamination of hardly accessible surfaces, such as the internal surface of pipes for example. This process is based on the modification of vacuumable gels by adding ferromagnetic particles in their formulations. Thus, the gels can be moved and spread using a magnet, placed more and less close to the gel, depending on the gel formulation and the magnet. After drying, the gel forms solid residues, which can also be recovered by the magnet. In this way, all the decontamination process is not necessarily implemented at the contact of the contaminated surface, and decontamination gels can be applied on hardly accessible surfaces.

It was demonstrated that the presence of ferromagnetic particles does not influence the inherently decontamination properties of a commercial gel, with similar corrosion efficiency and effect on the microstructure of the SS after treatment. However, the decontamination efficiency depends on the spreading of the gel and more particularly on the gel thickness. Notably, adding more particles increases the gel viscosity but does not particularly improve their spreading properties. Indeed, while ferromagnetic particles provide a magnetic response to the gel, adding more particles also increases the gel viscosity. That is why, a compromised has to be found between the ferromagnetic particles amount in the gel.

However, Fe_3O_4 particles react with the chemical solution of the Aspigel 100E and dissolve with time, inducing variation in the gel rheological properties. Consequently, spreading properties as well as the gel decontamination efficiency evolve with time, which is not compatible for a long time storage of the product, and it is recommended to formulate the gel just before application.

3. Conclusions

The decontamination of oxidized metallic surfaces needs the chemical dissolution of oxide layers to segregate the contaminated surface material from the bulk substrate. Among the different existing techniques, the vacuumable gels are interesting because they produced only secondary solid waste and limit the close contact of the operator with the contaminated surface. However, this technology currently also presents some limitations. This document reports the different studies performed during the PREDIS project with the objective to respond to these limitations.

Finally, after these different studies, it is of interest to compare the results with other decontamination techniques. Criteria such as the decontamination efficiency, the nature and volume of generated secondary waste, but also the application possibilities of the processes should be evaluated to identify the strong and weak points of the different techniques, depending on the decontamination operation context.

4.2.4 Secondary waste treatment

Katerina Cubova, Miroslava Semelova, Mojmir Nemec, Jan Houzar (CTU, Czech Republic)

katerina.cubova@fjfi.cvut.cz

Keywords: ionic liquids, extraction, decontamination

1. Introduction

Liquid waste minimization process based on application of Ionic Liquids

Research is focused on liquid waste minimization by ionic liquids based processes. Main emphasis is put on recycling of chemicals and media used and potentially also possible returning of radionuclides for other use. Two-step separation method consisting of extraction of radionuclides from the decontamination solutions by using the ionic liquids, followed by the separation of radionuclides from ionic liquids by electrodeposition was proposed and tested.

Optimization of decontamination of Ni-alloys - Optimization of known decontamination process

A modular laboratory system for application of chemical and electrochemical decontamination methods (the so-called decontamination loop) has been developed at FNSPE, CTU. The system consists of multiple components that can be arranged in various ways depending on the experiment, including among others a stirred reactor, flow-through heaters, an electrochemical setup, a column for filtration, ion exchange or adsorption, a dual extraction module, and flow-through sensors of temperature, pH, activity and flow rate. Decontamination loop was tested and optimised using on-purpose modified classic APOX (Alkaline Permanganate – Oxalate) chemical decontamination method for further use.

2. Description of work and main findings

Liquid waste minimization process based on application of Ionic Liquids

The ionic liquids used for the study of the separation of different activation and fission products were tested for the purpose of separation of the same radionuclides (Co, Fe, Tc, Mo, Sr and Ag) from the solutions containing organic complexing agents such as oxalic (HOx) or citric (HCit) acids simulating decontamination solutions. It was found out that even in the presence of HOx, HCit or mixture of both most of the radionuclides tested (except for Ag) were separated with high efficiency (around 90% or more). Considering the possibility of re-extraction (still under study) the extraction process based on the use of the ionic liquid offers a promising tool for the separation of radionuclides from different types of liquid wastes [1].

Optimization of decontamination of Ni-alloys - Optimization of known decontamination process

Chemical decontamination method based on APOX (Alkaline Permanganate – Oxalate) process was modified for the testing and optimization of the decontamination loop. A methodology was developed for the preparation of samples for decontamination (steel plates), followed by dissolution of corrosion layers formed by different methods (Figure 1). The behavior of two selected radioactive contaminants, 201Tl and 59Fe, was also examined. Based on the results, a decontamination procedure was designed, including methods for evaluating the efficiency of the process, as well as decontamination solution processing using an ion exchange resin.

Figure 1. Steel plates before and after the decontamination

3. Conclusions

Liquid waste minimization process based on application of Ionic Liquids

- $[C_4mim][NTf_2]$ as ionic liquid with acceptable properties, especially viscosity, can be used as solvent for metal extraction.
- Extraction with 8HQ or DCH18C6 in IL is suitable also at HCit + HOx concentrations present in common decontamination solutions
- Ionic liquids can be regenerated electrochemically
- As whole procedure, extraction of radionuclides from model decontamination solution offers a possibility to regenerate solution while concentrating them for the next step of electrochemical treatment.

Optimization of decontamination of Ni-alloys - Optimization of known decontamination process

- Decontamination loop was tested and optimised using APOX process for corroded steel
- During optimization, an ideal temperature for the process was found (65°C), a detailed procedure was devised and tested.
- The corrosion layer is completely removed after decontamination, the problem is the reverse formation of ferric oxalate on the surface
- As secondary output a laboratory task for students called „Decontamination of metal surfaces“ was developed. The task is available in two language versions including methodological instructions.

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4.3 Steel corrosion in MKPC (Task 4.4.6)

Crina Bucur, RATEN, Romania, crina.bucur@nuclear.ro
Aurel David, RATEN, Romania

Keywords: magnesium phosphate cement, carbon steel, corrosion, hydrogen release

1. Introduction

Magnesium phosphate matrices (MKPC) ensure a pH in the passivation range for aluminium and other reactive metals. To qualify this type of matrix for aluminium waste embedding not only the corrosion of the aluminium is assessed but also the corrosion of the carbon steel that is generally used as material for the primary waste package.

When C-steel container is in contact with the cement pore water, aqueous corrosion might occur producing steel oxidation and hydrogen gas generation. For all ferrous systems the optimal pH for minimizing the generation of corrosion products is ~ 9.5 and even higher (Figure 1). The corrosion products developed on carbon steel-water systems (at low temperatures) consist of ferrous hydroxides $Fe(OH)_2$ and hydrated ferrous species (α-FeOOH and γ-FeOOH) [1].

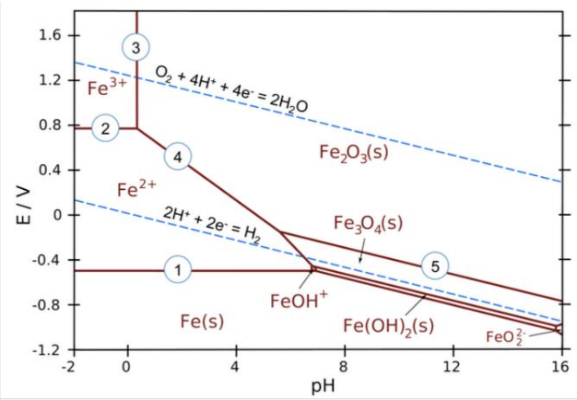

Figure 1. E_H-pH Pourbaix diagram for iron-water system at 25°C [1].

The steel corrosion is complex, corrosion mechanism involving a first oxidation step by water and a second step by dioxygen, with the kinetic of the second step depending on the O_2 content.

Two partners (CNRS/IJCLab and RATEN) performed under subtask T4.6.6 experimental studies on C-steel corrosion in chemical conditions relevant for MKPC matrices. The outcomes of the work conducted in the frame of this subtask are summarised in the final deliverable D4.11 [2], and only the work performed by RATEN is presented here.

2. Description of work and main findings

Electrochemical and chemical tests were performed by RATEN to determine the corrosion rate and volume of H2 released for C-steel in contact with MKPC. For comparison, the tests were also performed for ordinary Portland cement (OPC) matrix.

The reference MKPC formulation [3] was adapted to obtain a reasonable setting time by using low burned magnesium oxide instead of dead burned one, for water to solid ratio of 0.54 and retarder to ($MgO+KH_2PO_4$) ratio of 0.043 (Table 1). For OPC formulation CEM II type cement was used and the paste was prepared for a water to binder ratio of 0.4. Both types of tests (electrochemical and chemical) were performed on steel immersed in pore solutions characteristic for MKPC and OPC and on steel embedded MKPC and OPC pastes (after 28 days of curing at room temperature, with the steel embedded in the two pastes). The MKPC pore water composition is reported in Table 2, while as OPC pore water saturated portlandite solution was used (pH = 12.6).

Table 1. MKPC formulation.

Component	**wt.%**
MgO (light burned)	10.5
KH_2PO_4	38.5
H_2O	35.0
Ash	14.0
H_2BO_3	2.1

Table 2. MKPC pore water composition, ppm.

P	K	Mg	B	S	Ca	Na	Si	Al
3363	8161	76	258	432	17	29	20	0.2

Chemical tests were performed in controlled atmosphere (Ar) both for immersed and embedded C-steel samples, while the electrochemical tests on immersed steel were performed in controlled atmosphere and on the embedded steel in normal atmosphere. Details on the electrochemical and chemical set-ups and assumptions considered in the tests performed by RATEN are provided in the final deliverable D4.11 [2].

For C-steel immersed in pore-solutions, an increase of the corrosion rate for both pore-solutions was observed (Figure 2), with a larger increase for MKPC pore solution (to 50 and 100 µm/year) compared to OPC pore solution (~ 1 µm/year). In MKPC pore solution, after an initial increase of corrosion rate (characteristic for activation), a short relative passivation period in which the corrosion rate registered a sharp decrease is followed by a longer activation period (from 500 h up to ~1700 h) characterized by high corrosion rate. In the last part of the test, successive relative passivation (in which the corrosion rate sharply decreased from ~ 1 µm/year to almost 1 nm/y) and activation transitions were observed. Also for OPC pore solution similar “saw teeth” behaviour of corrosion rate was observed, but with a smaller increase or decrease amplitudes (Fig. 2).

The pH in MKPC pore solution was almost constant (~ 7.1) along the testing period (90 days), while in the OPC pore solution the pH slightly decreased at the beginning of the test (from 12.6 to 12.1).

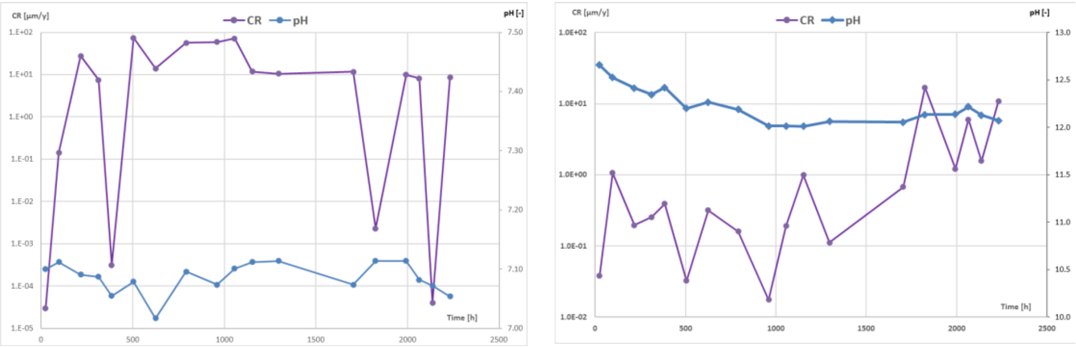

Figure 2. Corrosion rate and pH evolution during the electrochemical tests in MKPC pore solution (left) and OPC pore solution (right).

The volume of hydrogen computed based on the electrochemical parameters increased steeper for MKPC pore solution, reaching after ~ 1000 hours of testing 3 L/m^2 (Figure 3-left) and after this period, the hydrogen volume slowly increased (up to 3.5 L/m^2). For OPC pore water the hydrogen volume (Figure 3-right) slowly increased in the first 1800 hours of testing (to 0.05 L/m^2) and after this period, the hydrogen volume sharply increased (up to 0.3 L/m^2).

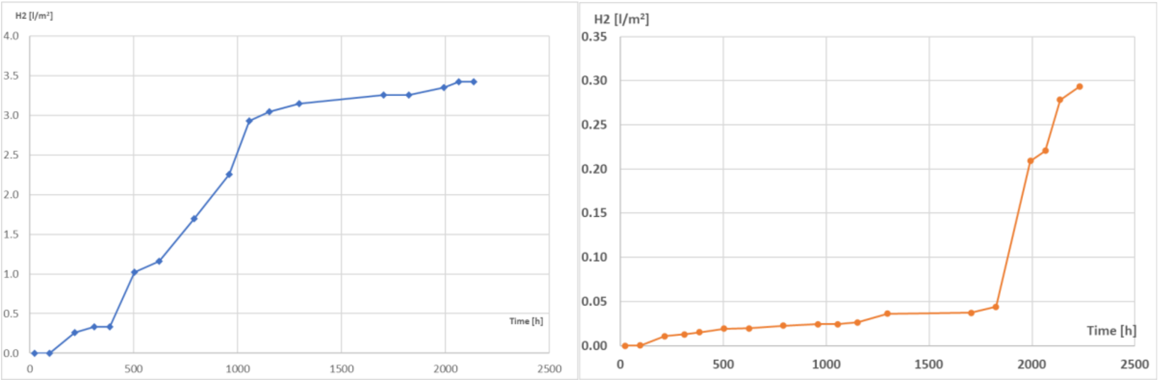

Figure 3. Cumulative volume of Hydrogen released during the electrochemical tests with C-steel immersed in MKPC pore solution (left) and OPC pore solution (right).

Similar trends for hydrogen evolution as those obtained by estimation based on the electrochemical parameters were obtained in chemical tests performed with C-steel immersed in the two pore solutions (Figure 4).

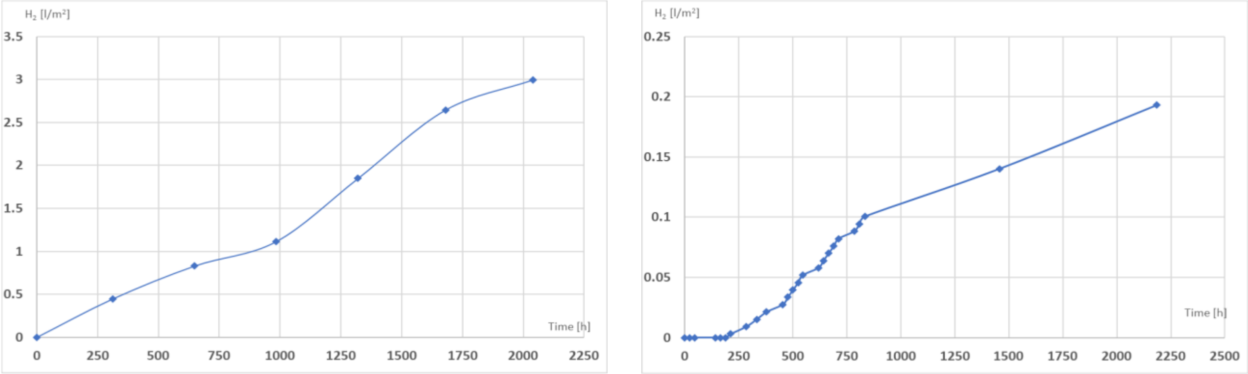

Figure 4. Cumulative volume of Hydrogen measured during chemical tests with C-steel immersed in MKPC pore solution (left) and OPC pore solution (right).

The hydrogen volumes estimated based on the electrochemical parameters for steel embedded in MKPC and OPC pastes are similar with those obtained in the pore solutions corresponding to the two matrices.

From the chemical tests, the hydrogen volumes (that are directly measured) are similar for both matrices.

3. Summary

The reactivity of C-steel in MKPC is similar to that in OPC, with the difference that in the MKPC initially the corrosion rate is higher and it decreases towards the end of the test, while in OPC it is initially lower and it increases towards the end of the test.

C-steel is more reactive when immersed in pore solutions compared to its embedding in MKPC and OPC pastes.

References

[1] H. Uhlig H., Corrosion and corrosion control, John Wiley and Sons Wiley Interscience, 2008. https://chem.libretexts.org/

[2] C. Bucur, M. C. Alonso, PREDIS Deliverable 4.11 “Report on Synthesis of formulation & process studies results Al and steel reactivity in magnesium phosphate cement (MKPC)”, 2024

[3] C. Cannes et all. Encapsulation of reactive metals in magnesium phosphate cement-based matrices. Deliverable 1.5 – Proceedings of PREDIS May Workshop 2021

4.4 Optimization of characterization techniques and waste minimization (Task 4.5)

A. Savidou, NCSR Demokritos, GREECE, T. Suzuki, IMT Atlantique
savidou@ipta.demokritos.gr
suzuki@subatech.in2p3.fr

Keywords: radiological characterization, metallic waste, non-destructive γ-spectrometry, MCNP simulations, simulation spectra, radiochemical analyses

1. Introduction

For minimization of metallic waste from decommissioning of nuclear reactors and increase the volume of recycling, methods for optimization of radiological characterization was proposed in T4.5 of the PREDIS project. Two non-destructive gamma spectrometry techniques as well as new radiochemical procedures for DTM radionuclides were developed. Both non-destructive gamma spectrometry techniques rely on γ-spectrometry measurements and MCNP simulations. By the first technique the SF for gamma emitters in activated components exhibiting contamination could be validated. The second technique concerns the monitoring of metallic segments after dismantling, aiming at the crucial reduction of the measurement uncertainties related to the distribution of density and activity. The radiochemical procedures focus on optimizing the detection and measurement of ^{59,63}Ni, ^{41}Ca, ^{93}Zr, ^{93}Mo in metallic samples by development of sensitive to ultra-sensitive methods of measurement, depending on the radionuclide. The optimization was achieved by highly selective and efficient separation and purification of the radionuclides in concern.

2. Description of work and main findings

The aim of the first non-destructive gamma spectrometry technique is the monitoring of activated components to differentiate between activation and contamination. HPGe and $CeBr_3$ spectra are produced by MCNP simulations, based on the activities of particular gamma sources (i.e. spectra for point, planar and volume sources as well as for an activated or surface contaminated metallic slabs). The simulation spectra characterize the geometry of the source (Figure 1). Then, the spectra of an activated or surface contaminated metallic slab were used to determine the activation and contamination on metallic slabs of nominal activities (Table 1).

The second non-destructive gamma spectrometry technique concerns the monitoring of metallic segments after dismantling. A new measurement set-up is proposed aiming at the reduction of the measurement uncertainties related to the distribution of density and activity lower than 30% while the measuring time is comparable to that of the existing methods (i.e. 100 kg, 2 min). The sensitivity of the technique for 2 min measuring time is 0.1 Bq/g for both the key radionuclides (^{60}Co, ^{137}Cs). The technique can be used for low activity metallic waste for better selection of the management route and the decontamination techniques. The specific activities of metallic waste are determined by using the activities of the key radionuclides and the SF.

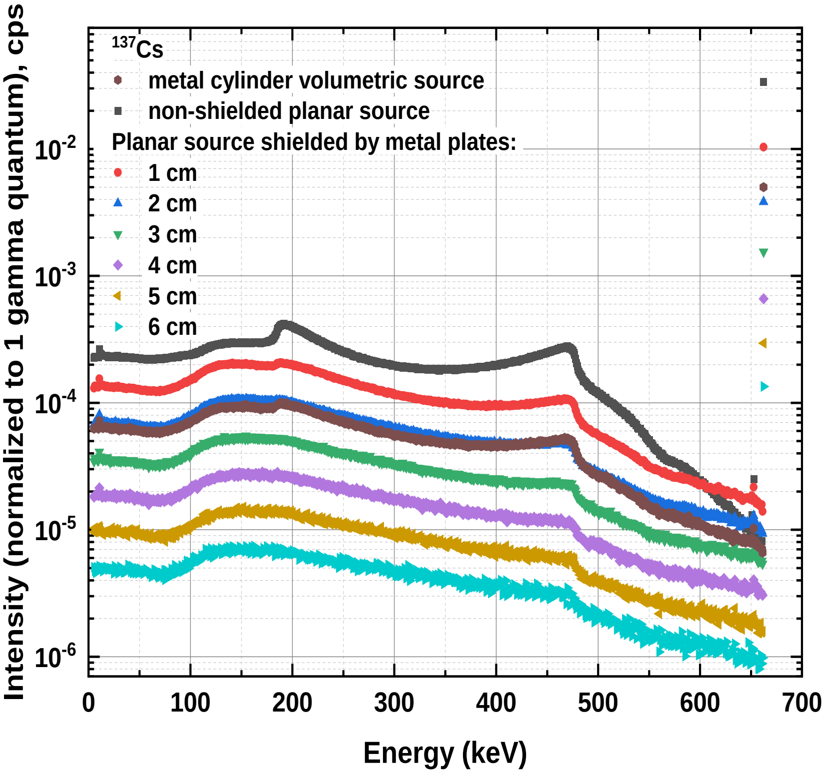

Figure 1. Comparison of MCNP simulation 137Cs γ-spectra in HPGe for different source cases (volumetric source, planar sources shielded by metallic plates of different thickness).

Table 1. Comparison of nominal and experimentally determined values of volume and surface activities in metallic slabs.

	Volume activity $A(b)$	Surface activity $A'(b)$
Nominal 1	4900 ± 500	610 ± 60
Experimental 1	4300 ± 700	300 ± 200
Nominal 2	2400 ± 200	1500 ± 150
Experimental 2	2500 ± 300	1000 ± 200

Sensitive to ultra-sensitive radiochemical methods were developed for determination of ^{59,63}Ni, ^{41}Ca, ^{93}Zr, ^{93}Mo in metallic samples. The samples used were: a) *synthetic*, prepared from chemical reagents; b) *solid* containing the radionuclide; c) *surrogate* to simulate the radionuclide in case of limited quantity or availability. The separation/ purification was performed by *chromatographic resins* to recover the radionuclide of interest or by *electrodeposition. The samples were prepared for the measurement* in liquid form or deposition on filters or on plates (Figure 2). For measurement an adapted analytical technique was selected for each case and the detection efficiency was optimized.

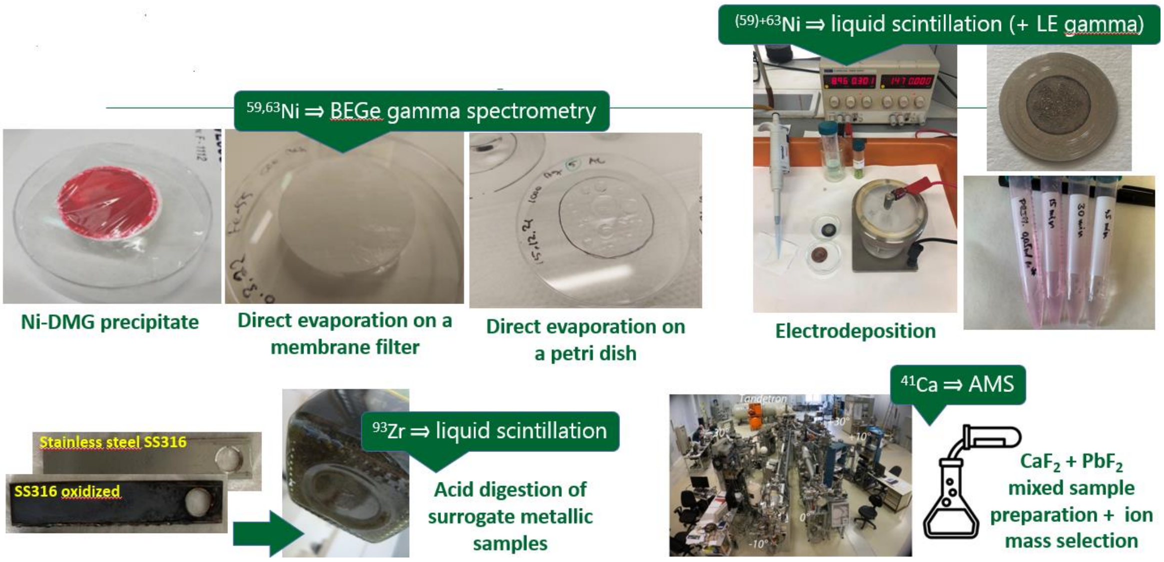

Figure 2. Innovation in sample preparation.

The main challenges achieved are the following:

I) Standard curves and calibration
  - Use of ^{55}Fe standard for the measurements of ^{59}Ni by BEGe spectrometry
    - Lowering the detection limits up to 20 Bq
    - Evaluation of ^{60}Co effect as contaminant on ^{55}Fe response: effect starting for activities at 200Bq of ^{55}Fe
  - Use of ^{63}Ni standard for the measurements of ^{93}Zr by liquid scintillation
    - Coupling chemical theory approach with experimental data
  - Selection of $[CaF_3]^-$ and $[CaF_4]^-$ ions for ^{41}Ca assessment by MILEA AMS

II) Optimization in sample preparations
  - Separation and purification of Ni and Zr using chromatographic resins from a complex solution (surrogate, radioactive)
  - Conditions achieved for efficient electrodeposition of Ni (Ni-63 with carrier) on planchette

III) Validation in the MoNi intercomparison exercise 2024 (coordination VTT) with a high activity steel

3. Conclusions and way forward

- Combination of gamma spectrometry measurements and MCNP simulation allows distinguishing surface contamination from volume activation by the shape or the peak/ Compton ratio (of key nuclides ^{137}Cs and ^{60}Co).
- The proposed set-up for measurement of metallic waste after decommissioning, resulting in a lower measurement uncertainty, can be used for better selection of the management route as well as the decontamination and clearance procedure while is sensitive enough and equally fast in comparison to the commonly used methods.
- The work will continue in EURAD-2.
- Regarding the radiochemical analyses, a collaboration started in January 2024 with Nordic Nuclear Safety Research Program. The project concerns 59Ni and 93Mo analysis in highly activated steel as well as other DTM radionuclides of interest, ^{55}Fe, ^{63}Ni, ^{93}Zr, ^{94}Nb. In 2025 the collaboration will focus on volatile DTMs e.g. ^{14}C, ^{36}Cl, ^{79}Se.

4.5 A non-destructive gamma spectrometry set-up for characterization of low activity metallic waste (Task 4.5)

D. Mavrikis and A. Savidou, NCSR Demokritos, GREECE
savidou@ipta.demokritos.gr
d.mavrikis@ipta.demokritos.gr

Keywords: radiological characterization, sorting of metallic waste, non-destructive γ-spectrometry, MCNP simulations

1. Introduction

For low and very low-level metallic waste from decommissioning, the aim of characterization is to decide if decontamination will be efficient and to select the most effective decontamination techniques as well as the clearance methodologies. The 90% of decommissioning waste is low activity, therefore the optimization of their sorting contributes crucially to waste minimization and recycling. A non-destructive gamma spectrometry set-up for characterization of low activity metallic waste is proposed in T4.5 of the PREDIS project. The characterization of metallic waste relies on γ-spectrometry measurements and MCNP simulations. The measuring technique concerns the monitoring of metallic segments aiming at the crucial reduction of the measurement uncertainties related to the inhomogeneity of density and activity.

2. Description of work and main findings

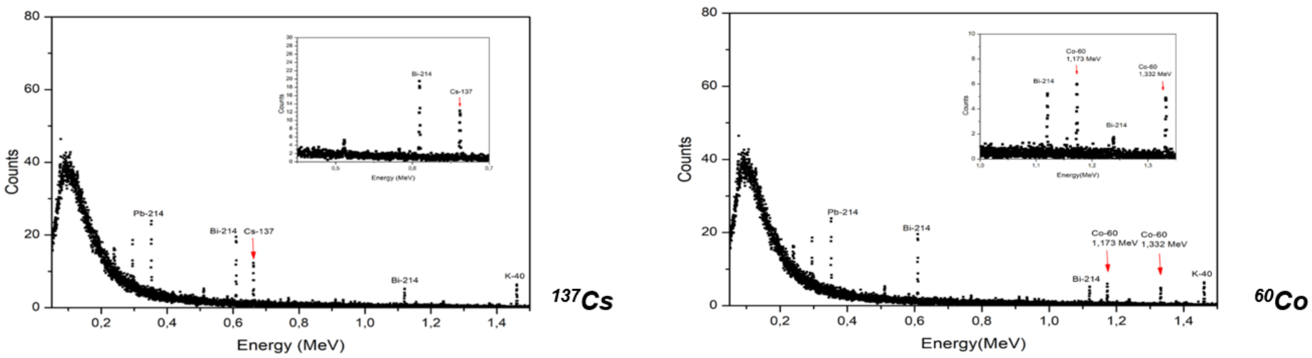

Figure 1. Simulation spectra resulted: a) from the summation of MCNPX spectra (of HPGe detectors 20%), for pipes of 10 cm diameter (total weight 100 kg) with 0.1 Bq/g homogeneous activity distribution, measured for 2 min; b) the background spectrum at an area of low background measured for 2 min.

The proposed non-destructive gamma spectrometry technique concerns the monitoring of metallic segments of several geometries (e.g. pipes of different diameter and thickness, slabs, screws, nets etc.). A new measurement set-up is used aiming at the reduction of the measurement uncertainties (lower than 30%) related to the distribution of density and activity. The time of measurement is comparable to that of the existing methods (i.e. 100 kg, 2 min). The sensitivity of the technique for 2 min measurement time is 0.1 Bq/g for both the key radionuclides (^{60}Co, ^{137}Cs) (Figure 1). The specific activities of metallic segments are determined by using the activities of the key radionuclides and the SF.

The results showed that by the proposed set-up, crucial reduction of the measurement uncertainty (less than 25%) for the examined geometries of metallic waste can be achieved. The direction of segments as well as if some segments are missing from the container of the measurement has no significant effect to the measurement efficiency.

3. Conclusions and way forward

- The proposed set-up for measurement of metallic waste after decommissioning, resulting in a lower measurement uncertainty, can be used for better selection of the management route as well as the decontamination and clearance procedure while is sensitive enough and equally fast in comparison to the commonly used methods.
- The work will continue in EURAD-2.

4.6 Possibilities of surface and volume activity determination in metallic waste by using experimental & MCNP modelling of γ-spectra (T4.5.2)

Angelos Markopoulos, Anastasia Savidou, NCSR Demokritos, GREECE

K. Mikalauskienė, E. Lagzdina, D. Germanas, A. Plukis & R. Plukiene, Center for Physical Science and Technology, LITHUANIA

angelos@ipta.demokritos.gr

Keywords: non-destructive γ-spectrometry, MCNP simulations, spectra comparison, Compton Effect, HPGe detector, $CeBr_3$ detector

1. Introduction

For the characterization of nuclear reactor components, several techniques are used (i.e. neutron calculations, models for radionuclide distribution, dose rate measurement, in-situ γ-spectrometry and sampling). For intermediate and high-level waste, the neutron calculations are used mainly for determination of DTM radionuclides in SF method. The accuracy of this technique depends on the composition and distribution of impurities in the materials, the flux and energy of neutrons, the nuclear data libraries, the methodology of the process and the simulation codes. For low and very low-level waste, the modelling the transport of radionuclides transport inside the primary cooling system is complicated and could be less accurate. The aim of this work is the monitoring of activated components to differentiate between activation and contamination. HPGe and $CeBr_3$ spectra are produced by MCNP simulations, based on the activities of particular gamma sources. The simulation spectra are compared with the experimental one to define the geometry of the source or to determine the activation as well as the contamination on a metallic slab. The proposed method could validate the SF for gamma emitters in activated components exhibiting contamination.

2. Description of work and main findings

Gamma ray spectra were produced by MCNP simulation code, using point and planar sources, placed between metal plates in an aluminium disk, as well as a volume source (Figure 1**Error! Reference source not found.**).

Figure 1. Modelled HPGe detector and ^{137}Cs photon flux for different geometry "metallic model samples".

Taking into account the Compton backscatter to photopeak ratio, one could separate different shielding between source and detector. The experimental and modelled spectra of ^{137}Cs and ^{60}Co point source using HPGe detector were compared, and the results set out that they are in good agreement. In case of $CeBr_3$

detector, the agreement of experimental and modelled results for ^{137}Cs point source was not very good because of lack of the accurate modelling of laboratory environment.

Volume source representing the activated metallic slab with ^{137}Cs (instead of ^{60}Co) as well as the contamination on the surface with ^{137}Cs were prepared. The experimental and modelled spectra by HPGe detector were in good agreement (Figure 2).

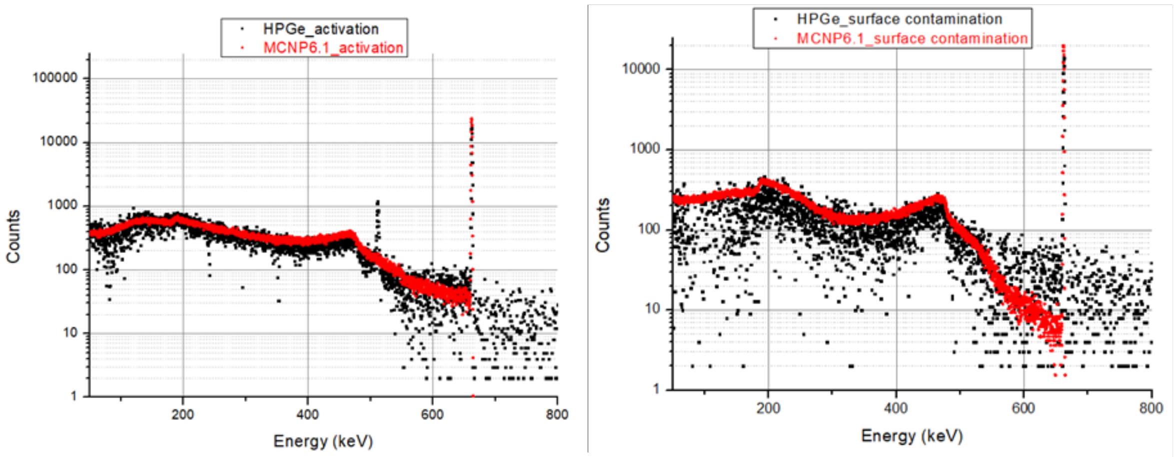

Figure 2. Comparing simulated and real spectra of volume sources representing a) the activated (^{137}Cs was used instead of ^{60}Co) and b) contaminated metallic slab.

From simulated spectra, the relation between Compton edge and photopeak intensity was determined and used in formulas to distinguish the activation and the surface contamination in metallic slabs of nominal volume and surface activity (Table 1).

Table 1. Comparison of nominal and experimentally determined values of volume and surface activities in metallic slabs.

	Volume activity $A(b)$	Surface activity $A'(b)$
Nominal 1	4900 ± 500	610 ± 60
Experimental 1	4300 ± 700	300 ± 200
Nominal 2	2400 ± 200	1500 ± 150
Experimental 2	2500 ± 300	1000 ± 200

3. Conclusions

- The quantitative agreement between the simulated and experimental spectrums justifies the validity of the simulation method procedure for spectra production.
- The simulating spectra show that not only the gamma peaks are characteristic but also the continuum is representative for each source.
- Combination of gamma spectrometry measurements and MCNP simulation allows distinguishing surface contamination from volume activation by the shape/ intensity or peak/ Compton ratio of γ-spectra (of key nuclides 137Cs and 60Co) analysis. This was checked by using CeBr3 and HPGe detectors for different known activity laboratory-made samples.
- The proposed method can be used for radiological characterization on activated reactor components.

4.7 Encapsulation of reactive metals in magnesium phosphate cement-based matrices (Task 4.6)

Task leader: C. Cannes (CNRS) celine.cannes@ijclab.in2p3.fr

Subtask 4.6.1 Studies on magnesium phosphate cements
R. Fernández, M. Dieguez, P. Padilla, A. I. Ruiz, J. Cuevas (UAM) *M. Cruz Alonso, C. Fernández (CSIC)*
Subtask 4.6.2 Cost optimization of magnesium phosphate cement-based matrix
L. Stefan (Orano), V. Shkuropatenko, Y. Svitlychyi, S. Sayenko (KIPT) *K. Le, S. Delpech, D. Rodrigues, C. Cannes (CNRS)*
Subtask 4.6.3 Behaviour of magnesium phosphate cements under leaching
L. Diaz Caselles, C. Cau Dit Coumes, P. Antonucci, A. Rousselet (CEA) *A. Mesbah (IRCELYON), V. Montouillout (CNRS)*
Subtask 4.6.4 Behaviour of magnesium phosphate cements under irradiation
I. Moschetti, L. Sarrasin, G. Blain, A. Abdelouas, (IMTA) *E. Mossini, F. Fattori, A. Santi, G. Magugliani, M. Giola, E. Macerata, M. Mariani (POLIMI)*
Subtask 4.6.5 Al corrosion in magnesium phosphate cements
M. Cruz Alonso, C. Fernández (CSIC) *M. Fulger, A. David, V. Lautaru (RATEN), J. L. Leganés (ENRESA)*
Subtask 4.6.6 Steel corrosion in contact with magnesium phosphate cements
A. David, L. Lautaru, M. Fulger, C. Bucur (RATEN) *K. Le, S. Delpech, D. Rodrigues, C. Cannes (CNRS)*
Subtask 4.6.7 Be corrosion in magnesium phosphate cements
S. Caes, V. de Souza, B. Kursten (SCK CEN) *A. Bukaemskiy, G. Deissmann, G. Modolo (FZJ)*

Keywords: magnesium potassium phosphate cement, formulation, leaching behaviour, irradiation, corrosion

1. Introduction

Magnesium potassium phosphate cements (MKPC) were identified as a promising alternative to Portland cements in encapsulation of nuclear wastes having high reactivity in alkaline media. Research was then developed on formulation, leaching and irradiation behaviour of MKPC, and the reactivity of reactive metallic waste (Al, Be) and a steel drum in MKPC. A reference formulation (Table 1) was provided by the CEA for the studies on MPC [J. Nucl. Mater. 541 (2020) 152411]. A formulation was also provided in the Milestone 29 for the studies on the low-cost magnesium phosphate cement, LC-MKPC (Table 2).

Table 1. MKPC formulation defined as a reference.

	m (g)
MgO (dead burnt)	131.39
KH_2PO_4	443.58
Sand MI 0.1/1.2 (Sibelco, 99,3 wt.% SiO_2)	574.97
Fly ash (class F, low CaO content)	574.97
Boric acid (H_3BO_3)	11.50
Distilled water	293.24

Table 2. LC-MKPC formulation

	B0T5	B2T3
	m (g)	m (g)
MgO (reactive)	128.72	128.55
KH_2PO_4	437.13	436.56
Sand MI 0.1/1.2 (99.3 wt.% SiO_2)	565.86	565.12
Fly ash (class F, low CaO content)	565.86	565.12
Sodium thiosulphate ($Na_2S_2O_3$)	28.30	16.95
Boric acid (H_3BO_3)	0	11.30
Distilled water	288.59	288.21

2. Description of work and main findings

Subtask 4.6.1 Formulation and characterization of MKPC

Considering the reference formulation presented in Table 1, the main objective of sub-task 4.6.1 consisted of optimizing the formulation for encapsulation of reactive metals. Several key factors of the formulation were studied, including the influence of the MgO source, the Mg/P ratio, the water/binder ratio, the nature of the filler and the retarder.

Increasing the MgO content increases the pH but, improves the mechanical strength and prevents or mitigates efflorescence. Formulations with Mg/P molar ratios from 1 to 4 were studied. A Mg/P molar ratio in the range 2–3 would be recommended to improve the mechanical properties and reduce potential efflorescence. Residual periclase increased with the MgO content but was observed at any Mg/P ratio. The pH would be influenced not only by the Mg/P ratio but also by the MgO and filler materials and would normally stabilize in the range 8–9.

The addition of filler materials increases the amount of inert solid in the mixture. They help to reduce the initial exothermic heat of reaction, and typically improves the workability and mechanical strength of the cement pastes, and simultaneously decrease production costs. Pumice, metakaolin, wollastonite and volcanic ash were studied with the objective to substitute fly ash, since its availability at long term is compromised. Volcanic ash showed good characteristics to be incorporated into MPC, however the distribution of this material and its homogeneity is not guaranteed.

The formulation should include the minimum amount of water to generate K-struvite (5 mols of water per mol of phosphate). Higher water content usually increases the initial workability of cement pastes but may produce higher instability at long term due to dissolution of other phosphates produced.
The role of boric acid and sodium thiosulfate were studied as retarder in the MKPC formulation. Rheological and mechanical properties were superior with H_3BO_3 using hard-burn and dead-burn MgO.

To design optimal and stable MKPC matrices for long-term aluminium immobilisation, the work carried out by the CSIC focused on evaluating two primary aspects on the MKPC physicochemical stability: 1) the Mg/P ratio and 2) the pore moisture content from curing. For this purpose, MKPC mortar samples with different M/P ratios of 1, 2, and 3M were prepared and cured under 100%RH. Additionally, 1M MKPC mortars were also prepared and cured under different moisture exposure conditions: 100%RH and isolated from the atmosphere. The physical (pore structure by EIS and MIP), and chemical properties (mineral structure by XRD and pore solution by pH and ICP-OES) were analysed at several ages over the test.

The main findings of this study reveal that the physicochemical stability of MKPC matrices is strongly influenced by both the Mg/P molar ratio and the moisture curing conditions. At a 1M Mg/P ratio, instabilities such as white efflorescences occurred due to the rapid dissolution of the excess of phosphates under high moisture curing. This condition also promoted the complete acid-base reaction, resulting in the formation of K-struvite and minor residual periclase in the 1M formulation. However, as the Mg/P ratio increased, the concentration of phosphate and borate ions in the pore solution decreased due to the progression of the reaction, raising the pore pH out of the aluminium passive domain. This increase was also influenced by the sulphur content from the fly ash. Despite this, higher Mg/P ratios promoted matrix densification by reducing capillary pores and supporting the coexistence of K-struvite and residual MgO. On the other hand, under isolated curing conditions with a lack of moisture in the pores, the MKPC reaction was not fully completed, resulting in a higher concentration of the main pore ions and unreacted products, maintaining near-neutral pH values for Al passivation over time, lower in 1M formulation.

Subtask 4.6.2. Cost optimisation of MKPC formulation

The results showed that reactive magnesia (less expensive than dead burnt MgO) can be used in MKPC, if a specific retarder is used. The high specific surface of reactive MgO enhances its hydration, which leads to a better use of the raw material. In dead-burned based grouts, anhydrous MgO can be beneficial in terms of mechanical properties. But the drawback is that it also induces anhydrous KH_2PO_4 that leads to efflorescence, instability and low properties for the material. The reactive MgO allows a better consumption of KH_2PO_4. Less efflorescence and a better durability are observed, as the depletion of KH_2PO_4 is enhanced by the total hydration of reactive MgO. Moreover, since the reaction with KH_2PO_4 is better complete, the quantity of cement can be reduced and the one of filler increased within the limit of keeping an acceptable mechanical resistance. Future works will aim to design formulations with equal K-struvite volume in the hydrated material compared to the reference formulation, rather than equal volume of initial cement (MgO + KH_2PO_4).

The best compressive strength (53 MPa for a reactive MgO mortar with 2wt.% H_3BO_3 and 3wt.% $Na_2S_2O_3$) is obtained at W/C of 0.5. This should be emphasized as usually much lower compressive strength are obtained for low Mg/P and high W/C ratios. The mortar prepared with reactive MgO, 2wt.% of H_3BO_3 and 3wt.% $Na_2S_2O_3$, presents very good compressive strength compared to other mixes at same W/C value, and for a lower Mg/P ratio. Enhanced hydration of this sample would be the main factor that impacts the result.

A study was also carried out on the nature of the filler. When fly ash (FA) is replaced by blast furnace slag (BFS), the content of K-struvite practically does not change. MPC-BFS samples demonstrate the highest compressive strength compared to MKPC-FA and MKPC-FA-BFS samples. The increased strength values are explained by the presence of a denser structure of the MKPC-BFS samples, in contrast to the structure of the MKPC-FA and MKPC-FA-BFS samples. Obtaining a denser structure of MKPC-BFS samples is due to the fact that BFS powder particles are more reactive compared to FA particles.

Subtask 4.6.3. MKPC behaviour under leaching

- The behavior of MKPC pastes or mortars under leaching was investigated with two main objectives:
  - (1) compare the behavior of MKPC prepared with different fillers (fly ash, and/or blast furnace slag) under leaching by demineralized water or 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 MKPC under well-controlled conditions.
- Two complementary approaches were implemented.

- "Operational" approach: Following ANS 16.1 standard, some leaching tests were carried out on MKPC mortars prepared with different fillers (fly ash (reference), blast furnace slag, or a mix (50/50) of the two components). The leachability indices and diffusivities of the different species released in solution were calculated from their cumulative concentrations in the leachates. Whatever the filler used, the leachability indices of K, Mg, P and B (LI>9) largely exceeded the LI index threshold of 6 defined by the US Nuclear Regulatory Commission. Blast furnace slag was shown to be an interesting filler, leading to denser materials than fly ash, and thus allowing, in most cases, to slow down the release of elements in the leachates.
- "Comprehension" approach: Leaching was performed on MKPC paste samples (reference formulation – fly ash used as a filler) under semi-dynamic and well-controlled conditions (pH maintained constant at 7 or 13.2, renewal of the leaching solution, nitrogen atmosphere, and temperature regulated at 25°C). The compositions of the leachates and solids (from the leached surface to the sound core) were characterized as a function of the leaching time using a large panel of techniques.
  - At pH 7, leaching was mainly governed by diffusion of dissolved species through the pore network of the paste. An interface retreat of the solid was observed. K-struvite was fully dissolved close to the exposed surface of the samples. Then, in an intermediate zone, K-struvite coexisted with cattiite.
  - At pH 13.2, a layer of Ca-deficient hydroxyapatite (CDHA) rapidly formed on the exposed surfaces and its thickness increased with the leaching duration. However, it was not sufficient to clog the porosity and protect the samples from further degradation. K-struvite dissolved near the exposed surface. In the intermediate zone, it mainly coexisted with brucite, CDHA and a hydrotalcite-like phase.

Based on these results, a first modelling approach based on reactive transport was proposed. Despite the simplified composition of the paste used for calculations, the model succeeded to reproduce the main mineralogical changes observed experimentally.

Subtask 4.6.4. MKPC behaviour under irradiation

This subtask aims to evaluate MKPC's durability under irradiation and its ability to meet Waste Acceptance Criteria (WAC). The MKPC samples were irradiated obtaining doses up to 1 MGy. A key test included hydrogen gas release, a critical factor when irradiating materials, which remained within acceptable limits. The observed low releases suggest that irradiation in MKPC do not give rise to excessive gas production, which is crucial to prevent pressure build-up in sealed disposal sites.

Mineralogical analyses, including X-ray diffraction (XRD) and scanning electron microscopy (SEM-EDX), reveal that gamma irradiation did not induce significant changes in MKPC's structure. This mineralogical stability is vital since changes in phase composition could lead to material weakening or loss of integrity. Moreover, the persistence of the K-struvite phase, a main component in MKPCs, suggests that the matrix can safely sustain doses up to 1 MGy, which is often a limiting factor for materials in nuclear environments.

The leaching tests, carried out following the ANSI/ANS-16.1-2019 protocol, further underscore MKPC's promising resistance, showing that even for 1 MGy the release of constituent elements like magnesium, potassium, and silicon after water immersion is limited. Moreover, the release of some noteworthy stable contaminants (caesium, strontium, cobalt, and europium), which were added to the MPC paste to simulate common radionuclides, was measured. The results were promising, particularly regarding caesium, which is very mobile and often abundant in radioactive waste. This is crucial for radioactive waste disposal since controlling the mobility of contaminants in case of flooding reduces environmental risks.

The mechanical strength of the material, tested under compression after exposure to radiation and immersion, adds another layer of confidence. Even after 90 d of immersion and up to 1 MGy of dose, MKPC retained most of its initial compressive strength.

Moreover, preliminary freeze-thaw cycle tests showed that MPC should be able to withstands environmental temperature fluctuations, adding to its versatility. The fact that MKPC can retain over 70% of its original mechanical strength after extensive leaching and irradiation ensures that it meets WAC, which are essential for safety in nuclear waste storage.

The studies demonstrate a robust consistency in MKPC's performance. The material's behaviour under different conditions is predictable and reliable—key traits for materials used in nuclear waste disposal.

Subtask 4.6.5. Al corrosion in MKPC

Effect of Portland and MKPC pore ion composition on Al corrosion

Simulated pore solutions were prepared, MKPC solution (pH 7.5) from a 7 d hydrated 1M MKPC and $Ca(OH)_2$-saturated solutions (pH 12.5) for OPC. High H_2 values for Al and AlMg alloy are detected in $Ca(OH)_2$ alkaline solutions simulating the OPC pore solution, which is not recommended for Al immobilisation. MKPC solutions show the lowest H_2 release, which becomes an alternative for Al immobilisation. The concentration of the main MKPC pore ions plays an essential role in the Al passivation mechanism. High phosphate content contributes to the Al passivation by forming a new passive film on the metal surface, lowering the H_2 release. A low borate content positively affects the Al passivation mechanism via adsorption in the Al_2O_3 layer, giving lower H_2 release. Differences are also appreciated with the method to determine the H_2 volume, higher with chemical than with electrochemical method.

Effect of cementitious composition (MKPC and OPC) on Al corrosion

Mortar and pastes were prepared using 1M MKPC and OPC (CEM I, IV or I+50%SF) and kept under water immersion curing. The type of binder significantly affects the H_2 volume and the Al/matrix interface. Al corrosion significantly decreases in MKPC than in CEM I mortar (El Cabril mortar). After 550 d of water immersion, the MKPC mortar (pH from 7 to 9.4) shows lower H_2 release than OPC (pH > 12.7), followed by CEM I+50%SF (pH close to 10). At the Al/CEM I interface, a heterogeneous layer of Al_2O_3 is formed (50 to 90 µm). Al ions generated due to the high alkaline pore pH of CEM I diffuse up to 1 mm depth in the matrix, forming expansive ettringite nodules, which affect the integrity of the wasteform. No significant metal reactivity exists in the interfase with an MKPC mortar due to its lower pH in the Al passive domain without Al_2O_3 corrosion product layer formation. A 30 µm dense protective microlayer rich in P, Mg, K at the Al/matrix interface is identified. Differences are also appreciated with the method to determine the H_2 volume, lower with chemical than from electrochemical estimation.

Effect of the MgO (hard-burnt or reactive) and the chemical retarder (sodium thiosulfate and boric acid)

LPR and EIS provided the same data, and both techniques can be used to study Al corrosion. Both chemical retarders and MgO type influence the Al passivation mechanism and H_2 release.Thiosulfate has a better behaviour than boric acid on the Al passivation mechanism on mortars. Lower H_2 release is detected with only thiosulfate.When both retarders are present, the synergy between the two products is unclear. Boric acid has a negative effect on the action of thiosulfate, showing the highest H_2 volume release.

Effect of the MgO/KH_2PO_4 (M/P) molar ratio and the pore moisture content from curing

Mortars with different M/P ratios (1, 2, and 3) were prepared and cured at 100%RH. Additionally, 1M MKPC mortars were prepared and kept under different exposure conditions, isolated and 100%RH. Due to matrix instabilities, the M/P ratio and moisture are modified. Al corrosion is affected by the pore moisture content and the M/P ratio. The increase of pore pH at a higher M/P ratio duplicates or triplicates the H_2 volume due to less phosphate ions in the pore solution. The pore moisture content influences the evolution of the acid-base reaction process in the MKPC. In isolated conditions with a lack of moisture, the progression of the acid-base reaction is not complete, and the presence of unreacted phosphates and borates in the pore solution decreases the pore pH and inhibits the H_2 release, contrary to 100%RH condition.

Study of the Al corrosion due to the realkalinisation of the MKPC and OPC

This study simulates the real engineers' barriers on the surface disposals for long-term immobilisation. 1M MKPC and OPC blended mortars (CEM I, IV and I+50%SF) were kept under pure water for over 300 d and alkaline water for another 250 d. A 1M MKPC mortar coated with a CEM I matrix was also prepared and kept under different exposure conditions to accelerate the corrosion: 100%RH and immersed in pure water for over 250 d. The alkaline media interaction confirms the reactivation of the corrosion response and H_2 release. In alkaline water, lower H_2 release is quantified in CEMI+50%SF mortar, followed by MKPC (pH 10). Both matrices are better alternatives to OPC (pH > 12.7) for long-term Al immobilization. In the interaction with a CEM I mortar, a diffusion of the alkaline media into the MKPC matrix exists, which increases in the water immersion curing. A reactivation of the corrosion process of Al and AlMg alloy is observed in the MKPC alkalinised matrix with an increase in the pore pH up to 11.3, reaching the Al/matrix interface. A higher H_2 volume is released in AlMg alloy than pure Al due to its less stability under high alkaline conditions.

Subtask 4.6.6. Steel corrosion in MPC

For all ferrous systems the optimal pH for minimizing the generation of corrosion products is ~ 9 .5 and even higher. When C-steel container is in contact with the cement pore water, aqueous corrosion might occur producing steel oxidation and hydrogen gas generation. The corrosion products developed on carbon steel-water systems at low temperatures consist of ferrous hydroxides $Fe(OH)_2$ and hydrated ferrous species.

As C-steel is generally used as material for the primary waste package, the experimental studies were achieved on C-steel corrosion in chemical conditions relevant for MKPC matrices (formulations based on low burned magnesium oxide) and comparison with the corrosion in CEM I. Electrochemical measurements and chemical tests were performed to determine the corrosion rate, volume of H_2 released and the effect of MKPC formulation on corrosion rate.

The test performed indicated that C-steel is more reactive when immersed in pore solutions compared to its embedding in MKPC and OPC pastes and the reactivity of C-steel in MKPC is similar to that in OPC, with the difference that in the MKPC initially the corrosion rate is higher and it decreases towards the end of the test, while in OPC it is initially lower and it increases towards the end of the test.

C-steel is significantly corroded in low cost MKPC compared to the reference MKPC. Differences of reactivity in the LC-MKPC prepared with only thiosulphate as retarder (B0T5) or with a mixture of thiosulphate and boric acid (B2T3) are minimal. However, the overall impedance of LC-MKPC formulations increases with prolonged exposure, suggesting a potential enhancement in corrosion resistance.

To overcome the higher corrosion of steel, concrete drums can be used for Al embedding in low cost MKPC. In cases the steel corrosion in the presence of thiosulphate exhibits linear kinetic corrosion, the consideration of concrete drums over steel ones could be warranted. The decrease in the cost of cement manufacturing could offset the high cost of concrete drums compared to steel drums.

Subtask 4.6.7. Be corrosion in MKPC

The corrosion of beryllium was studied in MKPC and Portland matrices, and in representative cement pore solutions (OPC solution (pH 13.5; Na^+, K^+, SO_4^{2-}), MPC solution (pH 8.1, K^+; PO_4^{3-}) and NaOH (pH 6.7 to 14). Two different Be grades were studied (99.8% pure be and S-200-F grade). Three different techniques were used for the determination of the Be corrosion rate: (1) mass loss measurement coupled with ICP-MS, (2) gas chromatography of the H_2 produced during corrosion and (3) electrochemical impedance spectroscopy.

In high pH solutions (OPC solution and NaOH solutions), similar corrosion behaviour was observed for both metal grade, whatever the technique used to determine the corrosion rate. From pH 12.5 to pH 14, the corrosion rate increases exponentially with pH. At pH ~13.5, the corrosion rate reached ~5 µm/y after 30 days of immersion and ~2 µm/y after 120 to 365 days of immersion. Moreover, the surface of both beryllium metal grade revealed pitting corrosion and a thin corrosion product layer. Mechanical defects (cavities, edges of scratches) on the initial beryllium surface acted as the initiation places for pitting corrosion.

In near neutral pH solutions (MKPC solution and NaOH solution), pure beryllium corroded slower (0.04 to 1.4 µm/y) than the S-200-F grade (~12 µm/y). SEM analysis of the surface of the metal after corrosion revealed the presence of $KBePO_4 \cdot H_2O$ crystals at the surface of both metal grade after corrosion in MKPC solution.

When beryllium was embedded in cementitious materials, the corrosion rates were lower than the ones measured in solutions. Initially, 0.8 to 0.9 µm/y was calculated from the H_2 production measurement in all matrices. This corrosion rate decreased to values lower or equals to 0.1 µm/y after ~10 weeks. Similar corrosion rates were calculated from EIS in OPC and low cost MKPC, while lower corrosion rates were observed in MKPC matrices (down to 4 to 40 nm/y). SEM characterization of the interface Be/matrix showed no corrosion product layer, but needle-like particles are present only in OPC close to the Be/OPC interface.

3. Summary

As the Al and Be wastes have previously been problematic with no real disposal route, most research conducted here has increased the knowledge of a promising conditioning material. Different magnesium potassium phosphate cements formulations were tested and optimised for mechanical, corrosion, irradiation, and leaching properties. The studies were carried out considering the waste acceptance criteria and the economic aspects. MKPC showed good performance as conditioning matrices for reactive metal radioactive wastes. The aqueous corrosion of Al and Be is low in MKPC, leading to a small production of hydrogen gas. Unfortunately, the leaching performance seems to be poor. More research on the topic is needed after adjustments of the material parameters.

5 Innovations in liquid organic waste treatment and conditioning – Overview of Work Package 5

Isabelle GIBOIRE, Arnaud POULESQUEN, Maria QUIROGA VALENCIA, CEA, France,
isabelle.giboire@cea.fr

Keywords: Alkali-activated materials, Conditioning, Geopolymer, Predisposal, Radioactive Liquid Organic Waste (RLOW).

1. Introduction

Radioactive Liquid Organic Waste (RLOW) is generated mainly by industrial nuclear facilities, such as nuclear power plants, spent nuclear fuel reprocessing plants, uranium enrichment plants. However, it can also be generated in other fields, including research and medical applications. RLOWs encompass a wide range of waste, e.g., oils, solvents generated from different decontamination operations, extraction solvents and scintillation liquids [1].

The management of RLOW remains a challenge. The available management routes and incineration have Waste Acceptance Criteria (WAC) that cannot be met by all existing RLOW in different European countries. Work Package five (WP5) objectives were to investigate and develop innovative RLOW direct conditioning solutions, implementing geopolymers and related alkali-activated materials as mineral binders. These solutions should meet the technical and economic requirements related to RLOW and lead to final waste showing properties and performance that are compatible with the safety and technical requirements associated with disposal but also with prolonged storage and transport.

WP5 of the PREDIS project WP5 involved 19 partners from 8 different countries. The partners represent a diverse range of organisations, including technical and scientific support organizations (TSOs), waste management organisations, research organisations and universities. The PREDIS (Pre-disposal of Radioactive Waste) project aims to increase the Technological Readiness Level (TRL) of treatment and conditioning methods for a range of waste streams other than nuclear fuel and high-level radioactive waste.

2. Description of WP5 and main findings

The work in WP5 was divided into six tasks. Two transversal tasks to ensure the organization of the management of WP5 and the exchange of information between the partners and the project coordination team (Task 5.1), and raise awareness of the achievements by providing documentation and dissemination materials as participation at scientific conferences and technical workshops (Task 5.6). The technical tasks (5.2 to 5.5) focused on exploring the possibility of using geopolymer and related alkali-activated materials.

At the beginning of the project, Task 5.2 in collaboration with other work packages, implemented an RLOW inventory questionnaire to PREDIS partners and the End User Group (EUG) members [2]. The results obtained were fundamental for the identification of the reference wastes and the selection of the raw materials and additives for the formulations of the matrices done in WP5.

During Task 5.3, the partners initially explore basic formulations and processes for direct conditioning of RLOW in geopolymer and related alkali-activated materials, all promising conditioning formulations were further investigated and grouped into three families of formulations based on: metakaolin (MK), blast-furnace slag (BFS), and a mixture of fly ash, BFS and MK. The optimisation and robustness of these formulations were studied with a surrogate RLOW, and the optimised reference formulations were further investigated with real waste and feasibility scale-up tests [1].

In Task 5.4, WP5 investigated the ability of geopolymer matrices to immobilise waste over long periods of time, focusing primarily on analysing the durability of matrices containing waste and their ability to withstand both radiation from the waste and accidental or seasonal thermal stress. Leaching and carbonation test were conducted to assess the capacity of the geopolymer matrices to physically immobilise RLOW and to ensure that chemical exchange with the surrounding environment would not be deleterious [3]. A disposability assessment was conducted as a preliminary step in evaluating the disposability of the geopolymer wasteforms [4].

Finally, Task 5.5 was dedicated to the preliminary technical, economic and environmental analysis of the direct conditioning route developed in WP5. The analysis, termed Value Assessment, brought together research results in terms of waste loading, conditioning matrix performance, process cost, and product disposability to capture the overall performance of the direct conditioning route. These results were compared with current waste management practices over a range of criteria [5].

3. Conclusions and way forward

All WP5 partners have collaborated closely over the past four years of the project, a total of 25 publications (e.g. journal papers, conference papers, deliverables of WP5, M.Sc. reports and Ph.D. theses) have been published with the main findings and research results of WP5 [6].The sharing of information and data has enabled the development of a deeper understanding of pre-disposal solutions for RLOW across different countries, which could be applied at national and European scales in the development of management strategies. Testing with real RLOW obtained a good incorporation rate for the MK-based and BFS-based formulations. The process scale-up tests conducted with both MK-based and BFS-based formulations and Nevastane oil provided valuable insights into the behaviour of geopolymers in larger-scale drums [1]. Results on the thermal behaviour for MK-based and MIX based formulations showed microcracking of the matrices under thermal cycling. Behaviour of the geopolymer matrices at high temperatures and under fire-like conditions needs to be studied in greater depth due to the important role of the thermal and hydric gradients in reducing the strength capacity of these matrices [3]. It is recognised that further R&D is required to advance the process towards a TRL of 9. This is reflected in the EURAD-2 proposals, which aim to go further in disposability assessment and contribute to the description of WAC across the different countries.

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5.1 RLOW pre-impregnation (Task 5.2)

Gabriele Magugliani, Eros Mossini, Andrea Santi, Francesco Galluccio, Elena Macerata, Marco Giola, Mario Mariani
Politecnico di Milano, Department of Energy, 32 Piazza Leonardo da Vinci, Milano, 20133, Italy
E-mail: gabriele.magugliani@polimi.it

Keywords: radioactive liquid organic waste, pre-impregnation, conditioning, geopolymer

1. Introduction

Pre-impregnation of radioactive liquid organic waste (RLOW) can be an alternative strategy to their direct conditioning. This approach aims at easing the incorporation of the waste into the matrix via its solidification onto an inert support, *e.g.* an absorbent. However, this strategy puts into play several factors which should be investigated and optimized, of which the most relevant are the waste-to-sorbent ratio, waste loading and manufacturing protocol [1]. Moreover, chemical compatibility between waste and sorbent and between sorbent and matrix must also be ensured to guarantee durability of the resulting waste form.

2. Description of work and main findings

Two materials were tested for the pre-absorption of the RLOW: recycled polyurethane (rPU) and NOCHAR N910. Various waste-to-absorber proportions were tested, ranging from 1:1 up to 6:1 mass ratios. As surrogate wastes, liquid scintillation cocktail (Ultima Gold LLT) and 30/70 v/v tributyl phosphate (TBP)/dodecane solvent were considered.

A tuff-based geopolymeric (GP) matrix was used for the encapsulation of the solidified waste. Its composition is reported in Table 1 [2].

Table 1. Composition of the tuff-based matrix.

Material	**Content (wt%)**
Volcanic Tuff	14.7
Fly ash	24.1
Blast furnace slag	24.1
Aluminium oxide	2.0
NaOH	8.1
H_2O	27.0

To prepare the samples, the RLOW was firstly added to the absorber. In parallel, the geopolymer paste was prepared by mixing the dry precursors with water. The solidified waste was then added to the paste, and specimens casted. All samples were cured for 28 days in endogenous conditions at 22 ± 2 °C. Specimens were tested for compressive strength and their resistance towards immersion in water was qualitatively assessed.

For both absorbers, no incompatibilities with the two waste types considered was noted. However, all samples prepared with rPU presented large cavities, and consequently proved of low mechanical strength. Also, their stability under water immersion was scarce, with high amounts of released waste. This low performance was attributed to the incompatibility of the absorbent, since rPU can undergo base-catalysed hydrolysis in the high pH environment found in the geopolymer, with a consequent release of CO2 which damages the structure of the matrix. This absorbent was therefore abandoned due to its intrinsic incompatibility with the conditioning strategy considered.

Both surrogate RLOWs could be easily absorbed onto NOCHAR, however higher organic liquid contents produced a thick gel (see Figure 1), which was difficult to homogenize with the GP paste due to its very high viscosity. Samples produced via the incorporation of this gel into the paste proved inhomogeneous and exhibited low mechanical strength (Figure 2 and Table 2).

To solve this issue, a preparation protocol different from the conventional pre-impregnation was tested. This approach, which can be described as a direct absorption, consists in mixing the absorber with the dry precursors of the geopolymer, and subsequently adding the liquid waste and the water, given that water is not absorbed by the NOCHAR N910. This protocol proved more effective, resulting in more homogeneous samples with fewer cavities (Figure 3). Also, the compressive strength of the specimens prepared with this improved protocol slightly improved, as reported in Table 2.

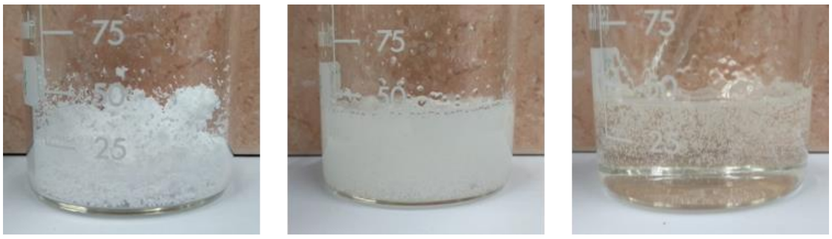

Figure 1. Absorption of TBP/dodecane on NOCHAR N910. From left to right: NOCHAR alone; immediately after the addition of waste (6:1 mass ratio); upon standing for 10 minutes.

Figure 2. Samples containing increasing amounts of TBP/dodecane prepared via pre-absorption on NOCHAR N910 (mass ratios from 3:1 to 6:1, constant waste loading of 30 vol%). Large cavities are visible due to the difficulties in homogenizing the paste with the absorbed waste.

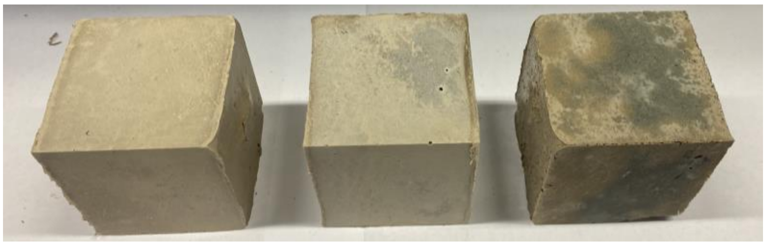

Figure 3. Specimens prepared with the modified direct absorption protocol (5 wt% NOCHAR). From left to right: with no waste, with 10 wt% LSC, and with 10 wt% of TBP/dodecane

Table 2. Compressive strength of samples prepared with different protocols. Waste loading 10 wt% TBP/dodecane, waste to absorber ratio 2:1.

Preparation protocol	**Compressive strength (MPa)**
No waste	23.7 ± 1.9
Pre-absorption	5.9 ± 0.7
Direct absorption	8.1 ± 1.4

3. Conclusions

The pre-impregnation approach can be an interesting method for the conditioning of RLOW, especially if the use of a surfactant is to be avoided. Both the tested absorbers presented some issues in their implementation. In particular, recycled PU exhibited chemical incompatibility with the alkaline conditioning matrix.

On the other hand, NOCHAR proved more stable and capable of solidifying high fractions of organic liquid. The effectiveness of the impregnation approach appears to depend also on the specific manufacturing protocol, which should be improved to further increase the achievable waste loading. Moreover, the leaching resistance of the waste forms would likely be improved if more stable interactions between the absorber and the organic liquid could be produced, *e.g.* via chemical bonding.

A comprehensive description of the obtained results is also reported in Deliverable D5.2 [3].

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5.2 Study of direct conditioning process (Task 5.3)

Federica Pancotti, SOGIN, Italy, pancotti@sogin.it; Crina Bucur, RATEN, Romania, crina.bucur@nuclear.ro

Keywords: Radioactive Liquid Organic Waste, direct conditioning, geopolymer, alkali activated materials, real waste, scale-up

1. Introduction

The task 5.3 of the PREDIS WP5 was dedicated to study the direct conditioning process of Radioactive Liquid Organic Waste (RLOW) in geopolymer and related alkali-activated materials.

The partners involved in this task investigated basic formulations and processes for the direct conditioning of RLOW. All the promising conditioning formulations were further studied and grouped into three formulation families, based on – metakaolin (MK), blast furnace slag (BFS) and mixture of Fly Ash, BFS and MK (MIX). The optimisation and robustness of these formulations were studied with surrogates RLOW. The optimised reference formulations were further investigated with real RLOW and upscaled.

The outcomes of the work conducted are summarised in the final deliverable [D5.2].

2. Description of work and main findings

The main objective of task 5.3 was to develop and study most promising reference formulations that can be used for conditioning of various types of RLOW. The work was organized in different sub-tasks, with the following main objectives:

T5.3.2 - Assess (feasibility/screening) exploratory conditioning options (5-10) and to select most promising reference formulations (3) to be further studied and developed

T5.3.3 - Optimize and assess robustness (waste, raw materials and process variability) of selected reference formulations

T5.3.4 - Further consolidate reference formulations from tests with real RLOW

T5.3.5 - Investigate feasibility of scale-up from exploratory pilot scale tests

Two additional sub-tasks were dedicated to:

T5.3.1 - Define experimental guidelines and protocols to be used

T5.3.6 - Elaborate a technical report including key results, information and data obtained

The partners involved in T5.3, first investigated basic formulations and processes for direct conditioning of RLOW in geopolymer and related alkali-activated materials. As reported in the Milestones [MS32] and [MS33], all the promising conditioning formulations were further studied and grouped into three formulation families, based on: metakaolin (MK), blast furnace slag (BFS), and a mixture of Fly Ash, BFS and MK (MIX).

For each family, 2-3 Partners were identified to work in the Optimisation and Robustness testing activities in the scope of the sub-task 5.3.3, and they worked at laboratory scale with surrogate RLOW.

Metakaolin (MK) based formulation - Major Achievements

Two partners were involved in the study of the Metakaolin based formulation: NNL and CIEMAT. The main results are summarised in Figure 2 and reported in the following.

Incorporation of up to 50 vol% of simple high viscosity oil (Nevastane EP100) for mid-point formulations was achieved

Incorporation of up to 30 vol.% of TBP-dodecane and scintillation cocktails was achieved

The addition of specific surfactant (Tween 80) is needed only for TBP-dodecane mixture

With high oil loadings (50 % vol.) the mixing methodology may become important in incorporating oil in the GP formulation (effect of shear)

RLOW loading affects GP viscosity/fluidity: by increasing oil loading, an increase of viscosity / decrease of fluidity is observed

The compressive strengths develop rapidly by 7d and are reduced by increasing RLOW loading

Mid-point formulations are characterised by high heats of dissolution of the MK powder, with lower heat of dissolution for Argicem® GP system compared to the Metamax® GP system

Severe cracking observed during water immersion if the MK specimens are stored in dry environment

No oil leaching was observed, but in the case of specimens containing scintillation cocktail positive TOC values were obtained in the leaching tests

Scintillation cocktail not stable in water: cracks were observed

Longer term monitoring of formulations is required to prove the long term RLOW retention and product stability

Blast Furnace Slag (BFS) based formulation – Major Achievements

Two partners were involved in the study of the Metakaolin based formulation: SCK-CEN and RATEN. The main results are summarised in the following.

Incorporation of up to 30 vol% of simple high viscosity oil (Nevastane EP100) and complex low viscosity oil (Shellspirax) can be achieved.

Addition of surfactant (Tween 80) is needed

It was not possible to achieve comparative waste loading with TBP-Dodecane (no incorporation) and scintillation cocktail (up to 20% vol.)

Need for in-oven curing during the first hours after preparation in the case of TBP-dodecane

w/b ratio and concentration of alkaline activating solution and affect the setting time: NaOH accelerates while high Sodium Silicate delays. Type of oil affects setting time while waste loading does not seem to have any significant effect on setting.

Oil in samples delayed the geopolymerization. Higher NaOH accelerates geopolymerization while high Sodium Silicate content seems to delay the process. The total alkaline content (both NaOH and Sodium Silicates) additionally controls the geopolymerization (heat release) after 7 days.

The strength of the samples is strongly affected by the w/b ratio and waste loading

The effect of the variability in raw materials has been studied and it was noted that the oil incorporation and mechanical strengths are affected by BFS composition and fineness

MIX based formulation – Major Achievements

Three partners were involved in the study of the Metakaolin based formulation: KIPT, Nucleco and CEA. The main results are summarised in the following.

up to 30 vol% of simple high viscosity oil (Nevastane EP100) and complex low viscosity oil (Shellspirax) can be achieved without any surfactant

RLOW loading affects GP viscosity: as the oils content increases the viscosity of paste and corresponding shear stress increases

Changing in raw materials (mainly different BFS), mixing protocols and curing conditions have a great impact on the oil incorporation and on the mechanical properties of the final waste form

The storage conditions and especially the relative humidity plays a crucial role on the hardened properties of the alkali activated materials composites

Robustness study conducted by varying in content of six different formulation parameters showed a compressive strength of 5 MPa and higher and a range of flowability between 75%-90%. Some bleeding has been observed in some samples, mainly with Nevastane oil

Surfactants are needed to correctly emulsify the TBP-dodecane. Using Glucopon as surfactant, it was possible to incorporate TBP-dodecane at a rate of 30 vol% and the resulted specimens had a compressive strength higher than 15 MPa

After the laboratory tests, it was possible to analyse the results and select a limited number of optimized formulations [MS34] to be used for the investigation of reference formulations with real RLOW (T5.3.4) and direct conditioning process scale-up (T5.3.5).

In parallel the possibility of an alternative route (a two-step pre-impregnation methodology) has also been investigated.

Real RLOW – Major Achievements

Three partners were involved in the tests with real RLOW: UJV, Nucleco and PoliMi. The main results are summarised in the following.

BFS-based geopolymer matrices are suitable for the incorporation of real scintillation cocktail and an ionic solution containing 63Ni and 14C with a waste loading of about 20 vol%.

For the real scintillation cocktail and solvent waste incorporation in MK-based geopolymer it was observed that compressive strength is significantly affected by the presence of real waste, with a maximum decrease of about 50% regardless of the waste considered. Regarding the leaching behaviour no significant differences were observed between the matrix without ROLW (assumed as reference) and the ones with real waste.

For the real oil waste, a good incorporation rate was obtained for the MK-based and BFS-based formulations while the MIX-based one didn’t incorporate the real oil waste and it was not possible to prepare specimens for testing. The real oil affected the compressive strength of the matrices and for the MK-based formulation it was highlighted that the curing conditions affect the stability of the samples if immersed in water. Good leaching resistance was observed for both MK-based and BFS-based formulations

Scale-up – Major Achievements

Two partners were involved in the scale-up tests: CVR and SCK-CEN. The main results are summarised in the following.

Process scale-up tests were conducted with both MK-based (50L – 100L) and BFS-based (50L) formulations and Nevastane oil (MK: 20-30 %vol. and BFS: 20 %vol.)

The MK-based scale-up experiments demonstrated the feasibility for direct solidification of liquid organic waste (TRL-6)

Further optimisation of the BFS-based geopolymer preparation protocol is needed (TRL-5)

Alternative route: two-step pre-impregnation methodology - Major Achievements

One partner was involved in the pre-impregnation tests: PoliMi. The main results are summarised the following.

N910 is a better RLOW absorber as it is compatible with alkaline matrices

The heterogeneity could reduce the waste form durability and mechanical strength

BFS-based matrix could produce better results, but further experiments are required to identify the best conditions

Other formulations (e.g. MIX-based) should be tested in the future with N910

3. Conclusions

The experimental activities conducted for the investigation, development, and assessment of innovative direct conditioning solutions for Radioactive Liquid Organic Waste, showed that specific formulations based on metakaolin, blast furnace slags and innovative mixes of raw materials have very promising results in terms of improving waste loadings and waste form properties compared to traditional cementitious waste forms.

The work involved the participation of different Partners coming from different European countries, with different background and experience in the field of RLOW conditioning. A continuous collaboration and exchange of information and data between the Partners allowed the project to reach its goal.

The results of the project can be used by Waste Management Organisations and Waste Owners who deal with RLOW that, due to their radiological and physicochemical characteristics, don’t meet the acceptance specifications for industrial treatment plants and constitute radioactive waste without management route.

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[MS34] F. Pancotti, C. Bucur, PREDIS Milestone 34 “Optimised formulations for reference formulations”, 2022

5.3 Investigation of direct conditioning process scale-up (Task 5.3)

Anna Sears, Vojtěch Galek, Petr Pražák, Martin Vacek, Research Centre Řež, Czech Republic,
anna.sears@cvrez.cz

Keywords: direct conditioning, scale-up process, metakaolin-based geopolymer, blast furnace slag geopolymer

1. Introduction

Within task 5.3, we conducted scale-up experiments involving directly conditioning a liquid organic RW surrogate to test the feasibility and effectiveness of the selected formulations on a larger scale. These included wet coring and sample analysis to ensure a uniform distribution of materials within the geopolymer matrix and compressive strength tests to evaluate the mechanical strength of the resulting geopolymer. The additional aim of the scale-up experiments was to provide temperature data to our project partner SCK-CEN for modelling to understand the thermal behaviour of the geopolymer matrices on a larger scale.

2. Description of work and main findings

For all scale-up experiments, a solidification device (Figure 1) equipped with a top mixer and independent drum rotator was used. The solidification device is compatible with 50 L and 100 L drums. Mixing was performed at a speed up to 1000 rpm; the mixing time was 35 - 45 min. Raw materials were added in parts during the mixing process to ensure good matrix homogeneity. After sample preparation, the thermocouples were inserted into the drum and attached to the drum surface to obtain temperature profiles.

Figure 1. Solidification device with the 50 L drum.

Selected geopolymer formulations, metakaolin-based (MK) and Blast Furnace Slag (BFS) based, were tested. A metakaolin Mefisto L05, commercially available from ČLUZ a.s., Czech Republic, with premix alkali activator, composed from potassium silicate solution (35 wt.%), were used for the MK-based formulation (Figure 2). For BFS formulation, a finely ground BFS sourced from Trinec Iron and Steel Works, Czech Republic, was used, along with locally obtained quartz sand as the added component, with sodium silicate solution prepared according to the SCK-CEN protocol.

Five scale-up experiments were performed:

MK-based

- 50 L, no oil
- 50 L, 10 wt.% Nevastane oil
- 100 L, 10 wt.% Nevastane oil
- 100 L, 20 wt.% Nevastane oil

BFS-based

- 50 L, 10 wt.% Nevastane oil, with added surfactant Tween®80

Figure 2. Preparation of 100 L samples with MK formulation.

After the curing, the samples were tested for homogeneity. Wet curing (Figure 3) was performed at 100 L tests, and the obtained samples were analysed for compressive strength. The compressive strength analysis of the samples was performed according to the Czech National Standard CSN EN 12390-3 Testing hardened concrete - Part 3: Compressive strength of test specimens. The average compressive strength was 21 MPa (100 L, 10 wt.% Nevastane oil) and 15 MPa (100 L, 20 wt.% Nevastane oil). The samples were then also measured for porosity using mercury porosimeter and pores measuring 0.01 µm in size were predominant within the sample matrix.

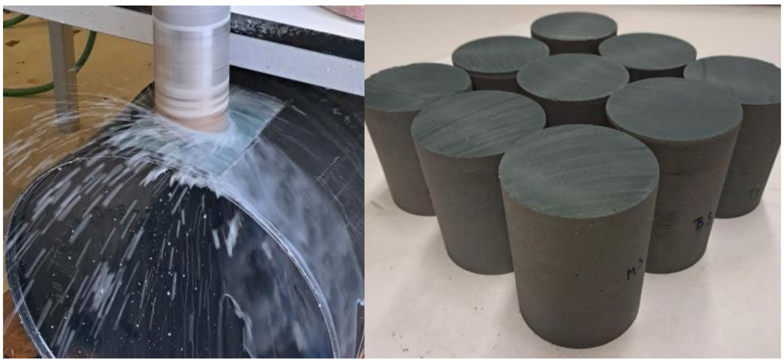

Figure 3. Wet curing of 100 L drum and extracted samples before compressive strength analysis.

The BFS solidified sample revealed suboptimal texture; the sample exhibited softness, preventing the extraction of a suitable sample for compressive strength testing (Figure 4). Additionally, visual observations indicated the likelihood of separated yet solidified phases, particularly at the upper section of the drum.

Figure 4. BFS formulation with 10 wt.% Nevastane oil and Tween®80 (50 L drum)

3. Conclusions

Process scale-up tests were conducted with both MK-based (50 L and 100 L) and BFS-based (50 L) formulations and Nevastane oil (MK 10-20 wt.%. and BFS 10 wt.%). The MK-based scale-up experiments demonstrated the feasibility of direct solidification of liquid organic waste surrogate, while BFS-based geopolymers showed suboptimal results, indicating a need for further optimisation of the BFS geopolymer preparation protocol.

5.4 Durability evaluation of the MK formulation (Task 5.4)

Sara Koubeissy, Matthieu Briffaut, Nicolas Gay, Franck Agostini (Centrale Lille Institut, France),
sara.koubeissy@centralelille.fr

Keywords: Geopolymers, organic liquid wastes, carbonation, leaching, permeability

1. Introduction

The aim of the study is to evaluate the durability of the metakaolin-based formulation developed within T5.3 in the following environments: endogenous, aerated and alkaline.

This document provides a brief overview of the results discussed in the student 5-minute presentation and elaborated in Deliverable 5.3 (Synthesis of experimental results on long term matrices performances for direct conditioning of liquid organic waste) and describes:

- The selection of the oil percentage for incorporation
- The pH levels of the various solutions selected for the leaching experiments
- The carbonation parameters used for both natural and accelerated carbonation
- The methodology followed for the preparation and the characterization of the specimens
- Various conclusions drawn from the different experiments

2. Description of work and main findings

Selection of oil percentage for incorporation

The optimized formulation developed by NNL in T5.3, whose ratios are presented below, was tested with Nevastane EP 100 oil.

$SiO_2/K_2O = 1.2$

$K_2O/Al_2O_3 = 1.2$

$H_2O/K_2O = 13$

The visual appearance using three different oil volume percentage are presented in Figure 1. Oil was coloured in red to detect obvious release. However, compressive strength results supported the choice we made.

Reddish, non-transparent water was released from the specimen containing 40% oil by volume. This led to the decision to use a 30% oil incorporation, which also meets the compressive strength requirements with a value of 25.5 MPa.

pH levels of the different conditioning environment selected and parameters opted

A reference state with 100% RH was established by storing specimens in airtight bags. For an alkaline environment, a Cem V solution with a pH of 13.3.

Due to limited references, we chose a pH of 3, using HCl acid, to represent an acid attack. For natural carbonation, conditions of 20°C, 65% RH, and 0.1% CO_2 were tested, while for accelerated carbonation, conditions of 20°C, 65% RH, and 1-5% CO_2 were used.

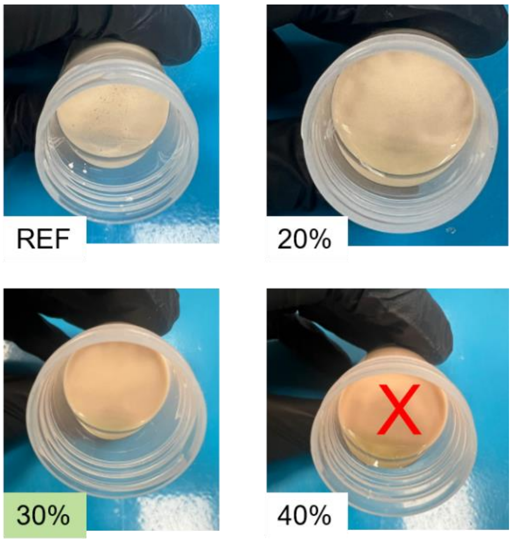

Figure 1. Visual aspect for the determination of waste loading factor.

Leaching experiments

The leaching experiments were conducted following the ANDRA specification [1] which consists on the following ratio for V_L to S:

$$\frac{V_L}{S} \geq 0{,}1 \text{ m};$$

V_L Leaching volume (m^3),
S surface area of the leached specimen (m^2)

The leaching solution was replenished at 3, 7, 14, 28, 56 and 90 days.

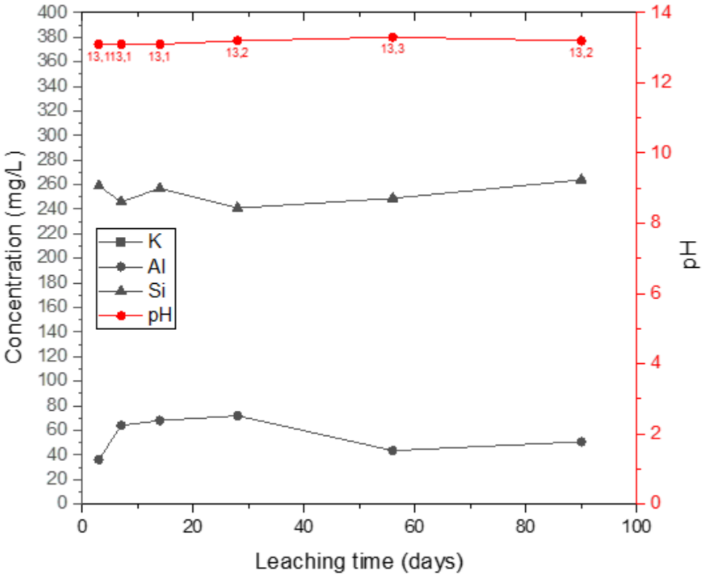

Figure 2. ICP measurement and pH evolution for sample leached in CEM V water (pH 13.3).

pH values remained constant from day 0 (using a 28-day aged sample) until 90 days of leaching. However, there was minimal Al and Si leaching from the GP matrix. K could not be measured in this environment because the leaching solution, prepared with KOH, saturated the water solution.

Permeability measurement has shown an improve when increasing the time of leaching. The permeability of the specimens has increased from 4.50E-17 at 14 days of leaching to 4.07E-18 at 28 days of leaching.

Natural carbonation

One of the experiments performed on the samples was the calculation of the carbonation penetration depth using phenolphtalein and alizarine yellow as a colour indicator. Table 1 shows the colour palette at different pH environments.

Table 1. Transition colours palette for alizarine yellow colour indicator.

Indicator solutions	Transition pH and colors					
Phenolphtalein	colourless	pH < 9	x	x	pink	pH > 9
Alizarine yellow	Yellow	Ph < 10,2	Orange	10,2 < pH < 12	Red	pH > 12

The colour indicator shows a penetration depth in Figure 3 corresponding to a decrease in the pH of the specimen. Reference state show a high alkalinity of the GP paste corresponding to a pH value above 12.

However, after 14 days of natural carbonation, samples without oil show a decrease of pH and a total carbonation when alizarine yellow is used. Samples with 30%. oil show a clear and uniform carbonation depth with both color indicators. This stems for less carbonation in the GP paste when physically incorporating oil within the samples.

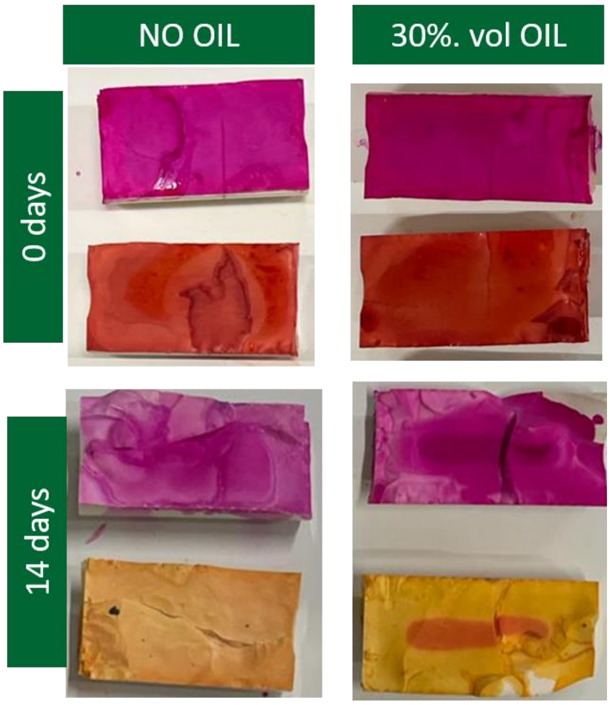

Figure 34. Carbonation depth of GP samples at reference state (0 days) and 14 days of natural carbonation.Phenolphtalein colored samples are presented.

3. Conclusions

During leaching in an alkaline solution, the pH remains stable, as the GP are within their safe range of alkalinity. In this environment, Permeability of GP matrix is enhanced by 10 after leaching in pH 13.

Tested samples containing oil exhibit, in our conditions, reduced susceptibility to carbonation. This association may stem from oil effectively blocking pores, thereby aiding in maintaining a higher pH level.

These results show that GEOIL materials seem to be stable material in different durability environments.

References

[1] Determination de la resistance a la lixiviation d'échantillons de blocs de dechets homogenes (E.T. 052), ANDRA

5.5 Investigation of reference formulations for real radioactive liquid organic waste

Eros Mossini[1], *Monika Kiselová*[2], *Gabriele Magugliani*[1], *Carlo Forconi*[1], *Andrea Santi*[1], *Francesco Galluccio*[1], *Marco Giola*[1], *Elena Macerata*[1], *Mario Mariani*[1], *Petr Večerní*[2]

[1]*Politecnico di Milano, Italy*

[2]*UJV-Rez, Czech Republic*

Corresponding authors: eros.mossini@polimi.it, monika.kiselova@ujv.cz

Keywords: radioactive liquid organic waste, real waste, direct conditioning, geopolymers, waste acceptance criteria.

1. Introduction

The purpose of the work was the investigation of the reference formulations developed in the task 5.3 with real radioactive liquid organic waste (RLOW). In particular, the aim has been the verification that the radionuclide content and the physico-chemical properties of the real waste would not affect the final matrix performances, already assessed with surrogate RLOW.

The general approach followed by Politecnico di Milano (POLIMI) and UJV-Rez (UJV) consisted of three steps: i) characterization of the available real RLOW (e.g. chemical and radiological composition); ii) conditioning of the real RLOW in the best matrix specifically developed and optimized; iii) characterization and validation of the waste-form according to the waste acceptance criteria (WAC).

2. Description of work and main findings

i) Characterization of the available real RLOW

At POLIMI, two types of waste were available, characterized and employed:

- A spent solvent employed in R&D activities aimed at investigating the recycling of minor actinides from the spent nuclear fuel. It consisted of a mixture of kerosene + 5% v. of 1-octanol, which dissolved 0.2 M of a lipophilic extractant N,N,N′,N′-Tetraoctyl diglycolamide (TODGA) selective for actinides and lanthanides. This real waste was contaminated with about 3-4 kBq/L of Eu-152, Am-241, and Cm-244 and also contained 1 g/L of stable lanthanides Eu, Nd, Ce.
- A spent liquid scintillation counting (LSC) cocktail employed in radioanalytical methods for the determination of hard to measure radionuclides. It consisted of a mixture of Ultima Gold LLT (Perkin Elmer) and AquaLight+ (Hidex) cocktails in unspecified proportions and 20 %v. of 1 M nitric acid. This real waste was contaminated with about 20 Bq/L of Ni-63 and also contained stable Ni and Cs at concentrations of 100 mg/L and 5 mg/L, respectively.

Two types of real liquid organic waste were available and used at UJV:

- A scintillation cocktail ROTISZINT R High-Capacity Cocktail provided by ROTH Company, Karlsruhe, Germany. It consisted of these ingredients: Diisopropylnaphthalene, nonylphenol ethoxylate, phosphate ester, butyldiglycol, sodium borohydride, 1,4-bis(2-methyl styryl) benzene, diethanolamine. The cocktail contained about 0.56 Bq/ml of ^{14}C and 0.84 Bq/ml of ^{63}Ni.
- An ionic solution from the Sigma-Aldrich Company, USA, used as a representative ionic liquid that is suitable for use as a carrier system for the electrochemical separation of a wide range of metallic elements including fission products such as lanthanides. The solution consisted of 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide containing about 12.05 Bq/ml of ^{14}C and 11.04 Bq/ml of ^{63}Ni. The uranium content was below the detection level.

ii) Conditioning of the real RLOW

At POLIMI, both real RLOWs were conditioned with 30% v. loading factor in the metakaolin (MK)-based matrix prepared according to the formulation developed by NNL and employing the high-shear mixing protocol [1]. The employed materials are MK-Metamax®, KOH and Betol K-5020T activators and water to obtain the following molar ratios: SiO_2:K_2O = 1.2, K_2O:Al_2O_3 = 1.2, and H_2O:K_2O = 13. The spent solvent was conditioned by pre-emulsification with the activation solution using a surfactant (5% wt. of surfactant with respect to the waste). The spent LSC cocktail was conditioned without adding a surfactant. The water content of the real LSC waste was subtracted from the water necessary according to the formulation to achieve the same W/B ratio. The water content in the solvent waste was negligible and so it was not accounted for. All samples showed acceptable workability, setting time and bleeding. They were cured for 28 days at >90% RH before further testing. After curing, all samples appeared homogeneous and without macroscopic cavities nor cracks. A slight bleeding was noted (below 1% of the total specimen volume) regardless of the presence of the real waste.

At UJV the RLOW was traced with an addition small amount (1.5 ml) of ^{14}C and ^{63}Ni due to the low levels of radioactivity of these monitored radionuclides in the real waste. Final activity concentrations in the real RLOW were: 2.5 MBq/100 ml of ^{14}C and 0.8 MBq/100 ml of ^{63}Ni in scintillation cocktail, 2.56 MBq/100 ml of ^{14}C and 0.81 MBq/100 ml of ^{63}Ni in ionic solution. Two matrices were used for the solidification of RLOW [1]. The precursors were respectively Blast Furnace Slag from Moravia Steel (Czech Republic) and Metakaolin & Activator Mefisto L05 from Czech Shale Plants Company, Nove Straseci. Other employed materials were: $Na_2O{\cdot}3SiO_2$ dissolved in the 10 M NaOH solution as alkali activator, sand and water as additives. For these initial lab-scale experiments, approx. 10% wt. of RLOW loading was performed. Samples were cured for 28 days under controlled wet conditions in a closed box.

iii) Characterization and validation of the waste-form

At POLIMI, compression resistance (R_c) was assessed in accordance with UNI EN 12390:2021. Porosity was measured following the water saturation method. It was demonstrated that R_c is almost halved due to the presence of the waste, regardless of whether surrogate or real RLOW is incorporated. Nevertheless, the R_c still nearly meets the national WAC (R_c > 10 MPa). Coherently, porosity slightly increased in samples containing RLOW. Moreover, water immersion generally induced loss of compressive strength in the order of few MPa. In addition, phase composition (XRD) was investigated to shine a light on possible changes caused by the RLOW incorporation. The material resulted to be almost completely amorphous. No differences due to ageing conditions (water immersion) nor RLOW loading were noticed.

Leaching tests were performed as specified in ANSI/ANS16.1-2019 protocol using ultrapure water as leachant, kept at room temperature (20 °C ± 1°C) and periodically renewed. The leachability indices (Li) of matrix constituents and contaminants were calculated and compared with the national WAC (Li_{Cs} > 6 for LLW). Due to their low concentration, the content of radioactive contaminants (Ni-63, Eu-152, Am-241, and Cm-244) in the leachates could not be measured, hence their Li were not assessed. Hence, those of stable isotopes (if present) were calculated: Ni and Cs for the spent LSC cocktail and Ce, Nd, and Eu for the spent solvent. All of them resulted well above the limit set by the national WAC, with negligible differences due to the presence of real or surrogate RLOW.

At UJV, compressive strength was performed using a ”MEGA 11-300 DM1-S Presser”. All tested samples showed suitable compression resistance, R_c > 10 MPa. No significant differences of values between the radioactive and inactive (without RLOW) specimens were obtained.

The leaching tests were performed following the ANSI/ANS-16.1.1986 method, which is a short-term test to measure the leachability of solidified low-level wastes. Ultrapure water was used as a leachant. A constant room temperature was maintained during the testing procedure. According to the acceptance conditions for storage in Czech Republic, Li must be above 8 for LLW. All tested samples met this required criterion, the maximum reached Li value was 11.18.

3. Conclusions

Different real RLOW were characterized and conditioned in geopolymeric matrices by POLIMI and UJV following the formulations and protocols developed by the partners of WP5. The properties of the waste-forms obtained with real RLOW resulted to be almost unaffected by the real waste content, with respect to previous results on surrogate RLOW. In particular, both R_c and Li satisfied the required WAC.

References

[1] Deliverable 5.2 – Report on synthesis of formulation & process studies results, RATEN, (WP5), February 2024

5.6 Disposability Assessment of Geopolymer immobolized wastes (Task 5.4.9)

Delhia Alby, Georges Daval, (Galson Sciences Ltd, UK), da@galson-sciences.co.uk

Keywords: Disposability assessment, criteria, evaluation, geopolymers

1. Introduction

Demonstration of the compatibility of the final waste package properties and performance of geopolymer waste forms, compared with safety and technical requirements related to disposal, is a key issue and challenge of WP5. Deliverable D5.4 [i] presents the activities carried out under Task T5.4.9, and summarises the resulting data and disposability considerations.

The objective of this work is to provide technology developers and end-users with an objective assessment of the likely performance of waste packages produced via the geopolymer direct conditioning route in terms of disposability. Due to the relative novelty of geopolymers as waste matrices, and uncertainties regarding their application to RLOW, such an assessment is not definitive; rather, it provides an easy-to-read dashboard of wasteform characteristics that shows which areas require improvement or substantiation if final disposability is to be demonstrated. Conversely, it also highlights areas assessed as already meeting disposability requirements.

2. Description of work and main findings

The three geopolymer formulations selected for the project are, namely:

- The Metakaolin (MK)-based formulation developed by NNL.
- The Blast Furnace Slag (BFS)-based formulation developed by SCK CEN; and
- The MIX formulation (based on MK, BFS, and Fly Ash (FA)), developed by KIPT.

Wasteform disposability was assessed according to the following radiological waste categories (VLLW, LLW/ILW-SL (Short Lived), and ILW-LL (Long Lived)) and according to disposal facility types, ranging from near-surface to intermediate-depth facilities, and Deep Geological Repositories (DGR). Assessments were based on a mix of qualitative and quantitative arguments. Due to the generic nature of this assessment, a traffic light system was established and, for each assessment area, a rating was given (Table 1).

Table 1. Assessment outcome definitions

Rating	Risk to disposability
Green	No foreseeable risk to disposability.
Grey	No, limited or partially applicable experimental data or industrial experience to substantiate disposability.
Amber	Limited risk to disposability, which may be addressed through further development work. Waste product behaviour falls at the frontier of what is typically considered acceptable for a given parameter.

Rating	Risk to disposability
🟥 Red	Significant risk to disposability. Waste product behaviour falls well outside what is typically considered acceptable for a given parameter.

Several factors can influence disposability, and their importance varies between different facilities and jurisdictions. Moreover, some assessment areas are of interest but cannot be assessed at this stage of the project because of the absence of data related to the package or the radioactive inventory of the wasteform. The criteria assessed included the physical form, mechanical stability, homogeneity, void space, free liquids before disposal, chelating/complexing agents and leaching properties. The evaluation is based on data from the WP5 partners and the results obtained are presented in Table 2.

Table 2: Summary table showing the disposability assessment of RLOW encapsulated in various geopolymer types.

Assessment area	Oil - MK	Oil - MK	Oil - Mix	Oil - BFS	Solvent - MK	Solvent - MK	Solvent - MK	SC - MK	SC - MK	SC - MK
	CIEMAT	NNL	KIPT	CVRez	NNL	POLIMI	UJV	POLIMI	UJV	CIEMAT
Physical form	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Mechanical stability	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟨	🟩	🟩
Homogeneity	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟩	🟨
Void space	▨	▨	▨	▨	▨	🟨	▨	🟨	▨	▨
Free liquids	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Chelating agents	🟩	🟩	🟩	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Leaching	▨	▨	▨	▨	▨	🟩	🟩	🟩	🟩	▨

3. Conclusions

In the absence of data on real packaged waste streams, a qualitative disposability assessment was implemented on oils, solvent and scintillation cocktails encapsulated in a geopolymer matrix, based on assessment criteria pertaining to the geopolymer wasteforms incorporating the different RLOW.

Disposability assessment is country-dependent as the criteria and their limits differ from country to country. The experiments were mainly realised at a laboratory scale, meaning that many criteria cannot be assessed, because they are waste package and/or dependant on radioactivity content. Moreover, the scale-up from desk scale to full scale can also result in different properties of the final package. The need for further research and development to bring the process towards a TRL of nine is acknowledged and is reflected in the EURAD-2 proposals. However, the analysis shows promising results for the encapsulation of oils, solvents and scintillation cocktails.

Note that Slovakia and the Czech Republic are already using geopolymer technology at TRL = 9 (SiAL and Alusil processes, respectively) to encapsulate problematic waste such as sludges and spent ion exchange resins for disposal.

References

[1] D. Alby, Disposability Assessment Report for Direct Conditioning, PREDIS Deliverable D5.4, 18 June 2024, Issue 1

5.7 Preliminary technical, economic and environmental analysis - Value Assessment of liquid organic wastes (Task 5.5)

Georges Daval, Tim Harrison, Delhia Alby, Jenny Kent, Stephen Wickham, (Galson Sciences Ltd, UK),
smw@galson-sciences.co.uk

Keywords: Value Assessment, radioactive liquid organic waste, technology selection, oils, solvents, scintillation cocktails, geopolymer

1. Introduction

Task T5.5 was dedicated to the preliminary technical, economic and environmental analysis of the direct conditioning route of RLOW. Deliverable D5.5 [ii] presents the activities carried out under Task T5.5.

This analysis, also termed Value Assessment, brought together research results in terms of waste loading, conditioning matrix performance, process cost, and product disposability to form a picture of what the overall performance of the direct conditioning route would be. These results were compared with current waste management practices to provide a comparison of how the novel direct conditioning route performs in comparison with current practices.

The overarching objective of this work is to provide technology developers and end-users with an objective assessment of the novel waste management routes across the full waste management lifecycle (from treatment through to disposal) to support decision making and industrial application of direct encapsulation technologies for three types of RLOW: contaminated oils, solvents and scintillation cocktails.

2. Description of work and main findings

The process starts with the identification of waste type and treatment/ conditioning technology combinations (called variant scenarios) for comparison with the typical current waste management approach used for these waste types, called the baseline scenario.

The five combinations of waste types and geopolymer formulations considered for Value Assessments as variant scenarios are:

- Contaminated oils, encapsulated in:
    - A metakaolin (MK)-based geopolymer.
    - A blast furnace slag (BFS)-based geopolymer.
    - A geopolymer based on a mixture of different raw materials, including MK, BFS and fly ash (FA). This formulation is referred to as the MIX formulation.
- Contaminated solvents, represented by a mixture of TBP and Dodecane, in proportions of 30/70 %vol encapsulated in a MK-based geopolymer
- Scintillation cocktails represented by the commercial product Instagel Plus, encapsulated in a MK-based geopolymer.

Baseline scenarios were selected for each waste type, thus enabling comparison of the direct geopolymer encapsulation routes for each waste type against a consistent baseline.

All the scenarios are presented in Table 1.

Table 1. Waste type / formulation selected as scenarios for value assessment.

Waste Type	Scenario ID	Formulation / process description	Waste
Oil	5.1.1	Encapsulation in metakaolin (Metamax) geopolymer	Nevastane oil
	5.1.2	Encapsulation in composite metakaolin (Metamax), blast furnace slag (Ecocem), fly ash (Italy) geopolymer	Nevastane oil
	5.1.3	Encapsulation in blast furnace slag geopolymer	Nevastane oil
	5.1.B	Two-step process: Step 1: absorption onto Experlite and transfer to a 115 L drum. The sorbent is then encapsulated with cement. Step 2: 115 L is placed into a 216 L drum. Cement is used to fill void between the two drums. Cement assumed to be ordinary Portland cement.	Nevastane oil
Solvents (TBP-Dodecane)	5.2.1	Encapsulation in metakaolin (Metamax) geopolymer	TBP-Dodecane (30/70)
	5.2.B	Step 1: transport to, and incineration at an incinerator using the IRIS process (assumption: at the CEA in France) Step 2: cement encapsulation of ashes in 200 L drum (assumption: co-located with incinerator).	Solvents (incl. TBP-dodecane 30/70) used in the PUREX process (spent fuel reprocessing).
Scintillation Cocktails	5.3.1	Encapsulation in metakaolin (Metamax) geopolymer	INSTAGEL Plus
	5.3.B	Two-step process: Step 1: absorption onto Experlite and transfer to a 115 L drum. The sorbent is then encapsulated with cement. Step 2: 115 L is placed into a 216 L drum. Cement is used to fill void between the two drums. Cement assumed to be ordinary Portland cement.	Scintillation cocktails in drums with or without stabilisation, conditioned or unconditioned, modelled for value assessment by INSTAGEL Plus

The criteria studied are the following ones:

Table 2. Summary of Value Assessment criteria.

Area	Criterion	Metric examples
Cross-cutting	Waste loading	Number of packages /m^3 of waste. Waste loadings (%vol).
Operational safety	Facility construction and decommissioning	Size of the facility. Recorded H&S accidents during construction. Judgement on facility complexity.
	Safety during pre-treatment operations	Shielding requirements. Operator dose rates. Sorting and segregation requirements.
	Safety during treatment and conditioning	Shielding requirements. Operator dose rates. Known or anticipated operational issues. Number of treatment and conditioning steps. Number of packages (waste loading).
	Safety demonstration requirements	Availability of safety case. Existing safety demonstrations / regulatory approvals.
Environmental impacts	Material environmental Impact	Known environmental impact of material excavation (qualitative). Calculated in LCA. Calculated (LCA) energy requirements for material manufacture and/or excavation.

Area	Criterion	Metric examples
		Number of waste packages (waste loading). Material requirements of alternative treatment options.
	Process energy requirements	Calculated (LCA) process energy requirements. Number of waste packages (waste loading).
Disposability / long-term safety	Secondary waste produced during the process	Type and quantity of secondary waste. Known and/or existing management routes for secondary waste, including its disposability.
	Disposability of final waste product	Existing disposability assessments. Known or anticipated issues with waste product characteristics.
Implementation	Process throughput and impact on waste management strategy	Full-scale facility throughput (m^3 of waste processed per unit time). Experimental facility throughput and estimated ease of scale-up. Inventory of waste for treatment and conditioning. Other implementation considerations (e.g. anticipated issues during scale-up, throughput-limiting steps).
	Material availability	Known and/or anticipated issues in sourcing materials, including considerations of material purity and consistency. Waste loading / number of waste packages.
	Technical Readiness Level (TRL)	TRL (1-9).
Financial	Cost of facility and of treatment and conditioning	Construction cost. Design cost. Decommissioning cost. Cost per m^3 of waste processed. Waste loading.
	Material costs	Calculated cost of materials (LCC).
	Cost of secondary waste management	Cost of secondary waste management per m^3 of waste.
	Disposal costs, including cost of disposal containers	Cost of disposal containers. Total volume of waste to be disposed of (waste loading).

For each evaluation, each criterion was considered in turn and the strengths and weaknesses of the variant scenario in comparison with the baseline scenario were discussed, identified and recorded. For each criterion, the panel was asked to agree on an outcome, or rating (geopolymer direct encapsulation vs. baseline), on a scale of -2 (much worse) to 2 (much better), via -1 (worse), 0 (neutral), and 1 (better).

3. Conclusions

Direct conditioning of contaminated oils and scintillation cocktails using Metakaolin-based, Blast Furnace Slag, or the MIX-based geopolymer formulations was found to result in better operational safety outcomes, compared with the current two-step cementation approach. The environmental impact of the overall process is also lower, whilst significantly reducing conditioning, storage and disposal costs. Several challenges were identified in the form of raw material procurement and purity. The need for further research and development to achieve a TRL of nine was also acknowledged and is reflected in future work described in the EURAD-2 proposals.

Direct conditioning of solvents using MK-based geopolymers was compared against a baseline comprising incineration followed by cementation. Geopolymer conditioning was found to result in improved safety and environmental outcomes. The same challenges to implementation as those highlighted above were identified. The economic impact of implementing this management route was not fully evaluated due to unavailability of cost data associated with incineration facilities. Current findings indicate, however, that disposal is likely to be more costly due to the relatively lower geopolymer waste loading compared with the loading achieved when thermal treatment is used.

Overall, direct conditioning of RLOW using the geopolymer formulations developed in PREDIS WP5 was found to result in positive economic, safety, and environmental outcomes.

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6 Scientific progress in Innovations in solid organic waste treatment and conditioning (WP6)

6.1 Economic, Environmental and Disposability Impacts of Novel Treatment Technologies for Radioactive Solid Organic Waste (Task 6.2)

Callum Eldridge, Georges Daval, GSL, ce@galson-sciences.co.uk

Keywords: Value Assessment, RSOW, Thermal Treatment, Disposability, Geopolymer

1. Introduction

PREDIS Deliverable 6.3 presented a high-level assessment of the economic, environmental and disposability impacts of some of the novel treatment technologies for solid radioactive waste studied in the PREDIS project [1]. This extended abstract summarises the approach taken to the assessment of these impacts and the overall conclusions of the task.

Understanding the 'value' of a given technology is highly contingent on the specific context in which the technology will be implemented and involves the consideration of a wide array of factors spanning the whole lifecycle of the treatment facility and waste. The Value Assessment work in PREDIS adopted the definition of value presented in THERAMIN Deliverable D2.5: *"the realisable benefit in safety, monetary and environmental outcomes that will arise from implementing this technology at a specified time" [2].* Recognising the very contingent nature of value, the Value Assessment work across the PREDIS project focused on producing a strategic assessment of value that would be suitable for adapting for different national contexts. Within Work Package 6 (WP6) there was a focus on a subset of the treatment technologies for Radioactive Solid Organic Waste (RSOW) studied in the PREDIS project.

2. Description of work and main findings

The Value Assessment methodology was developed collectively by all of the work packages in the PREDIS project to be generally applicable to variety of technologies studied in the project. The assessment was broken down into a set of attributes which each encompass a set of more specific data categories which were assessed against relevant phases of the facility and waste lifecycle. The attributes and data categories used in the Value Assessment work of the PREDIS project are presented in Table 1.

Table 1. Value Assessment attributes and data categories used in the PREDIS project.

Attribute	Data Category
Operational Safety	Waste pre-treatment requirements
	Waste post-treatment requirements (conventional and radiological safety implications)
	Waste operational safety issues
Environmental Impacts	Secondary waste generated per cubic metre waste treated
	Waste volumes generated during decommissioning
	Infrastructure material requirements
	Energy requirements
Timescale	Design, construction and active commissioning timescale
	Lifetime operating timescale
	Decommissioning timescale
Technical Readiness	Maturity of technology (TRL)
Strategic Impact	Indicative lifetime feed (m3)
	Throughput for process (full-scale facility) (m^3/year)
	Impact on disposability
	Potential to treat a wide range of waste groups (flexibility)
Strategic Cost Impact	Impact on total packaged waste volume
	Impact on total waste storage capacity
	Impact on total disposal capacity
	Infrastructure capital cost

Not all of the technologies studied in PREDIS WP6 were assessed; instead a subset of technologies were selected to provide a representative sample of the technolgies studied in the work package. Rather than consider each technology in isolation, a set of ‘treatment scenarios’ were defined which comprise a set of treatments which together convert a raw waste into a disposable product (typically thermal treatment followed by conditioning). A standard 200 litre drum was selected as the treatment endpoint for consistancy. This allowed for a like-for-like comaprison between different types of technologies as each scenario had equivilent start and end points. In addition to the novel treatments considered in PREDIS, a set of ‘baseline scenarios’ were defined to provide a comparison point which reflects typical current waste management practices for the waste types treated by the novel treatments. The scenarios selected for consideration are presented in Table 2.

Table 2. Treatment scenarios assessed in the WP6 Value Assessment.

Scenario ID	Raw waste	Treatment baseline or novel technology	Treatment output
6.1	Mixed organics and IERs	Thermal treatment with **IRIS process** and then **HIP of ashes** (USFD, NNL)	Cement encapsulated HIP cans in a 200 L drum.
6.2	Mixed organics and IERs	Thermal treatment with **IRIS process** and then **compaction of ashes** (CEA)	Cement encapsulated compacted pellets in a 200 L drum.
6.3	Mixed organics and IERs	Thermal treatment with **IRIS process** and then **encapsulation in Tuff-based geopolymer** (POLIMI)	Waste conditioned in a geopolymer matrix in a 200 L drum.
6.4	IERs	Thermal treatment by **Molten Salt Oxidation** then **encapsulation in geopolymer** (CVRez)	Waste conditioned in a geopolymer matrix in a 200 L drum.
6.0.A - Baseline	IERs	Direct cementation	Waste conditioned in a 200 L drum
6.0.B - Baseline	Mixed organics	Compaction and cementation	Waste conditioned in a 200 L drum

A mixed quantitative and qualitative approach was used to assess each Value Assessment catagory. To inform the Value Assessment ratings data were gathered on each treatment technology; the inputs to the Value Assessment process are outlined in the points below:

- Data from PREDIS partners involved in technical development of each respective technology. PREDIS partners provided data on aspects such as energy use, throughput, material inputs and secondary waste production for the technology.
- Preliminary data from the Lifecycle Assessment (LCA) and Lifecycle Costing (LCC) work undertaken in WP2 (D2.9) was used to provide information on the environmental impact of technologies for which data was available.
- Where data was not available, data from literature for comparable technologies was used as an approximation for the novel treatments, or expert judgement was used to estimate appropriate figures. Data for the baseline technologies were also taken from literature.

This data was curated and presented at the WP6 Value Assessment workshop. Workshop attendees assessed the relative performance of each treatment scenario in each Value Assessment category and arrived at a rating which indicated the performance relative to a baseline from -2 (much worse) to +2 (much better). The detailed Value Assessment ratings for each scenario are presented in D6.3 [1]. An overall rating for each technology was not derived as each assessment category will have a different relative importance for any given user, and should be weighted accordingly to determine the relative value of each technology combination.

For the ‘impact on disposability’ category, a bespoke approach was taken which evaluated the disposability risks associated with the final product produced in each scenario. Disposability considerations were taken from the list of parameters and requirements for waste acceptance to disposal facilities as identified in PREDIS D2.4 [3]. The disposability risks were evaluated for a number of disposal facility types representative of the range of potential disposal options that may be considered for the wastes included in the assessment; the assessed disposal facility types are presented in Figure 1. The outcomes of the assessment of disposability risks were incorporated into the Value Assessment by considering the extent to which each treatment scenario mitigated or exacerbated the disposability risks associated with the baseline scenario.

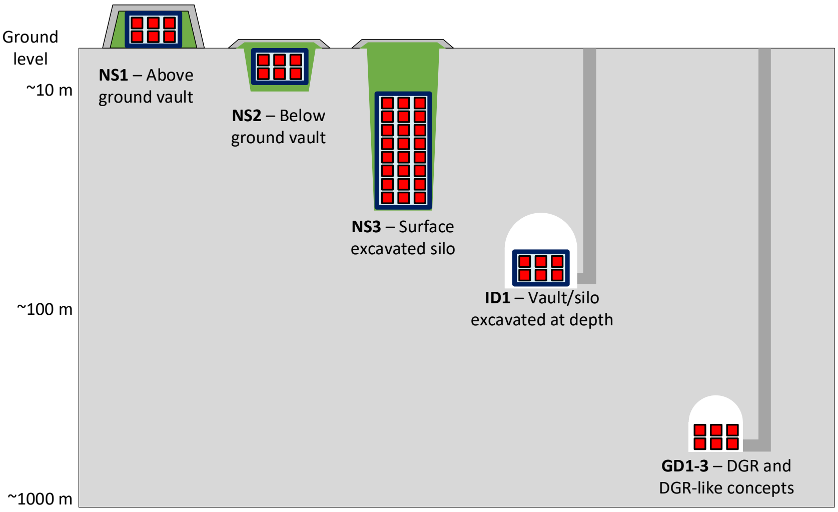

Figure 1. Disposal facility types considered in the evaluation of disposability impacts of the scenarios.

3. Conclusions

Overall, it was found that the evaluated novel treatment technologies typically provide benefits in terms of material environmental impact, package disposability and the disposal and storage costs for the product drums. This is offset however by the energy consumption, the safety and cost impacts of the additional facilities as well as the uncertainties associated with a novel technology. Further development of the new technologies to the point where operating TRL 9 versions of these treatment facilities are available would remove or lessen many of the negatives or uncertainties, in which case they could in future become more sustainable, less costly alternatives to the baselines. Which technology will perform 'best' in any situation will be highly dependent on the context and the priorities driving waste management. The unweighted assessment outcomes presented in D6.3 may be used at the basis for more detailed, context specific evaluations.

Acknowledgements

The Authors would like to thank to everyone who provided input to the Value Assessment, including all attendees at the WP6 Value Assessment Workshop, the technology developers Helene Nonnet, Samuel Walling, Ewan Maddrell, Andrea Santi, Eros Mossini and Vojtech Galek, and the Work Package 6 lead, Thierry Mennecart.

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6.2 Thermal treatment of the RSOW and characterization (Task 6.3)

H. Nonnet (CEA) ; E. Torres, A. Bahillo (CIEMAT) ; E. Mossini, F. Galluccio, A. Santi, E. Rizzi, G. Magugliani, E. Macerata, M. Giola, M. Mariani (POLIMI) ; Yu. Zabulonov, B. Zlobenko, A. Pugach, A. Rozko, Yu. Fedorenko (SIIEG) ; Veli-Matti Pulkkanen (VTT) ; Hélène Nonnet (CEA); Josh Radford (USFD), Claire Corkhill (USFD); Vojtěch Galek (CVRez), Anna Sears (CVRez), Petr Pražák (CVRez), Martin Vacek (CVRez), Jak Hadrava(CVRez)
helene.nonnet@cea.fr

Keywords: Thermal treatment, waste characterization, radioactive solid organic waste (RSOW)

1. Introduction

This report presents descriptions of the different organic solids treatment processes used and developed at CIEMAT, POLIMI, SIIEG, VTT, CEA, UFSD and CVRez.

2. Description of the thermal treatment processes and main characterization of the waste

CIEMAT:

In Spain, thermal treatment, in particular, incineration is used for the management of liquid organic wastes, mostly scintillation cocktails. Scintillation cocktails (from non-nuclear producers) are incinerated at El Cabril disposal site and subsequently, ashes are solidified in mortar to solidify them in monolithic blocks. The incinerator used in the disposal facility is of the excess air type, with a double combustion chamber. A temperature of 800°C is reached in the first reactor, and 1000°C in the post-combustion chamber. At the chamber outlet there is a silicon carbide high-temperature filter. The fumes are cooled by dilution in fresh air to 140°C. The flue gases then pass through very high efficiency filters and once filtered are discharged through the stack.

Currently, experiments are ongoing abroad to treat decontamination effluents by incineration (slags and fly ashes will be sent back to Spain). Regarding SIERs, once they are spent, slurries from different purification systems are radiologically characterized and later, immobilized by cementation. After the radiological characterization of the waste packages, if they meet the WAC for disposal, they are shipped to the storage facility.

For PREDIS project, two types of IERs of frequent use in Spanish NPPs were chosen: a strong acid cationic type (Amberlite™ IRN-77) and a strong base anion type (Amberlite™ IRN-78). Both resins have a scaffold based on copolymers of styrene and divinylbenzene, being its characteristic functional groups sulphogroup –SO3H (H-form of a resin) for cationic IRN77 and quaternary aminogroups anionic IRN-77.

Prior to the preparation of the surrogates, different waste streams from the primary and secondary circuits were examined, considering both chemical and radiological aspects. Doping of the SIERs surrogates was tailored assuming a target Volume Reduction Factor (VRF) of 5 so that, the activity of the final manufactured waste package could meet the WAC of the disposal facility.

Surrogates used for thermal treatment consisted of a mixed form of 50/50 cationic and anionic IERs, doped according to the specifications provided by two of our end users. Resins were saturated with boron and traces of Sr, Cs and activation products (Co, Cr, Zn, Fe, Ag, Ni). For the saturation of the resins, doping solution was buffered to pH 10.2.

Before carrying out the thermal treatment of any material, a previous chemical analysis of the material is needed. In this case, a detailed chemical analysis of raw IRN77 and IRN78 and the doped mixture of IRN77/IRN78 (50:50) was carried out.

Chemical composition of the ashes basically consists of a carbon (~ 75%), hydrogen (~ 5%), nitrogen (~1%) and sulphur (~7%). Trace analysis suggest that no volatilization of minor doping elements have occurred during the thermal treatment of the surrogates.

For the safe storage and disposal of SIERs, thermal treatment can be an interesting option to avoid problems such as gas and organic complexants generation by radiolysis, cracking of cemented waste forms due to the swelling of SIERs.

Prior to this thermal treatment, removal of the moisture from the IERs is required. Reducing this moisture content is important in order not to excessively penalize the thermal efficiency of the reactor. For this reason, a pre-dehydration step is needed to optimize the energetic balance of the process.

For this project, thermal treatment of SIERs surrogates was conducted in a low-temperature range (375 to 450ºC). Main advantages of treating SIERs at low-temperature (375-450ºC) consist basically of:

- an easier-to-handle product from a radiological point of view, as volume reduction factor is in the range of 4 to 5.
- preventing the loss of volatile elements, such as Cs.

Under such operational conditions, resulting product of the thermal treatment of the SIERs surrogates seems to avoid traditional problems associated to the cementation of SIERs. Currently, in the cementation of traditional OPC matrices, swelling of SIERs results in the cracking of cemented drums, limiting the SIERs content in waste packages to a typical range of 12-15%wt.

Thermally-treated waste obtained seems to be chemically stable. However, stability in highly-alkaline environments could be an issue of concern and further assessment needs to be carried out in order to guarantee the long-term performance of the reconditioned waste.

POLIMI:

Spent ion-exchange resins (IERs) produced in nuclear plants and used for the decontamination of radioactive effluents come in huge amount as low-level waste. They comprise a material which is challenging to encapsulate as it stands: it is physically and chemically unstable, and it is incompatible with the inorganic matrices developed so far. Hence, spent IERs are preferably treated to obtain a proper by-product, suitable for conditioning. POLIMI is currently working on two different treatment processes: an oxidative pyrolysis and a Fenton-like wet oxidation.

The oxidative pyrolysis process was run in batches, mildly heating samples of spent cation-exchange resins in a muffle furnace. The surrogate waste was prepared by contacting pristine beads with aqueous solutions containing at least one of the following stable isotopes of Co, Ni, Sr, Cs, Nd, and Eu, chosen as representatives of fission and activations products, and for their different chemical behaviour. The ashes obtained downstream of the process have been analysed and characterised to assess the possible loss of the contaminants, to measure the achieved reduction of waste mass, and to identify the chemical form. These data are needed to understand the feasibility of their encapsulation in geopolymers.

POLIMI has also investigated Fenton-like wet oxidation as it is an alternative and green strategy to manage radioactive organic waste such as spent ion-exchange resins.
A surrogate waste was prepared by loading nuclear grade cation-exchange AmberLite IRN77 beads (DuPont) with nitrate salts of stable Co, Ni, Sr and Cs. Anion-exchange resin is AmberLite IRN78 (DuPont) and is doped with KCl and KI salt (Sigma-Aldrich, analytical grade) solutions. The saturation factor with respect to the ion exchangeable resin sites ranges from 10 eq.% to 40 eq.%. Some experiments are performed on cationic resin alone, other with a mixed bed resin.

SEIIG:

When decommissioning nuclear facilities, it is necessary to process large volumes of radioactive waste, an industrial problem. Over the past few years, there have been several innovative projects to develop specific heat treatment processes. The literature broadly describes studies of the low-temperature pyrolysis of spent IERs. An earlier study by Matsuda et al. investigated the influence of the functional sulfonic acid group on the pyrolysis characteristics of cation exchange resins. These studies focused on the pyrolysis conditions that allow the retention of radioactive elements in a pyrolysis residue. The papers studied low-temperature pyrolysis of spent ion-exchange resins in a pebble bed at approximately 500°C with keeping radioactive cesium species in the solid pyrolysis residue, have led to valuable reductions in waste volumes.

The decomposition of IER by thermal gasification results in significant volume reduction, which was demonstrated successfully in many projects. The State Institution “Institute of Environmental Geochemistry” NASU (IEG) research group with partners has worked for several years to develop a hybrid process of gasification of IER and has designed new and innovative equipment for safe and efficient deep processing of thermal treatment of the RSOWs, with obtaining useful energy products (electricity, hot water, heating). The system for the thermal treatment of radioactive waste consists of a thermal treatment unit with a plasma torch and gas cleaning technologies, a heat exchanger, and a control unit.

The thermal treatment unit consists of a hopper for loading waste, a gasification chamber, a gas afterburner, a heat exchanger, and a smoke exhauster. The lining is made of high-temperature ceramics.

The primary material used in this study is KU-2-8 cation exchange resin supplied by the VAT "AZOT", GOST 20298-74. The resin consists of sulfonic acid groups (-SO_3H) and an insoluble skeleton formed by copolymerisation of styrene and divinylbenzene.

Cation-exchange resins represent spherical granules of high-molecular polymeric compounds (styrene-divinylbenzene copolymer) with gel structure. The diameter of granules is 0.315-1.25 mm.

During the experimental work, a surrogate waste cationic IER has used for loading. Processing occurs with the sintering of the IER ash. Methods of DTA, SEM, and XRF to study decomposition and the resulting ash. Solid residue (ash) is dependent on thermodynamic parameters and process speed. The thermal degradation study of acid (–SO3H+) cationic IER shows a slight mass loss of 55% up to 900°C. The slight weight loss of acid IER was attributed to forming of sulphonyl and sulphur bridges between base polymers after the dehydration reaction.

VTT:

VTT’s thermal gasification process was successfully used to produce enough amounts of thermal treated waste for further testing in Tasks 6.4 and 6.6. The process was verified to be a suitable thermal treatment method for organic IXR in EU-THERAMIN-project.

The gasification test trials were carried out with an atmospheric pressure bench-scale Bubbling Fluidised Bed (BFB) gasifier (**Error! Reference source not found.**) at Bioruukki - VTT’s Piloting Center (THERAMIN, 2019). T he bed diameter of the reactor is 100 mm and the freeboard diameter 150 mm. The test facility is heated with external electrical heaters to compensate heat losses, and fluidising gases are preheated electrically to about 310°C below the grid.

The start-bed was added into the reactor as a batch before the fuel feeding was started. Al_2O_3 was used as a bed material. The IXR was fed from the live-bottom fuel tank equipped with the screw feeder. The gasification product gas was cleaned by a high-temperature filter unit. Easily volatile compounds condensate to the particles when the gas is cooled down to the temperature low enough and harmful compounds (e.g., Cs) are removed from the process with the filter dust.

IXR has such low ash content that bottom ash removal was not needed during the treatment process. No additional bed material was needed after the start-up. Minimised need for make-up bed material reduces the overall bottom ash waste, which has to be immobilised and disposed in a similar way as filter ash.

Concentrations of Al, As, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, K, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, Ti, V, Zn, Ba in 11 solid samples were measured with ICP-OES (5100 SVDV, Agilent Technologies) and ICP-MS

CEA:

The ashes considered in these studies come from the IRIS incineration pilot process (Installation for Research on Incineration of Solids) developed at CEA Marcoule for R&D support and devoted to the treatment of the organic waste contaminated by α-emitting actinides from glove boxes in the nuclear industry.

This pilot is working exclusively under inactive environment, and the ashes produced come from the incineration of a mix of different organic solids and IER resins. This leads to achieve a volume reduction of the waste to about a 30 factor. IRIS is a three-step process implemented in rotating kilns.

The ashes have a high flying behaviour with a density of 0.2 $g.cm^{-3}$ and their particle size is mainly centered between 0.1 to 1 mm.

Elementary chemical characterisations have been done. The ashes are mainly composed of aluminium, silicon, calcium and zinc.

SEM and structural characterizations have been done. The micro particles have a very porous aspect and are partially amorphous. The crystallized phase are composed of ringwoodite, anohrtite and chlorapatite $Ca_5(PO_4)_3Cl$.

USFD:

The use of Plasma vitrification for the treatment of nuclear waste has been assessed, showing that vitrified waste products can be successfully produced with less requirement for waste pre-treatment compared to other thermal treatments. A case study has demonstrated the viability of plasma vitrification and the chemical and physical properties of the pre-treated waste and the final wasteform are presented here.

Plasma vitrification has been demonstrated to be a possible immobilisation route for several wastestreams. The key benefit to using plasma vitrification over other thermal treatments is the minimal pre-treatment of wastes prior to the vitrification process as the study discussed here demonstrates the capability of processing wastestreams directly from storage drums. In addition to the lack of pre-treatment required, plasma vitrification is capable of producing durable and stable wasteforms comparable to those produced using alternative thermal processing routes. The samples discussed in this report represent the variation in chemical composition found in PCM wastes in the UK. Despite the difference in the composition of the wastestream, all wasteforms were successfully produced to be within the target compositional envelope, demonstrating the operational flexibility of plasma vitrification.

CVREZ:

The CVRez’s main contribution to this report was using their Molten Salt Oxidation (MSO) thermal treatment process. During this process, waste is generated, which needs to be reprocessed or disposed of. This report shows the MSO process and characterises the generated waste.

MSO is a thermal process designed for the disposal of organic waste. Technology has been well-known since the end of the fifties of last century. This process is based on the flameless decomposition of organic wastes in high molten salt temperatures. Dosing an oxidising medium with the waste below the molten salt's surface is necessary to complete the organic material's oxidation [1]. Other non-combustible inorganic substances, i.e., heavy metals or possibly radionuclides, are trapped in the molten salt and can be easily separated. [1-3] All organic carbon-containing wastes, together with excess combustion air, are conducted in the reaction vessel below the level of the salt melt, which has a temperature of 800-950 °C. The melt is usually Na_2CO_3, K_2CO_3, Li_2CO_3, or their eutectic mixtures.

The MSO process has several advantages over combustion. The operating temperature depends on the used alkali salts, but it is generally lower than in direct combustion. Alkaline carbonates and mixtures have melting temperatures from 400 °C K to 850 °C. The alkaline molten salt also acts as a scrubber for other acidic substances such as SO3, SO4, and NOx, eliminating the need for a flue gas cleaning system. The molten salt has the function of a stable heat transfer medium which resists thermal shocks and is thus able to maintain rapid process fluctuations. This technology is also suitable for disposing of explosive materials, detonators, or other energetic materials.

Despite many advantages, MSO technology has its drawbacks. One of the main disadvantages is the increased economic cost when compared to combustion processes. It is necessary to heat the alkali salt to its melting point and keep it in a liquid state. After the initial heating, onward heating is ensured by the supply of waste and oxidising medium during the disposal of energy-rich wastes. Another disadvantage is the high corrosivity of the environment. Construction materials do not have a long service life if they are in contact with molten salts at high temperatures and in an oxidising environment.

As the main generator of RSOW from the thermal treatment process of Molten Salt Oxidation CVRez was able to supply this waste to other partners. This waste must be removed from the storage tank and reconditioned for encapsulation. That means waste was pre-dried in the air, ground for smoother particles, and dried in the oven for 65 °C to get low moisture levels as the moisture could negatively affect the final product. XRD analysis of the dried-up waste salt samples have been performed. The phase distributions in each sample have been identified with Natrite (Na_2CO_3) as the primary phase.

This deliverable shows the MSO thermal treatment process and its possibilities to decompose organic waste, especially IER. The technology is suited as a two-stage reactor system to fully decompose residual organics and completely oxidise flue gas into CO_2 and H_2O with only tracers of CO, SO_3 and NO_x. After releasing the waste molten salt into the water tank, the undissolved salt needs to be physically prepared for immobilisation. This process included air drying, grinding to fine particles, and drying in the drier. The waste was then analysed via XRD and XRF analysis. The moisture content was also determined. The XRD analysis showed that Natrite, Essenite, Trona and Thermonatrite mainly composite MSO waste.

The samples of this improved salt were sent to the PREDIS partners to study their immobilisation techniques.

3. Conclusions

The expectations set at the start of the project for this task have been largely met and have enabled us to provide several options for the thermal treatment of the RSOW in order to change their initial characteristics and physico-chemical properties. This leads to their direct immobilization thanks to the good stability of the end-products (plasma slags or glassy materials), or to their immobilization using geopolymer, cement-based materials or molten glass coating (ashes, residues…).

In addition, the TRL levels of certain processes have progressed and can be estimated to have evolved from 4 to 6 for the Molten Salt Oxidation process and from 2 to 3 - 4 for the Wet Oxidation route.

Acknowledgements

The Authors would like to thank to everyone who provided input to this Task 6.3.

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6.3 Enhanced salt preparation and immobilisation of solid organic wastes (Task 6.3)

<u>Vojtěch GALEK</u>, Petr PRAŽÁK, Martin VACEK, Jan HADRAVA
Research Centre Řež, Hlavní 130, Husinec-Řež, 250 68, Czech Republic, cvrez@cvrez.cz

Keywords: Geopolymer, Molten Salt Oxidation, molten salt waste

1. Introduction

Through the PREDIS project, the Molten Salt Oxidation (MSO) waste became a challenge to immobilise properly in the cement or geopolymer matrix. In task 6.4, the involved partners were trying to find a suitable recipe for stabilising this sort of waste. Several recipes were developed with cement-based or metakaolin-based matrices, but the stability rapidly decreased with a higher waste loading. Samples exposed to the water or humid environment showed a blooming effect or break after a short time. Some recipes had promising results. Nevertheless, a higher number of low-performance samples led to the waste improvement before stabilisation process. The Enhanced salt (chemically changed MSO waste) was developed for better stabilisation performance.

We aimed to prepare several Enhanced salt samples and immobilise them in the metakaolin-based geopolymer. The samples were analysed using a compressive strength test to evaluate their mechanical strength and XRD and SEM analysis to evaluate the structure.

2. Description of work and main findings

The process started with the preparation of Enhanced salt. The laboratory setting is shown in Figure 1. After discussing the work with colleagues from POLIMI and SCK-CEN, the reaction of MSO waste solution with calcium hydroxide solution was carried out. The formed sediment was then filtered, dried, and analysed with XRD analysis to determine the quantitative amount of Na_2CO_3 and $CaCO_3$.

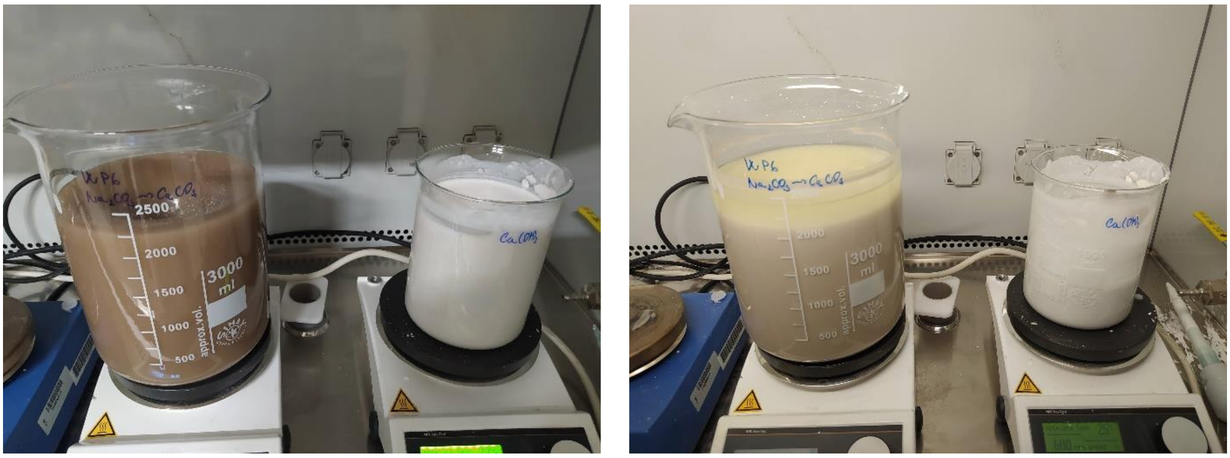

Figure 1. The preparation of Enhanced salt: Before the reaction (left), after reaction (right).

The prepared salt had an average composition of 52.6 w.% Na_2CO_3 and 47.4 w.% $CaCO_3$. It was then immobilised in the LK10 recipe.

The aim was to immobilise from 5 to 15 % waste loading, and the samples were cured in three different environments. The results of compressive strength are shown in Figure 2.

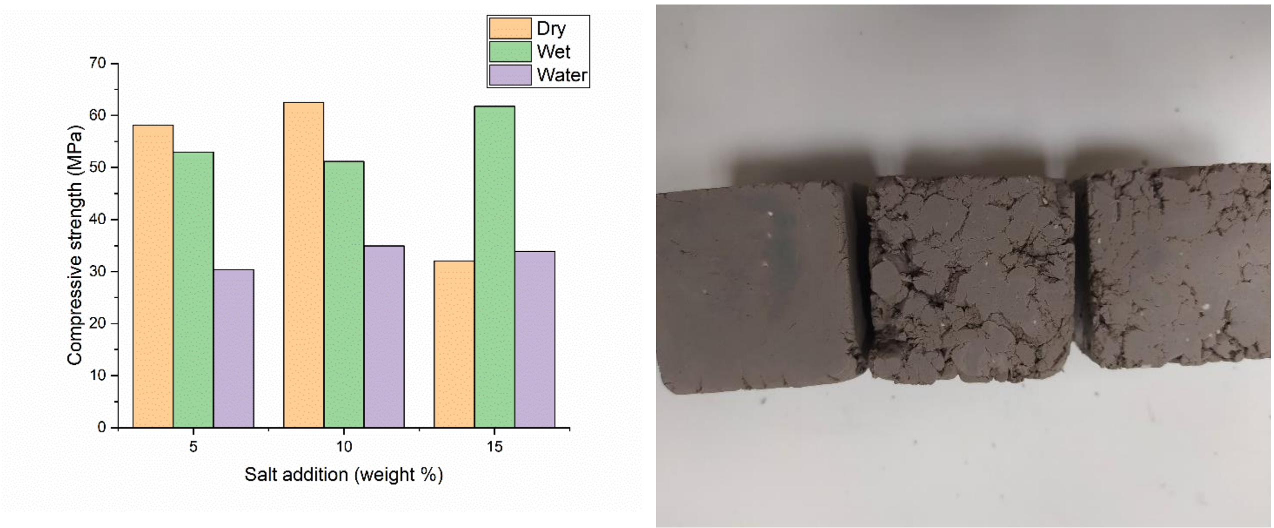

Figure 2. The results of the compressive strenght test (left) and fast setting time of the samples with 15 % waste loading before curing (right).

The compressive strength test results showed promising outcomes as samples did not crack, and no blooming effect was observed even in water-immersed samples. The results ranged from 30 MPa up to 60 Mpa. However, samples showed a very fast setting time with a 15 % waste loading set before moulding. It is showed that first sample (Figure 2) was still liquid and the other samples were almost solid. The time for each sample to cast was 15 seconds. This phenomenon was not ideal as it prevented more waste-loading samples from being prepared and evenly mixed. Therefore, the adjustment to the recipe was needed. The additional 5 w.% of water content was aimed to prolong the setting time. Another batch of samples was prepared and left to cure in three different environments. The results are shown in Figure 3.

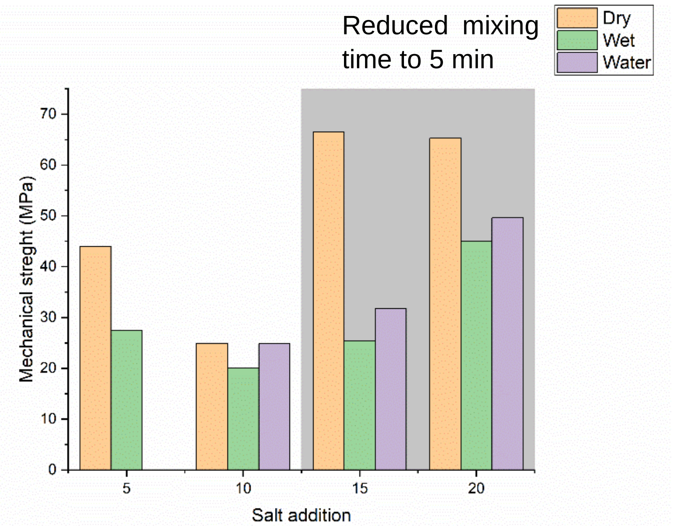

Figure 3. The results for second batch of samples with 5 w.% of additional water.

The results showed that the additional water content did not prolong the setting time as intended. The 5 and 10 % waste loading showed worse compressive strength than the first batch of samples. Therefore, for 15 and 20 % waste loading, the mixing time was reduced from 10 minutes to 5 minutes. With additional water, the homogeneity of the mixture was increased, as shown in the results, and the lower mixing time enabled more waste loading to be integrated with the smooth structure of the samples shown in Figure 4. The compressive strength increased gradually with waste loading, and samples showed good structural integrity after exposure to the high moisture environment and water immersion.

Figure 4. The second batch of prepared samples.

3. Conclusions

The conducted experiments were focused on preparing and immobilising the Enhanced waste arising from the MSO technology. The original waste consists mainly of Na_2CO_3, and the previous immobilisation had satisfactory results. However, when exposed to a high-moisture environment, the samples cracked or had a significant blooming effect, which would lead to high leaching. Therefore, enhanced salt was chosen for preparation.

The results obtained with Enhanced salt showed that this is a new approach to immobilising persistent waste into a stable form. Samples were stable in a highly humid environment and showed promising results after curing and immersing in water. Preparing this improved waste type is not difficult, and a chemical reaction tank can be added to the MSO waste stream processing. The continuing research will focus on increasing waste loading and optimising the mixture preparation.

6.4 Densification (Task 6.5)

Russell Hand, Lucy Mottram, University of Sheffield, UK r.hand@sheffield.ac.uk

Keywords: Densification, Hot Isostatic Pressing (HIPping), wet oxidation waste, IRIS ashes

1. Introduction

Densification has primarily focussed on the use of hot isostatic pressing (HIPping) supported by some cold-press and sinter work. Specifically, the densification of wastes from different parts of the PREDIS programme (polymeric ion exchange wastes, wet oxidation or wetox wastes and ash wastes) has been investigated and the outcomes of these investigations are summarised below.

2. Densification experiments and outcomes

Wasteform production using a hot isostatic press (HIP) typically involves the conversion of a powdered or granular material into a solid block. This is achieved by packing the loose material into a steel canister, which is sealed and then transferred to the HIP pressure vessel where both heat and pressure are applied, producing a solid product fully encased within the steel container with significant volume reduction (see Figure 1).

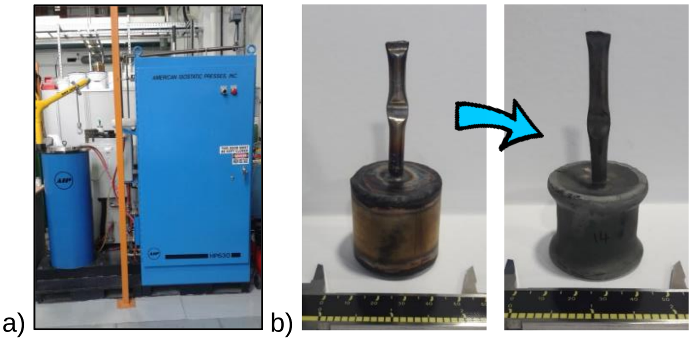

Figure 1. a) AIP6-30H: Research HIP at USFD and b) before and after of a canister HIPped at 1250 °C and 103 MPa for 4 hrs.

2.1. IRIS ashes

HIPping of ashes arising from the IRIS process (WP 6.3) supplied by CEA was successful. Four different compositions were HIPped at 1250 °C, 100 MPa for 2 hours: the as-received ash; ground ash; ground ash with the addition of 5 wt% sodium tetraborate; and ground ash with the addition of 5 wt% sodium aluminate. Grinding improved the homogeneity of the HIPped wasteform. HIPping with 5 wt% sodium tetraborate produced the most successful outcome with most of the ash melting and no crystalline silicates (see Figure 2); this composition was also least aggressive to the HIP canister. Samples of these materials were sent for long term dissolution trials at SCK-CEN and USFD as part of WP 6.6.

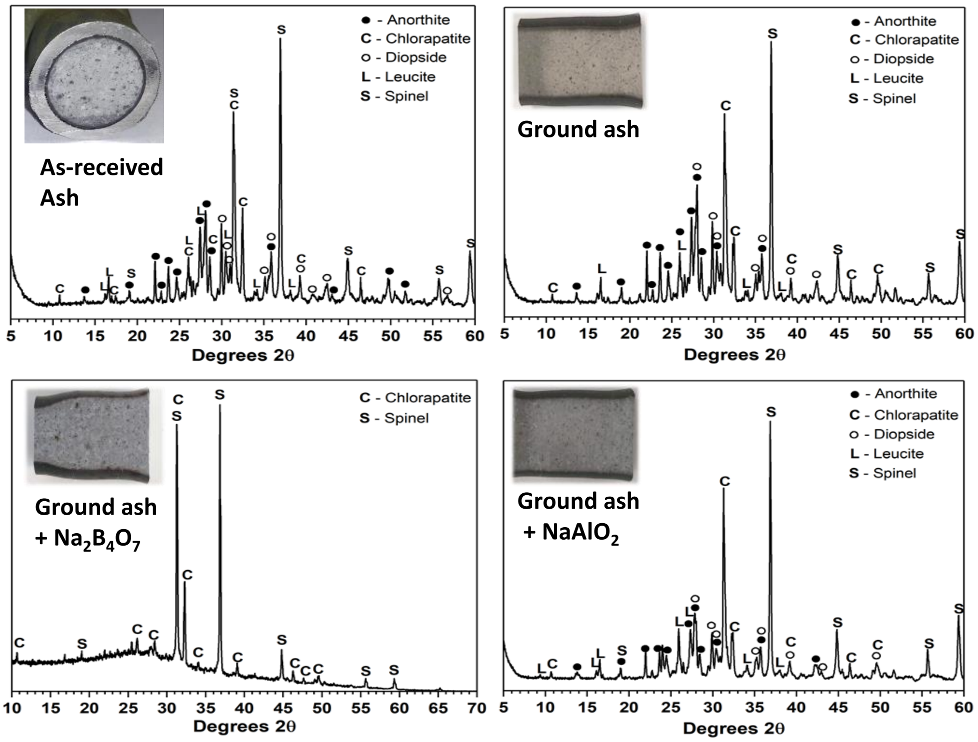

Figure 2. HIP canister cross sections and associated X-ray diffraction patterns for the different IRIS ash HIPping trials.

2.2. Wet oxidation wastes

Preliminary attempts were made to densify samples representative of wet oxidation (wetox) sludges from WP 6.3 using cold press and sintering. The CuO-Fe_2O_3 phase diagram [1] indicated that the wetox composition should form delafossite ($CuFeO_2$) whereas the addition of extra iron could form more beneficial spinel ($CuFe_2O_4$) compositions (see Table 1). The materials were milled, dried, pressed and heated to 1050 °C for 4 hours. A pure spinel wasteform was obtained with the highest iron additions (see Table 1).

Table 1. Target phase and phases obtained by cold press and sintering of wetox wastes

Composition	Fe_2O_3:CuO	CuO/(CuO+Fe_2O_3)	Target phase	Phases obtained
1 (wetox)	0.5	0.67	$CuFeO_2$	$CuFeO_2$, CuO, $CuFe_2O_4$ (minor)
2	0.67	0.60	$CuFe_2O_4$	$CuFeO_2$, CuO, $CuFe_2O_4$
3	1.21	0.45	$CuFe_2O_4$	$CuFe_2O_4$

HIP trials of wetox wastes have been undertaken both at the University of Sheffield and on a larger scale NNL. HIPping was successful at the small scale (see Figure 3) but both of the larger scale trials at NNL were unsuccessful, with the second trial resulting in a cracked wasteform arising from the presence of excessive nitrogen (see Figure 4). The reasons for this are being investigated.

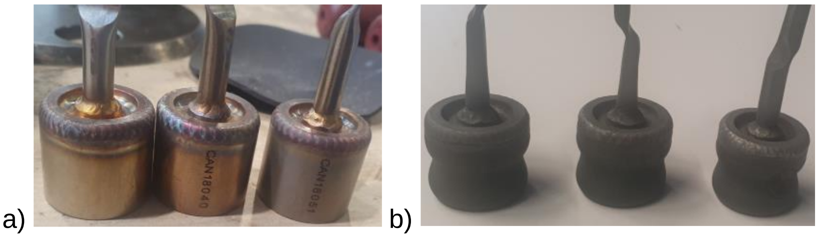

Figure 3. USFD HIP canisters of wetox waste a) pre-HIPping and b) post HIPping.

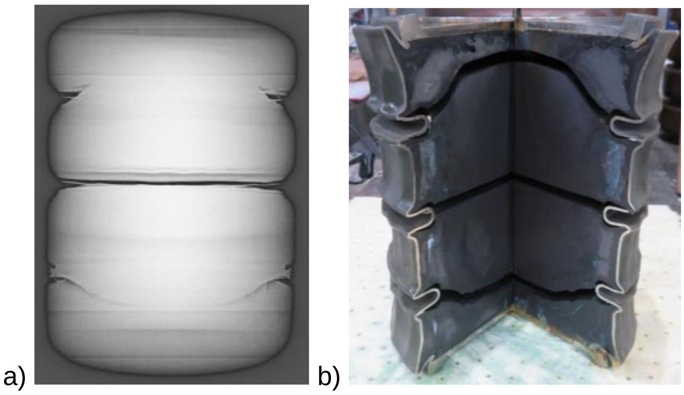

Figure 4. HIP canister from the second scale up trial showing cracking: a) X-ray radiograph of the canister and b) sectioned canister.

2.3. Ion exchange wastes

Attempts were made to HIP Amberlite IRN-150 ion exchange resin and a 1:1 mixture of Amberlite IRN-150 and low density polyethylene. Both attempts were unsuccessful as the HIP canisters could not be welded shut without causing melting or thermal degradation of the waste (see Figure 5).

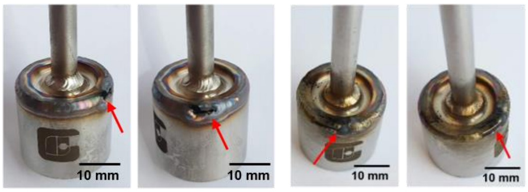

Figure 5. Canisters containing Amberlite IRN-150 showing welding failure.

A potential solution might be to use larger, taller canisters, with 50% packing, where the top of the canister could be filled with steel spacers to mitigate the degradation of the polymer although there would still be a high risk that the polymer within the canister would be exposed to high enough temperatures to cause polymer melting or thermal degradation. However using the equipment and canisters available at USFD, it was deemed that HIPping of polymeric material is not achievable.

3. Summary

Overall densification of a wetox waste and the IRIS ash waste have been demonstrated at the small scale.

Cold press and sinter of the simulant wetox wastes demonstrated that the phase assemblage of the wasteforms can be driven towards spinel by the increasing the fraction of Fe_2O_3 in the batch. Small scale HIP trials have also been successful but thus far larger scale HIPing of simulant wetox wastes to demonstrate the potential for scale up has not been successful.

HIPping of the as-received IRIS ashes formed a solidified product which, at least partially, melted to form a crystalline multi-phase wasteform. Gentle dry grinding of the IRIS ash produced a solidified and dense mutli-phase wasteform. The addition of 5 wt. % sodium aluminate into the IRIS ashes appears to have successfully formed a solidified wasteform. Sodium tetraborate was the most successful additive, resulting in a glass-ceramic material in which the ash was almost completely melted. Although some canister-wasteform interaction occurred, it appeared to be less aggressive towards the canister than other formulations. All of the latter three compositions were taken forward for durability testing under WP 6.6.

HIPping of polymeric ion exchange resins was unsuccessful as the polymeric wastes started to break down during the process to weld on the canister lid meaning that the HIP canisters could not be sealed.

Acknowledgements

The authors thank Hélène Nonnet (CEA) and Ewan Maddrell (NNL) for their contributions to the work. At the University of Sheffield we specifically thank Sam Walling, Josh Radford, Neil Hyatt and Claire Corkhill who conducted the earlier parts of the USFD contribution.

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6.5 Physico-chemical characterization of reconditioned waste forms and stability testing (Task 6.6)

E. Myllykylä (VTT); E. Torres (CIEMAT) E. Mossini, A. Santi (POLIMI), M. C. Alonso (CSIC), R. Fernández (UAM), G. Vettese, G. Law (UH), B. Zlobenko, A. Rozko, Yu Fedorenko (SIIEG NASU), K. Ferrand, L. Frederickx (SCK CEN), H. Nonnet (CEA), L. Mottram, R. J. Hand (USFD), L. Stefanini, T Oey (VTT)
emmi.myllykyla@vtt.fi,

Keywords: Radioactive solid organic waste, RSOW; long-term performance, durability, formulation, metakaolin, blast furnace slag, fly ash, material behaviour, durability.

1. Introduction

The main objective of this task was to study the chemical and mechanical durability of different waste forms produced from low and intermediate level waste or waste surrogates in previous tasks of work package, WP6 (6.3, 6.4, and 6.5). The materials which were studied can be classified to 3 different categories: geopolymers, cements and glass/ceramic materials. The disposability performance can be compared to “waste acceptance criteria” (WAC).

Studies contained characterisation of the initial form of produced waste forms, leaching experiments, and post-mortem characterization of the leached materials after leaching periods from 3 months to 24 months. The aim was to estimate the expected mechanical and chemical behaviour of these waste forms during disposal and increase the scientific understanding behind the observations.

During the project special attention was paid to increase the comparability of the results. Most of the leaching experiments were conducted according the PREDIS leaching protocol and the calculations and presentation of the results was also unified.

2. Description of work and main findings

When disposed, the reconditioned RSOW waste forms might end up in contact with water during the lifetime of the repository. The interaction of waste matrix with leachant might lead to; 1) release of radionuclides from the conditioned waste form, 2) degradation and chemical alteration of matrix under disposal conditions, and 3) changes in the physical properties of the waste matrix. These three points were the main objectives of this research.

In the beginning of the project, partners defined together a reference leaching protocol based on the feedback given by End-Users Group. A synthetic cementitious water with pH ~12,7, defined already in ACED-EURAD project [1], was selected as a leachate. The chemistry of this solution simulates the cementitious surroundings, which will prevail in the most disposal facilities in the case the intruded water gets into contact with conditioned waste. The protocol also contains parameters as the surface area to leachant volume ratio, temperature, sampling intervals to enable the comparison of the results provided by different partners. Priorities for elemental analyses of leachate samples and characterization of post-mortem solid samples were also defined to provide data for comparison [2]. For leachate analyses the pH, electrical conductivity, and main elements (Si, Al, Ca, B) were listed to the protocol to be followed. Whereas, trace elements, main anions, TOC and colloidal particle size were defined as optional analyses. The characterization of solids contained compressive strength, XRD and SEM-EDS according to protocol and MIP/BET, FTIR, TG/DTA, NMR, Micro-tomography and EXAFS were listed as additional analyses.

Some additional leaching experiments were also conducted either by following the ANSI standard protocol [3] or national requirements. In these experiments either deionized water or water sampled from disposal site was used as a leachant.

The leached geopolymer, cement and glass/ceramic samples are listed in Table 1.

Table 1. Different candidate waste matrices, fabricated in previous tasks and used is T6.6 for physico-chemical characterization and for leaching experiments.

Institute	Matrix composition	Type of waste	Waste loads tried (%w/w)	Challenges found	Homogeneous distribution of waste	Compatibility waste-matrix
Geopolymer						
VTT - UH	Metakaolin-based (2 types)	Ashes	15 & 50	Mechanical strength decreases with waste load (but > 10MPa)	Yes	Good
SCK·CEN	MK+BFS+$Na_2Si_2O_5$	Molten salts	10 & 20	Unable to mix high viscosity salt slurries	Yes	Good
CSIC/UAM/CIEMAT	MK+BFS+Na_2SiO_3	IERs ashes	Up to 30	Waste reduces compressive strength	Yes	Acceptable, but porosity increased
POLIMI	Volcanic tuff, BFS, FA, NaOH	IRIS ashes	Up to 50	Delayed setting	yes, by visual inspection	Good but setting time increases
		Molten salts	Up to 20		yes, by visual inspection	Good
		Ashes (dryox)	Up to 40	Not yet assessed	yes, by visual inspection	Good
		Ashes (wetox)	Up to 35	Poor mechanical properties	yes, by visual inspection	Good
Cement						
VTT-UH	CEM I	Ashes	15 & 50	Mechanical strength decreases with waste load	Yes	Good
SCK·CEN	CEM I (BFS, limestone filler and sand, lime & silica fume)	Molten salts	10 & 14	Unable to mix: high viscosity salt slurries	Yes	Good
CSIC/UAM/CIEMAT	CEM I/42.5 SR	IERs ashes	Up to 30	The waste substantially delayed setting and reduced the mechanical properties	Yes (μ-CT)	Low compatibility: poor adhesion waste/matrix and the porosity increased
	CEM III/B32.5	IERs ashes	Up to 30	The waste delayed setting and reduced the mechanical properties	Yes (μ-CT)	Acceptable compatibility, but the porosity increased
Glass/ceramic						
USFD	Glass	IRIS ashes	95	------		
	Glass-ceramic	IRIS ashes	95 & 100	------		
SCK·CEN	Glass-ceramic	IRIS ashes	95	------		
CEA	Borosilicate & ashes (SiO_2, Al_2O_3, Na_2O, CaO, B_2O_3)	IRIS ashes	30	------	No, some crystalline phases	Good, some crystals and increased porosity
	Densified thermally-treated ashes (SiO_2, Al_2O_3, CaO, ZnO)	IRIS ashes	100	------	Yes, sintered pellets	

For results of the experiments, shared data sheets were used to calculate and collect the achieved data. The data inserted into these sheets includes e normalized mass loses, leaching indices and pre and post characterization observations.

The leaching results indicated that glass/ceramics materials had greater durability in comparison to geopolymer and cement matrices. For all studied candidate waste matrices the leachability indices were above the threshold limit > 6. The release rates of contaminant elements (e.g. Cs, Ce, Sr) and elements (Al, Si, B) degrading from the matrix is dependent of the leaching solution. For geopolymers the synthetic cementitious water with higher pH results in increased leaching rates in comparison to 0.1 M NaOH. Whereas, for the CEM waste forms the DI water is the most aggressive leachant. The leaching rates of radionuclides does not increase linearly with ash loading (e.g. 1%, 15% and 50%), which suggest that the ash % can be optimized. The results of this task will be reported more in detail in the PREDIS deliverable D6.6 “Final Report on the Physico-chemical characterization of reconditioned waste form and stability testing”.

3. Conclusions and way forward

The leaching response was dependent of the composition of the leaching solution. In general, higher release rates were detected during first 30 to 60 days of the leaching. However, the matrix degradation was not significant after 1 to 1.5 years of leaching and good dimensional stability was sustained. The mechanical strength decreased slightly with increasing leaching time, but still in most cases the strengths were much higher than the limits defined by waste acceptance criteria (WAC).

For the future, it would be necessary to conduct some experiments with real radioactive waste or surrogates containing more contaminants. In reality, the conditioned waste form will be exposed to gamma radiation, and possibly also for thermal cycling or chemically aggressive solutions (e.g. containing chlorides or sulphates). The timescale of the disposal is long, and thus for extensive understanding of the long-term durability it would be very beneficial to execute experiments with longer timescales to produce data more relevant to disposability assessment.

Acknowledgements

All partners, who took part in research activities in task 6.6 are greatly acknowledged for their contributions. The research leading to these results has been conducted by Politecnico Milano, University of Sheffield, University of Helsinki, Univesidad autónoma de Madrid, CEA, CIEMAT, CSIC, SCK CEN, SIEEG NASU, and VTT.

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7 Scientific progress of Innovations in cemented waste handling and predisposal storage (WP7)

7.1 Dissemination and Reporting (Task 7.7)

Yannick Caniven, Abhishek Mishra, Slimane Doudou, Galson Sciences Ltd, UK, sd@galson-sciences.co.uk

Keywords: cemented waste, monitoring technology, digital twin, data management, digitalisation

1. Introduction

The objectives of task 7.7 of Work Package 7 (WP7) were to disseminate the work carried out and produce a project summary report documenting the outcomes of WP7. The dissemination activities included participation at scientific conferences and technical workshops to raise awareness of the achievements, preparation of specific dissemination materials for distribution, engaging in dialogue with the End users Group (EUG), and preparation of open access publication and finalising project results for publication.

2. Description of work and main findings

The dissemination activities by WP7 partners over the duration of the PREDIS project covered a range of topics, including digital tools for waste management, innovative pre-disposal treatments, and management of cemented wastes. At the end of the project, a total of 28 dissemination activities were recorded. These included:

- 14 oral presentations at several conferences including the international conference on nuclear decommissioning (ICOND), DigiDecom 2022, EURADWASTE 2022, international Conference on Nuclear Engineering (ICONE30) , international conference on environmental remediation and radioactive waste management (ICEM 2023) , and the 67th International Atomic Energy Agency (IAEA) general conference .
- Nine articles and journal publications [1, 2, 3, 4, 5, 6, 7, 8, 9], including several which are publicly available.
- Five poster presentations at the IAEA international conference on radioactive waste management, EURADWASTE 20223, IGD-TP symposium 2022, Waste Management 2023 (WM2023), and ICEM 20235.
- One webinar on the DT tools [10].

The WP7 dissemination activities reached a diverse audience, including industry professionals, researchers, and the public. These activities were communicated internationally across Europe and beyond. This widespread reach is consistent with the aim of engaging with global audiences to increase the impact of the project.

The economic, environmental, and safety impacts of the innovative technologies and approaches tested in WP7 were also evaluated by means of a “value assessment” approach to compare these technologies against current practices in terms of key assessment areas relating to operational safety, environmental impact, long-term safety, implementation, technical readiness, and strategic cost impact. This process involved close collaboration between technology developers and the EUG through workshops to discuss the outcomes of the value assessment and incorporate EUG feedback into the final value assessment D7.9 report [11]]. D7.9 provides further details on the assessment methodology and its application and identifies key findings on each technology in terms the advantages and challenges associated with its implementation during storage of cemented waste packages.

A WP7 summary report was also produced as part of the Task 7.7. For each technical task within WP7, the report documented the task objectives, approach followed and deliverables produced, and the main outcomes of the work, including any potential future needs and opportunities if identified. A summary of the outcomes is given in the next section.

3. Conclusions

The main outcomes of the six technical tasks of WP7 are summarised below. Task 7.1 relates to project management and coordination and is not discussed.

Task 7.2: State of the Art (SoTA) in Packaging, Storage, and Monitoring of Cemented Wastes

Task 7.2 aimed to conduct a gap analysis in the early phases of the project and compile a comprehensive SoTA report on the existing methods and procedures for managing cemented waste packages. This task also involved identifying a reference package and degradation mechanisms for use in further activities in WP7 and provided necessary data for Life Cycle Assessment (LCA) and Life Cycle Costing (LCC) activities in WP2 of PREDIS. The gap analysis aimed to evaluate industry and stakeholder needs to help inform the WP7 scope and plans. The approach to the SoTA report included distributing a questionnaire to collect information on cemented waste management practices across Europe, which highlighted the widespread use of cement grouting for various waste streams and the common use of metallic drums and prismatic concrete containers. Monitoring strategies revealed a reliance on visual inspection and periodic data collection. Key degradation phenomena identified were corrosion, cracking, and alkali-silica reactions (ASR). Based on this, a reference package with specific characteristics was recommended for further studies and demonstrations within WP7.

Task 7.3: Innovative Integrity Testing and Monitoring Techniques

The advancements made in Task 7.3 have significantly improved the monitoring and integrity testing of radioactive waste drums. The technologies covered included: SciFi/SiLiF gamma and neutron radiation monitoring, acoustic emissions (AE) for measuring ASR, non-contact ultrasonic inspection, radio frequency identification (RFID) embedded sensors, sensorised long-range radio (LoRa) wireless sensor network, and muon tomography. The tests and development activities with Task 7.3 demonstrated the potential of these technologies for continuous remote monitoring of a store and revealed the need for further optimisation and processing of data collection to enhance the reliability and accuracy of these monitoring systems. Future work will focus on developing and validating these technologies through extended testing and optimisation in real-world end-user facilities.

Task 7.4: Digital Twin (DT)

Task 7.4 successfully achieved its primary objective of developing a proof of concept for certain aspects of DT technology in the pre-disposal management of radioactive waste packages, demonstrating the use of machine learning (ML) algorithms to predict the geochemical and mechanical evolution of waste packages over time. The DT dashboard developed on the geoml platform provides a valuable tool for real-time monitoring and decision support, integrating complex geochemical and mechanical models. Continued development and testing of the surrogate models and Bayesian inference methods are essential to improving the accuracy and efficiency of parameter estimation methods used for the evolution prediction. Experimental results of the characterisation of a LLW cemented waste drum, stored in a facility in Switzerland for 30 years, can be used in the future to obtain more detailed DTs for cementitious waste drums. Additionally, ongoing drum-scale experiments will provide further insights into ASR kinetics and the role of recycled concrete aggregate in waste packages.

Task 7.5: Data Handling, Processing and Fusion

Task 7.5 of WP7 successfully established a framework for secure data management and processing, integral to the efficient management of cemented radioactive waste. The task achieved its key objectives, including the development of a comprehensive data management system, the translation of non-destructive evaluation (NDE) and monitoring data into engineering parameters, and the integration of multi-method monitoring data for informed decision-making.

Ensuring data integrity and secure storage over the medium to long term required the development of sophisticated models and methods, including the potential use of ontologies and advanced preprocessing techniques. The project outlined areas for enhancing long-term data management in radioactive waste storage. Creating non-fungible tokens (NFTs) for each waste drum on Web3 could provide a certified digital life for the drums, ensuring continuous data integrity and traceability. Additionally, using ML based on visual artificial intelligence for property recognition can streamline data handling and reduce storage requirements.

Task 7.6: Demonstration and Implementation of Monitoring, Maintenance, and Automation/Digitalisation Techniques

The main outcome of Task 7.6 was the successful demonstration the technologies developed in other WP7 tasks within a realistic storage environment at UJV in the Czech Republic and at other locations at NNL (UK) and INFN (Italy). The tested technologies were evaluated for monitoring waste packages over a three-month period. A dedicated dashboard was also created to integrate and display data from the technologies and provide a visual user interface for interpreting the monitored data. The demonstration highlighted the strengths of the technologies and various areas for improvement. Further testing in a representative industrial setting is necessary to validate the practical usability and effectiveness of these technologies.

Task 7.7: Dissemination and Reporting

The primary focus of Task 7.7 was on disseminating the findings of the project and engaging with stakeholders and the EUG to raise awareness of its achievements. This was accomplished through various means, including participation at scientific conferences and technical workshops, and production of open-access publications. The EUG were also involved and provided feedback on the value assessment task which analysed the economic, environmental, and safety impacts of the technologies developed and tested in WP7. This feedback was incorporated into the analysis.

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7.2 Data management framework for concrete package studies – Summary of Task 7.5

Tuula Hakkarainen, Joonas Linnosmaa, Teemu Mätäsniemi, Jukka Aho, Tero Jokinen and Petri Kaarmila
VTT Technical Research Centre of Finland Ltd, Finland

Enrico Botta and Paola Castagna
Ansaldo Nucleare SpA, Italy

Tom-Robert Bryntesen, Réka Szőke, Hans Olav Randem and Svein Tore Edvardsen
IFE Institute for Energy Technology, Norway

Bas Janssen
NRG Nuclear Research and Consultancy Group, Netherlands

Corresponding author: tuula.hakkarainen@vtt.fi

Keywords: data management, database, decision framework

1. Introduction

Task 7.5 of the PREDIS project was dedicated to data handling, processing, and fusion. Its goal was to produce a conceptual model for data handling and storage, and database and software prototype.

Task 7.5 was subdivided into three sub-tasks: data handling, processing, and fusion platform (T7.5.1); ML and advanced signal processing (T7.5.2); and decision framework (T7.5.3). The work was strongly connected to Task 7.3 on innovative instrumentation and Task 7.4 on simulation and digital twins. Figure 1 presents the three subtasks within Task 7.5 and the relationship of Task 7.5 to Tasks 7.3 and 7.4 of WP7.

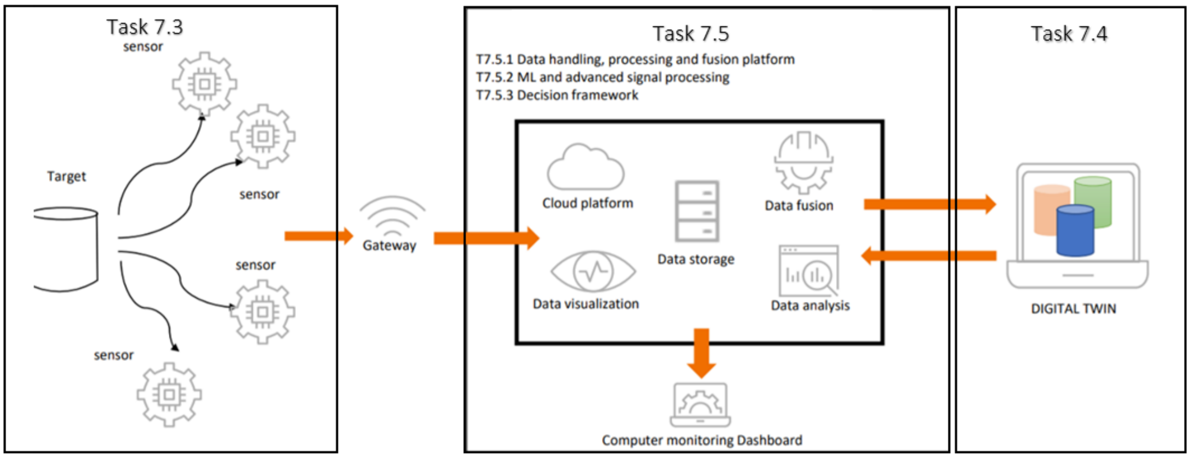


Figure 1. Scope of Task 7.5 and its relationship with Tasks 7.3 and 7.4 within WP7.

2. Description of work and main findings

The tools and methods developed within Task 7.5 are collectively referred to as the data management framework. The data management framework consists of a data platform, data processing and integration scheme, and decision framework.

More details of the work performed, and the results achieved are provided in Deliverable 7.7 [1].

Data platform

The data platform is the central data repository of the data management framework, interfacing with the various data input and output flows. A reference metadata model, accessible as a web service, was set up by using a Django Virtual Environment. This metadata model holds four database tables describing the information needed for traceability, reproducibility, and long term storage of measurement data. Tables (waste packages, sensors, nodes, images) were associated with the possibility of managing data by the administrator and user groups with the necessary permissions. An SQLite3 Database was preliminarily filled (by using Django syntax) with the relevant metadata from the project. Once the waste packages were defined as a master table, any changes associated with them were automatically traced in a change history. Data was visualised in three different ways: admin mode, public mode (webpage), and other external open-source tools (i.e., HeidiSQL) to analyse the database structure and its consistency. To store the actual timeseries telemetry data from the waste packaging, an InfluxDB Database was setup with buckets storing data from each organisation.

Data processing and integration

The Azure cloud computing environment was tested to be suitable for performing the data processing and integration operations, and simple trials were done with Azure artificial intelligence (AI) studio to confirm its suitability for possible advanced analytics. While ML and advanced signal processing were considered to be more part of the scope of Task 7.4, Task 7.5 focused on the other parts of the data-driven workflow: data collection, integration of the data management framework subsystems, and administration of the different development platforms. Azure Data Lake was used to preliminary store the data, allowing processing and metadata linking before migrating to the InfluxDB. Azure Virtual Machines were used to run the databases, allowing ease-of-access through different project partners and locations.

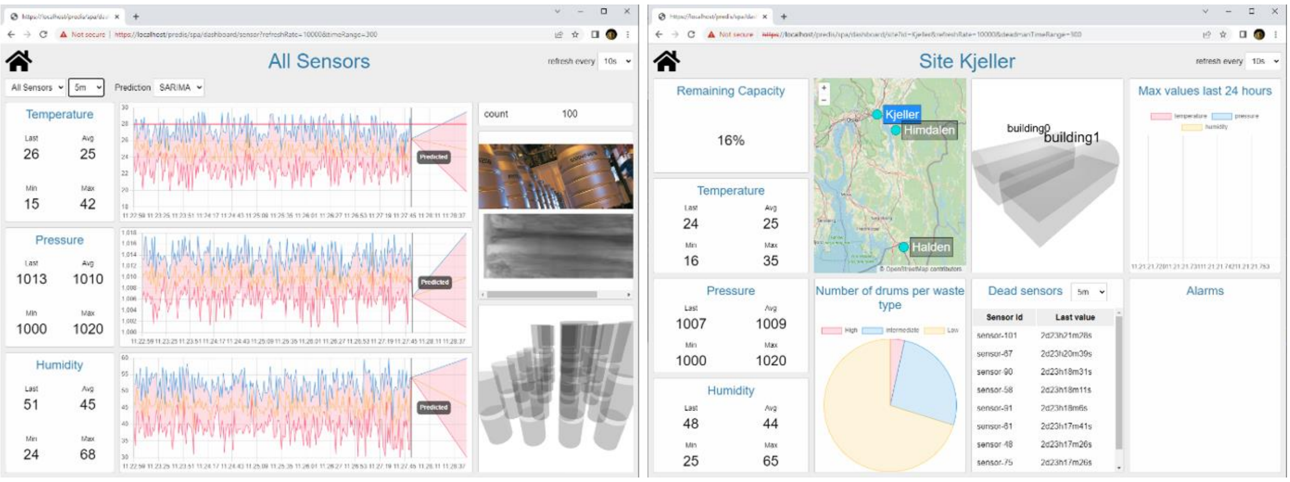
There are various options for modelling and structuring the data. The possible use of ontologies in the context of the PREDIS project was studied. Potential benefits of ontologies, such as information integration, compatibility, and shared terminology, were described and considered within this task.

There are several types of data preprocessing methods for different purposes. Methods on data integration, data cleaning, time series data handling, handling time-dependent sequences, labelling, and data transformation were examined. In addition, software libraries intended for data processing using the Python programme language were briefly considered and compared.

The data management framework was implemented in Azure. Automatic setup and management of this framework using scripts and Azure Resource Manager (ARM) templates was outlined. Several advantages achieved by using scripts and ARM templates were highlighted. In addition, a list of steps with which a partially corresponding system can be deployed was compiled.

Decision framework

The decision framework is the user interface to the data management framework and aims to provide visualised information to end users to assist with the decision-making process based on information about the condition of the monitored packages and the predictions provided by the digital twin (DT) by interfacing with the databases designed within the task. As part of the decision framework initiative, a prototype for a decision platform was designed and implemented as a web application. This platform incorporated multiple dashboards, each tailored to present information from distinct perspectives, tailored to the specific needs of different users. Users can access 3D analysis views that facilitate the visualisation of both waste storage sites and containers. Example dashboards developed within this task are shown in Figure 2. Furthermore, the decision platform offers Online Analytical Processing (OLAP) analysis of radioactive waste and dose analysis reports (As Low As Reasonably Achievable (ALARA) based planning or briefing option). Additionally, the platform goes beyond presenting only the current situation by showcasing future predictions derived from a DT, which can be conveniently viewed on a dashboard. This comprehensive approach ensures that the decision platform not only addresses immediate needs but also provides valuable insights for long-term planning and management.



Sensor id	Last value
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sensor-67	2d23h20m39s
sensor-90	2d23h18m31s
sensor-58	2d23h18m11s
sensor-91	2d23h18m6s
sensor-61	2d23h17m41s
sensor-48	2d23h17m26s
sensor-75	2d23h17m26s

Figure 2. Example dashboards: dashboard for a single drum (left) and for a whole site (right).

Utilising a decision platform that integrates ML and DT powered predictions and OLAP analysis holds the potential to significantly support informed decision-making. Through the integration of sensor data and other monitoring systems, the PREDIS platform provides immediate insights facilitating improved performance and safety in waste management processes. The real-time monitoring capabilities facilitate the instant detection of deviations from normal conditions and automated alerts upon the detection of irregularities for prompt corrective actions. The OLAP analysis empowers users to selectively extract and query data, allowing for analysis from various perspectives. This proactive approach ensures timely interventions, thereby minimising the likelihood of incidents/accidents or environmental impact.

Joint showcase

To demonstrate the data management framework concept of Task 7.5 and its link to other WP7 tasks, a showcase common between the different tasks and involving several partners was performed. This joint showcase demonstrated the advancements made in the project.

Selected technologies were tested in a realistic environment in a storage configuration at UJV using a set of mock-ups. The commissioning of the UJV mock-up facility was completed in October 2023. Preliminary data collection tests were conducted locally at UJV to ensure seamless integration and data transmission to the Azure Platform. Remote troubleshooting procedures were established for any potential issues during the three-month testing period, which concluded in January 2024.

The joint showcase produced data in the form of the metadata file, and the measured data from three sensors from the sensing and monitoring systems was transferred and stored to the cloud data platform through IoT applications. The data was processed and displayed to the end users through the decision framework. The final data connection with the DT of Task 7.4 may be subject of future work and the decision framework dashboard has capabilities to display the analysis data originating from the DT.

3. Summary

A conceptual model for data handling and storage was developed, and a practical implementation was performed. The demonstration test at UJV confirmed that monitoring data from sensors can be automatically uploaded to the Microsoft Azure cloud platform, and it can be visualized on the decision platform. A web-based decision platform with multiple dashboards was developed to present information from different perspectives customized to different users. The functionality of the decision platform has been proven in the UJV demonstration test. This joint showcase of Tasks 7.3, 7.4 and 7.5 demonstrated the advancements made. It exemplified the collaborative, iterative, and integrative approach of the project, weaving together various strands of research and development.

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7.3 Sensitivity analysis with 1 million cases generated by digital twin of cement waste package

Guang Hu, PSI, guang.hu@psi.ch; Dan Miron, PSI; Wilfried Pfingsten, PSI; Rainer Dähn, PSI

Keywords: Digital twin, Surrogate model, Cement waste package, Sensitivity analysis

1. Introduction

Ensuring the stability of materials used in waste packaging is critical for long-term environmental safety and integrity. Essential indicators of material stability, particularly chemical changes, play a pivotal role in predicting potential threats to the integrity of waste packages. By understanding these chemical alterations, it becomes possible to foresee and mitigate risks, thereby enhancing the durability and reliability of containment solutions.

A groundbreaking approach in this domain is the use of digital twins to link reaction rates with material properties. This innovative method allows for a comprehensive assessment of waste containment stability by creating a virtual replica of the physical system. The digital twin facilitates real-time monitoring and analysis of chemical reactions, providing invaluable insights into the dynamic interactions between materials and their environments.

2. Description of work and main findings

The efficacy of neural network-based surrogate models is demonstrated in significantly enhancing computational efforts, reducing the generation time of 1 million cases from nearly 79 days to under 2 seconds. Sobol sensitivity analysis across this extensive dataset reveals both the direct contribution and total contribution of an input to the output parameter. Such digital twins might also be used in the future for the optimization of waste conditioning recipes, improving (interim) storage integrity.

3. Conclusions

The integration of neural network-based surrogate models into the analysis of material stability and waste package integrity marks a substantial advancement in computational efficiency. These models demonstrate remarkable efficacy, drastically reducing the generation time for extensive datasets. For instance, the time required to process 1 million cases has been cut down from nearly 79 days to under 2 seconds, exemplifying a quantum leap in computational capabilities.

Furthermore, the application of Sobol sensitivity analysis across this vast dataset offers profound insights into the factors influencing output variance. By elucidating both the direct and total contributions of various inputs, this analysis enhances our understanding of the complex interactions governing material stability.

The potential applications of digital twins extend beyond current methodologies, promising future innovations in the optimization of waste conditioning recipes. Such advancements could significantly improve the integrity of both interim and long-term storage solutions, ensuring safer and more reliable waste management practices.

In conclusion, the synergy of advanced neural network models, comprehensive sensitivity analysis, and digital twin technology heralds a new era in predictive modelling and waste containment optimization. These breakthroughs not only streamline computational processes but also pave the way for more resilient and sustainable waste management strategies.

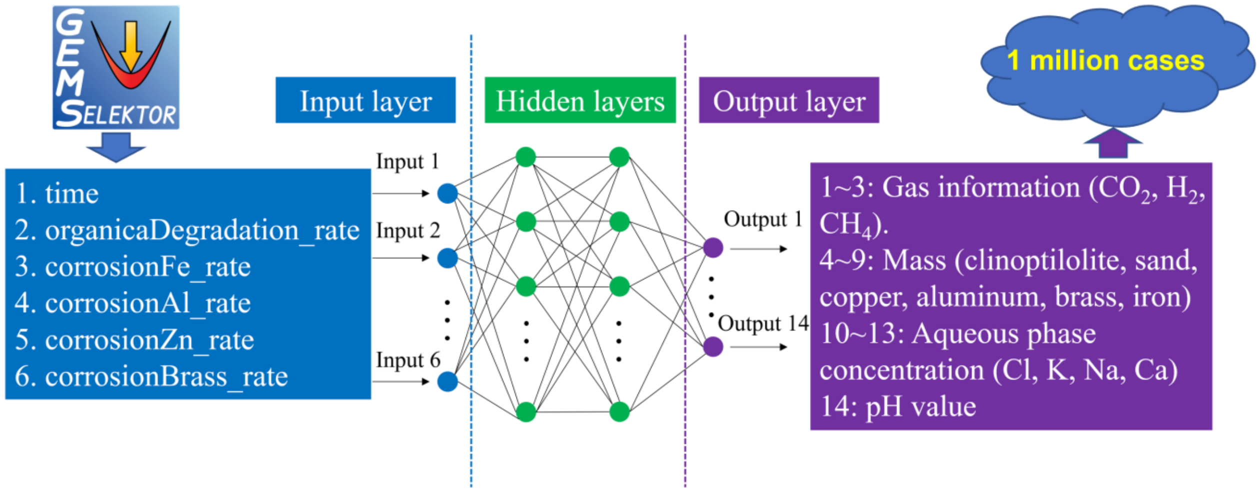

Figure 1. Six inputs and 14 outputs in neural network machine learning model for the digital twin of cement waste package.

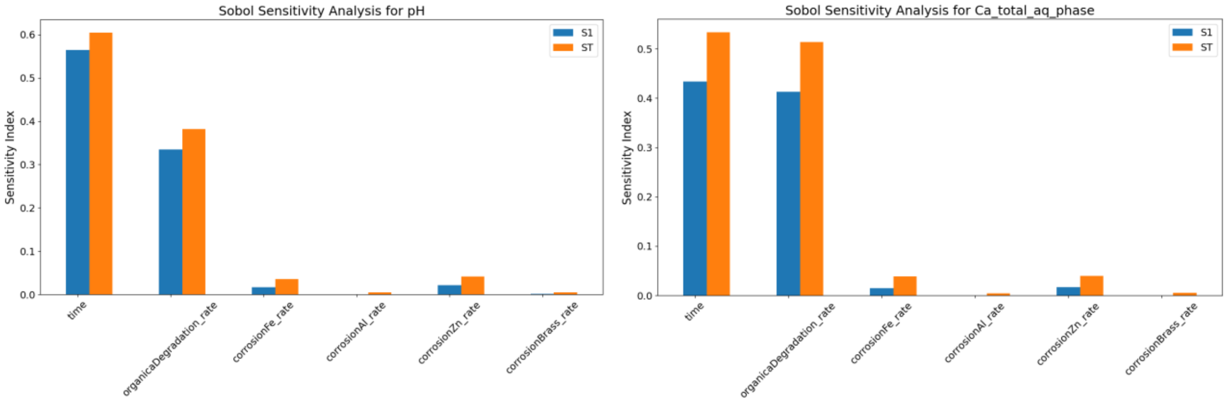

Figure 2. Sensitivity analysis of 6 input variables on 14 output parameters with 1 million cases generated by digital twin of cement waste package.

Acknowledgements

This work was partially funded by the European Union’s Horizon 2020 research and innovation programme **pre-dis**posal management of radioactive waste PREDIS [Grant No. 945098]. We express our gratitude and thanks to PD Dr. Georg Kosakowski from PSI for providing assistances concerned with the GEMS python scripts in our research.

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Appendix 1 – Agenda of the Final Conference

PREDIS Final Conference - June 2024

Final AGENDA

Time: 3-7 June 2024

Location: 7 June 2024 at Novotel Avignon Center, Avignon, France

Meeting is organised **in-person.**

MS TEAMS link below for Wednesday-Thursday sessions.

Tuesday – 4 June 2024 - Consortium Partners Only

***Project Consortium Meeting, Review of WP completions** – all PREDIS partners*

Time: 9.00-17.00 CET

8:00-9:00 Registration

9:00-9.15 **Welcome** by Maria Oksa and Erika Holt, VTT, as Coordinator and Florence Bart, the deputy head department, CEA, as local host

9.15-9.35 **EC welcoming words**, including EC review findings by Seif Ben Hadj Hassine and Hans Forsström

9.35-10.00 **WP1 Management & Dissemination**

- PREDIS project status update, Maria Oksa, VTT
- Status on EURAD collaboration
- Financial review, Sirkku Hoikkala, VTT (online)
- Dissemination activities

10.00-10.40 **WP2 Strategic Studies (40 min)**

- WP updates, Anthony Banford, NNL and Laurence Stamford, UoM

10.40-11.20 **WP3 Knowledge Management (40 min)**

- WP updates, Alba Valls, A21

11.45 **Parallel Sessions of Each WP** (part A) *(separate/own room for WP4-7)*

- *WP4 room PEGASE (1st floor)*
- *WP5 room CASSIOPEE*
- *WP6 lounge (4th floor)*

- *WP7 room ANDROMEDE (1st floor)*

14.30-17.00 Parallel Sessions of each WP continue (part B)

Wednesday – 5 June 2024 – PUBLIC Technical Workshop

Open technical workshop*, Time: 9:00 – 17:30 CET*

- *Location: Room ANDROMEDE (1st floor)*

Possible to participate on-line

Chairperson all day: Maria Oksa, VTT

9:00 Welcome by Coordinator (VTT), including WP1-3 overviews

9:15 Status updates and scientific presentations on Technical Work Packages, part 1

- 9.15-10.30 **WP4 Innovations in metallic treatment and conditioning**
  - Summary by WP leader, Abdel Abdelouas, IMT Atlantique (20 min)
  - Scientific presentations (40 min)
    - Developing and optimizing decontamination processes (T. Suzuki, IMT Atlantique)
    - Optimization of characterization and waste minimization techniques (A. Savidou, NCSRD)
    - Advances in encapsulation of materials in magnesium phosphate cement-based matrices (C. Cannes, IJCLab)
  - Student presentations (10 min)
    - A non-destructive gamma spectrometry set-up for characterization of metallic waste (D. Mavrikis, NCSRD)
    - Decontamination of radioactive effluents (M. Robin, IMT Atlantique)

- 11.00-12.15 **WP5 Innovations in liquid organic waste treatment and conditioning**
  - Summary by WP leader, Isabelle Giboire, CEA (20 min)
  - Scientific presentations (40 min)
    - Study of direct conditioning processes:
      - Investigation of reference formulation for real waste Real Waste (POLIMI + UJV)
      - Investigation of direct conditioning Process scale-up (CVRez)
    - Study of conditioning matrix performances (SCK+ ECL)
  - Student presentations (10 min)
    - Sara Koubeissy (ECL)
    - Gabriele Magugliani (POLIMI)

12.15-12.45 Discussion on WP4-WP5 topics

14.00 Status updates and scientific presentations on Technical Work Packages, part 2

- 14.00-15.15 **WP6 Innovations in solid organic waste treatment and conditioning**
  - Summary by WP leader, Thierry Mennecart, SCK CEN (20 min)
  - Scientific presentations (40 min):
    - Thermal treatment of the radioactive waste forms and characterisation (CEA)
    - Encapsulation (CVRez)
    - Densification (USFD)
    - Physico-chemical characterisation of reconditioned waste form and stability testing (VTT)
    - Economic and environmental impact (GSL)
  - Student presentation (10 min)
    - Francesco Galluccio (Polimi)

- 15.45-17.00 **WP7 Innovations in cemented waste handling and pre-disposal storage**
  - Introduction to WP7 (Christian Köpp, BAM, 5 min)
  - Innovative Instrumentation summary (Paolo Finocchiaro, INFN, 5 min)
    - Michele Di Giovanni, Unicampania, Student presentation 10 min (*online*)
  - Digital Twin summary (Rainer Dähn, PSI, 5 min)
    - Student presentation (10 min)
  - Database and decision framework summary (Tuula Hakkarainen, VTT, 5 min)
    - Student presentation 10 min
  - Demonstration in a realistic environment (Thibaut Hémédinger, ORANO, 10 min)
  - Conclusions & Value Assessment (Slimane Doudou, GSL and Christian Köpp, 10 min)

17.00-17.30 Discussion

17.30 Summary & Adjourn

Thursday – 6 June 2024 – PUBLIC Project Outcomes/Impact Workshop

***Open technical workshop**, Time: 9:00 – 16:00 CET*

- *Location: Room ANDROMEDE (1st floor)*

Possible to participate on-line

9:00 Welcome by Coordinator (Maria Oksa & Erika Holt, VTT)

9.10 Welcome by EC Officer (Seif Ben Hadj Hassine, Euratom)

9:20 -10.45 Highlights of Project Impacts – Chairperson Erika and Seif

- Introduction on the Value Assessment Process & Case Studies (10 min) – Jenny Kent, GSL

- Geopolymers for Waste Immobilization (WP5, WP6) (9:30-9:50)
  - Putting results into practice
    - PREDIS partner's view: Quoc Tri PHUNG (SCK CEN) – perspectives of using geopolymer for immobilization
    - End User perspectives: Denise Ricard (ANDRA), WP5's perspectives; Peter Ormai (PURAM), WP6's perspectives

  - Open discussion/ feedback from stakeholders

- Decontamination & Supporting Waste Hierarchy principles (WP2, WP4) (9:50-10:10)
  - Putting results into practice
    - PREDIS partners' view: Thomas Carey (NLL)
    - End User perspectives: José Luis Leganes (ENRESA)
  - open discussion / feedback from stakeholders

- Digitalization advancements, for monitoring (WP7) (10:10-10:40)
  - Putting results into practice
    - PREDIS partners' view: Suresh Seetharam (SCK CEN)
    - End User perspective: Massimo Morichi (CAEN)
  - open discussion / feedback from stakeholders

- Closing of the session (5 min)

11.15-12.45 ***Panel discussion – EU Project Impacts on French Programme***

Moderated by Erika HOLT (VTT)

Guided Panel discussion of French stakeholders, with Q&A from the audience:
  - Virginie WASSELIN, ANDRA (WMO)
  - Magali SALUDEN, CEA
  - Fabrice MOGGIA, ORANO (industry)
  - Hélène DENIAU, VEOLIA (industry)
  - Henri LE MONIES DE SAGAZAN, EDF (Industry)

14.00-15.30 Panel discussion –EU Projects Impacts on International Community

View from each panellist on the impacts of PREDIS and Euratom projects (3 minutes each, followed by guided Q&A). Moderated by Erika Holt (VTT, Co-coordinator).

- European Commission (Euratom) views, Seif Ben Hadj HASSINE
- EC Project Evaluator - Impact views, Hans FORSSTRÖM
- IAEA Waste Management division views, Rebecca ROBBINS
- SNETP Technical Area on Waste/Decommissioning views, Anthony BANFORD
- EURAD cooperation with view on KM, Paul CARBOL
- JRC views, Vaidas MATUZAS

15.30-16.00 Workshop Summary & Closing

Appendix 2 – PREDIS Posters

PREDIS project has been prominently figured in the international conferences. Appended to this report some of the posters of PREDIS project.

1. Innovative and green pre-impregnation solution for the disposal of radioactive liquid organic waste, I. Moschetti et al. at NUWCEM 2022, 4th International Symposium on Cement-Based Materials for Nuclear Wastes, 4.-6.5.2022, Avignon, France
2. Stability and Physico-Chemical Characterisation of a Reconditioned Waste Form Relevant to Radioactive Wastes, F. Vettese et al. at the 19th International conference for radiochemistry 2022 (RadChem 2022), 15.-20.5.2022, Mariánské Lázně, Czech Republic
3. International cooperation on predisposal waste management − The PREDIS project, M. Oksa el. at EURADWASTE´22, 30.5.-3.6.2022, Lyon, France
4. Innovations in liquid organic waste treatment and conditioning, K. Hamadache et al. at EURADWASTE´22, 30.5.-3.6.2022, Lyon, France
5. Development of formulations for direct conditioning of Radioactive Liquid Organic Wastes, F. Pancotti et al. at EURADWASTE´22, 30.5.-3.6.2022, Lyon, France
6. The Immobilisation of Radioactive Liquid Organic Wastes (RLOW) in Geopolymers, S. Irving et al. at Cement and Concrete Science Conference 2022, 12.-13.9.2022, Leeds, UK
7. Stability, Physico-Chemical Characterisation, and Leaching of Reconditioned Waste Forms Relevant to Radioactive Wastes, G. Vettese et al. at MIGRATION 2023, 24.-29.9.2023, Nantes, France
8. Innovations in liquid organic waste treatment and conditioning, I. Giboire et al. at WM 2023 Symposia 26.2.-2.3.2023, Phoenix, Arizona, USA
9. Conditioning of liquid organic waste into a geopolymer matrix, A. Sears et al. at The 32nd International Conference Nuclear Energy for New Europe (NENE2023), 11.-14.9.2023, Portorož, Slovenia
10. Data handling, processing and fusion (WP7.5), PREDIS Final Conference, 3.-7.6.2024, Avignon, France

NUWCEM2022
4th International Symposium on Cement - Based Materials for Nuclear Wastes
Avignon, France
May 4 to 6, 2022

POLITECNICO MILANO 1863

UNIVERSITÀ DI PAVIA

Innovative and green pre-impregnation solution for the disposal of radioactive liquid organic waste

I. Moschetti[1,2], E. Mossini[1*], G. Magugliani[1], M. Giola[1], E. Macerata[1], L. Brambilla[3], C. Castiglioni[3], D. Vadivel[4], D. Dondi[4], D. Cori[5], A. Abdelouas[2], M. Mariani[1]
[1]*Department of Energy, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milan, Italy*
[2]*SUBATECH, CNRS-IN2P3, IMT Atlantique-Université de Nantes, 4 rue Alfred Kastler, BP 20722, 44307, Nantes cedex 03, France*
[3]*Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133, Milan, Italy*
[4] *Department of Chemistry, Università degli Studi di Pavia, Via Taramelli, 12, 27100, Pavia, Italy*
[5]*Nucleco S.p.A., via Anguillarese, 301, 00123, Roma, Italy*
*Corresponding Author: eros.mossini@polimi.it

INTRODUCTION

Radioactive Liquid Organic Waste (RLOW) is challenging due to the combination of radiological and physico-chemical risk. RLOW requires a careful managment system for treatment and conditioning prior to disposal [1, 2]. In order to simplfy the waste management, preliminary and complicated treatments should be avoided.

Figure 1 - Nochar N910

Figure 2 - Recycled polyurethane powder (rPU) from the reprocessing of refrigerators

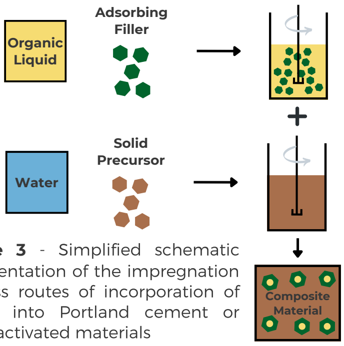

Figure 3 - Simplified schematic representation of the impregnation process routes of incorporation of RLOW into Portland cement or alkali-activated materials

OBJECTIVES

The aim of this work is to propose an innovative and green pre-impregnation solution for RLOW management.

1. Evaulate the **binding mechanism** and **retention capability** of the absorbent matrix by comparing it with the properties of Nochar N910 [3]
2. Determine the best formulation for the **cement matrix** from the promising one used in construction [4]
3. Verify the accomplishment of Waste Accetance Criteria (**WAC**)

EXPERIMENTAL

Step Zero: Verification of the absorption and retention capacities of polymers (see Figure 4)

1st step: Different types of RLOW (oils, scintillation liquids and solvents) were mixed with the absorbent material

2nd step: The different samples were characterised by FT-IR, Raman, TGA and DSC analysis to understand the type of interaction between polymer and waste.

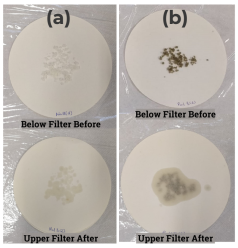

Figure 4 - Filters before and after the release test. (a) Nochar N910 and (b) Oko-Pur loaded with Vacuum Pump Oil (1:3)w.

Figure 5 - Qualitative scheme of specimen composition. 1 part OPC [gray], 0.6 parts water [blue] and 3 parts sand [orange], replaced at 50% by volume with rPU [green]

3rd step: The mixture was encapsulated within containement matrices, based on Ordinary Porland Cement (OPC)

4th step: The conditioning matrices were tested by Compressive analysis, Leaching Test and Thermal analysis

CONCLUSION

The results are very encouraging: rPU is capable of **absorbing different types of RLOW** and the leaching test and thermal analysis demonstrate the **strength of the conditioning matrix**. Better performance could be achieved in compressive strength by changing the formulation of the cement matrix and increasing the sample size to reduce the effect of expansion of rPU and sample inhomogeneity.

RESULTS

rPU and Nochar N910 produce a physical bond with surrogate wastes and the absence of chemical bonding requires an additional immobilisation step to accomplish WAC. The thermal behaviour of rPU shows resistance up to about 200 °C.

The compressive strength was determined in two different samples, one reference and the other with rPU, obtained by substituting 50% by volume of sand.

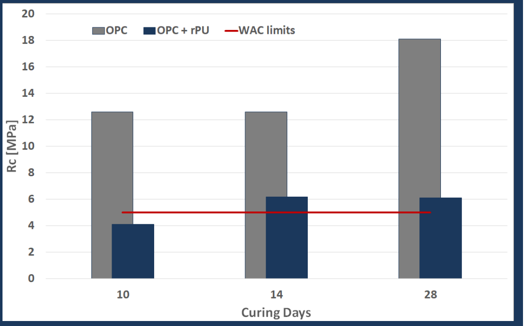

Figure 6 - Compression Resistance of Reference matrix, only OPC, and matrix with OPC and rPU

The leaching tests were performed following the ANSI/ANS-16.1-2003. The leachant solutions were renewed after 2, 4, 24, 48, 96 and 168 hours and then tested.

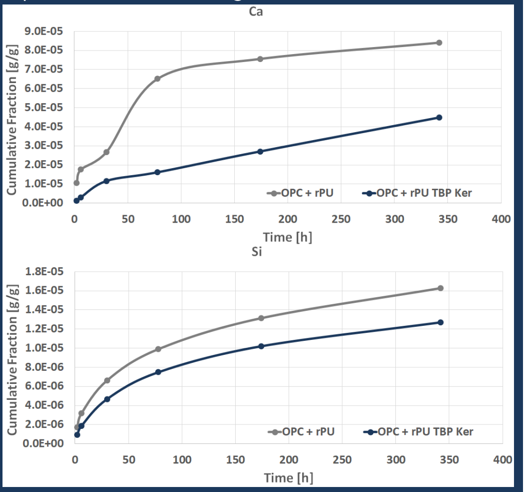

Figure 7 - Cumulative trend of Ca and Si release in the leaching solution of samples with and without surrogate waste.

The leachability index for organic liquid release was calculated equal to **10.56**, which is higher than the value required by the WACs (>6).

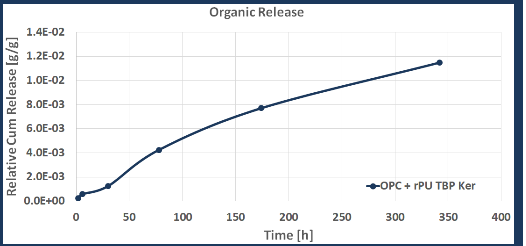

Figure 8 - Cumulative organic liquid release in the leaching solution

Thermal analysis was performed by TGA to evaluate the behaviour of surrogate waste absorbed into rPU alone or contained within the conditioning matrix.

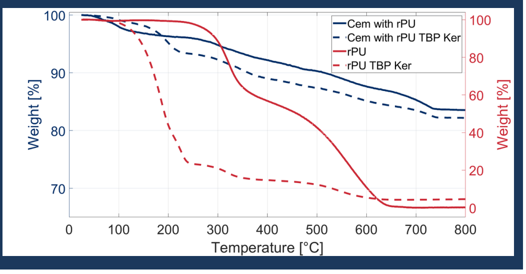

Figure 9 - Thermal decomposition curves of [blue] cement matrix (OPC and rPU) with and without surrogate waste and [red] OkoPur with and without surrogate waste

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Pre-disposal management of radioactive waste

Stability and Physico-Chemical Characterisation of a Reconditioned Waste Form Relevant to Radioactive Wastes

Gianni F. Vettese[1]*, Taavi Vierinen[1], Tandre Oey[2] , Matti Nieminen[2], Suvi Lamminmäki[2], Markku Leivo[2], Tapio Vehmas[2], Jaana Laatikainen-Luntama[2], Emmi Myllykylä[2] & Gareth T. W. Law[1]
[1]The University of Helsinki, Radiochemistry Unit, Helsinki, Finland, [2]VTT Technical Research Centre of Finland, Helsinki, Finland

1. Introduction

Low and Intermediate Level radioactive Waste (LILW) typically includes operational wastes (*i.e.,* contaminated materials) and ion-exchange resins (IXR) used in the cleaning of process water at nuclear plants. Although LILW represents only about 1 % of the total radioactivity of waste, it represents more than 95 % of the total volume. Finland alone generates over 300 m^3 of LILW annually.

Generally IXR waste is immobilised in a solid matrix and contained in a steel drum, where it is held in interim storage until the final disposal concept is ready. LILW final disposal in Finland is via burial in geological disposal, with waste emplaced in rock caverns ~ 100 m below surface.

In this research, ion-exchange resins have been thermally treated via gasification (Figure 1A) and immobilised in a novel metakaolin geopolymer by VTT (Figure 1B). Here, treatment enables substantially higher loading of the LILW (more than 90% volume reduction) into the geopolymer without loss of matrix strength or cohesion.

Currently, the chemical stability of the geopolymer and the encapsulated contaminants remain unknown. Here, we share early results on the characterisation and leachability of a novel geopolymer.

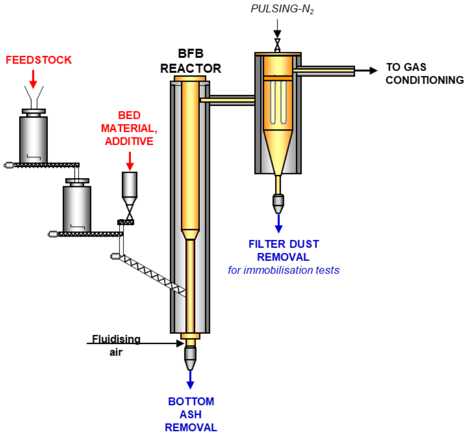


Figure 1: Schematic of the gasification process.

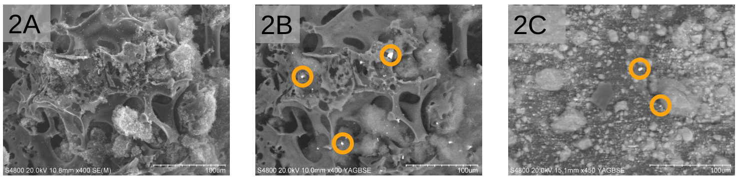


Figure 2: [A] Scanning Electron Microscopy (SEM) imaging of ion-exchange resin ash; **[B]** SEM-Back-Scattering Electron (BSE) image of ion-exchange resin ash; **[C]** ESEM-BSE of metakaolin geopolymers. Circles highlight dense agglomerations.

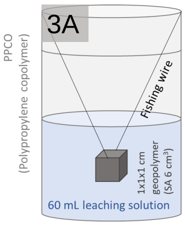
2. Geopolymer Characterisation

- The gasified ash represents 1% of the final geopolymer matrix and contains stable isotopes of Cs (200 mg/kg), Sr (20 mg/kg) Cr (3000 mg/kg), Co (40 mg/kg), and Ni (3000 mg/kg) representative of nuclear fission and activation products.
- Contaminants in ash are heterogeneously concentrated as dense agglomerations observable in electron imaging (Figure 2B).
- Geopolymer general structure is a –Na/K-Al-Si-(H)- network, heterogeneous particles from ash are retained after encapsulation into the geopolymer matrix (Figure 2C).

3. Geopolymer Leachability

During the final disposal of LILW, passing water will come into contact with concrete structures present in the facility creating a high ambient pH (~12, CaOH buffered) rich solution that may leach the immobilised radionuclides from the geopolymer. Semi-dynamic leaching experiments (Figure 3A) assess the short- and long-term (1 month – 2 years) behaviour (see section 4) of the matrix and contaminants (Figures 3B-D).

- pH and conductivity remain stable at 12.5 and 8.5 mS/cm respectively.
- Bulk: Na, Al, Si leach into the solution, Ca and K are removed from solution into the geopolymer.
- Trace: Co, Cs, Cu, and Ni leach into the solution. Sr, Cr are below the LOD (0.7 and 0.09 μg/kg, respectively).
- No colloids observed in leachate using dynamic light scattering.



Leachant recipe	
Ca (ppm)	96
Na (ppm)	668
K (ppm)	650
pH	12.6
Cond (mS/cm)	8.9

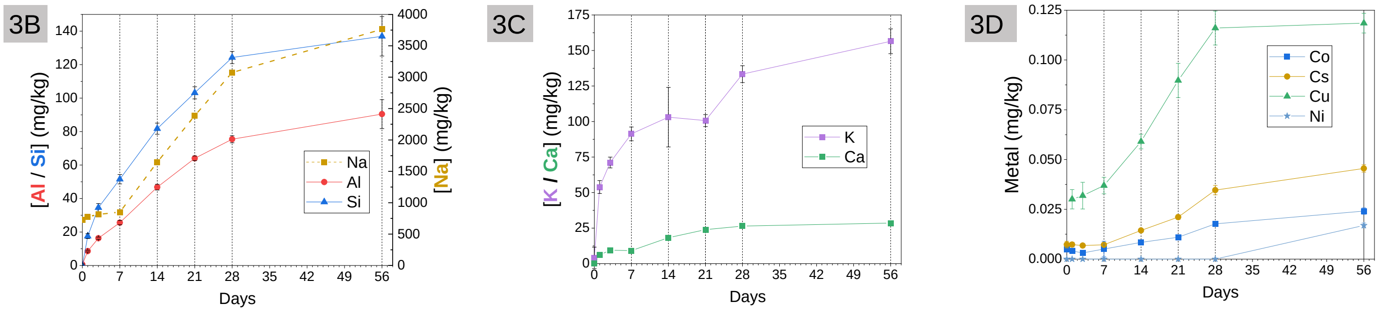


Figure 3: [A] Experiment setup; **[B]** Cumulative **leaching** of Al, Si, and Na; **[C]** Cumulative **absorption** of K and Ca; **[D]** Cumulative **leaching** of Co, Cs, Cu, and Ni.

4. Post-Mortem Analyses (ongoing):

- Leached geopolymers are sacrificed, preserved, and dissected after 1 month, 6 months, 1 year and 2 years of leaching.
- Post-mortem analyses (XRD, μ-CT, ESEM-EDX, EMPA & ^{29}Si NMR) of the end points will yield information on the changing crystallinity and pore structure, evolution of the geopolymer matrix elements and trace contaminants.

5. Conclusions & Future Work:

- VTT has successfully developed a process to treat spent resins that significantly reduces the volume of resin to be disposed of and enables more efficient immobilization prior to disposal.
- Current experiments assess the stability of the geopolymer when high pH leachate eventually passes through the stored waste.
- Soon we will receive a new set of geopolymers spiked with: *i)* higher ash loadings to assess the extremities of potential waste loading using thermal treatment; *ii)* elevated concentrations of Cs and stable actinide analogues Eu and Ce. Here, concentrations sufficiently high enough for nano-microscale analysis (XRF, XRD, and XAS) of local structure and bonding environments, will be used.

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

Always happy for a chat!

Email: gianni.vettese@helsinki.fi

PREDIS

EURADWASTE'22

predisposal management of radioactive waste

International cooperation on predisposal waste management – The PREDIS project

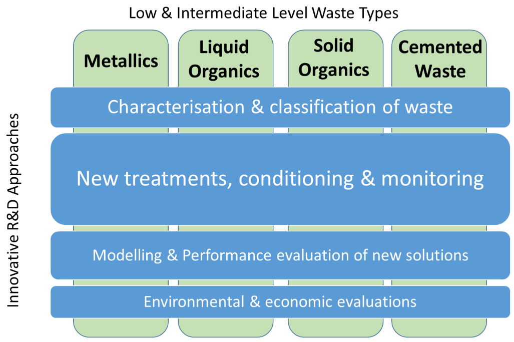
M. Oksa & E. Holt (VTT, Finland), A.W. Banford (NNL, UK), C. Bruggeman (SCK CEN, Belgium)

The PREDIS project, ‘Predisposal Management of Radioactive Waste’, addresses innovation and break-through technologies for improved handling of the different low-level and intermediate-level radioactive waste streams, in close cooperation with related projects, international organisations and the PREDIS End User Group.

PREDIS project

The PREDIS project focuses on treatment and improved handling of metallic materials, liquid organic waste and solid organic waste which can result from nuclear power plant operation, decommissioning and other industrial processes. The project also addresses digitalisation solutions for improved safety and efficiency in handling and assessing cemented-waste packages in extended interim surface storage.

This 4-year Euratom project began in September 2020, with 46 consortium partners from 17 countries. The project also includes an additional 25 industrial partners engaged via the end user group (EUG) to advise the project on their most pressing needs and challenges. The project budget is 23.7 M€ total, of which 14 M€ is provided by the EC.



Low & Intermediate Level Waste Types

Metallics

Liquid Organics

Solid Organics

Cemented Waste

Characterisation & classification of waste

New treatments, conditioning & monitoring

Modelling & Performance evaluation of new solutions

Environmental & economic evaluations

Innovative R&D Approaches

Figure 1. *Project scope addressing waste streams and approach, where the majority of effort is focused on the issues of treatment, conditioning and monitoring.*

Cooperation activities

PREDIS engages the wider international community, allowing cross-fertilisation and interaction between different national programmes. Numerous collaborative dissemination activities, including with EURAD, SNETP, IAEA and NEA, have already been held and further events will continue to maximise the impact of PREDIS for all the identified Stakeholders in the predisposal waste management domain.

12 open webinars presenting information and resources as well as needs, challenges and opportunities on different topics have been arranged so far, with over 1500 registered participants. The topics covered the different technical work areas of the project, but also other issues were addressed, including waste acceptance criteria or waste characterisation.

Gap analysis of predisposal activities

A gap analysis was performed to identify predisposal technology gaps, their urgency and importance and the current technology readiness of potential solutions. For the gap analysis, existing Strategic Research Agendas (SRAs) were reviewed, discussions and surveys took place to assess scientific impacts and the technology gaps. According to the gap analysis, the PREDIS project covers mostly the priority predisposal development activities. Some topics are to be added to the future SRA of predisposal.

Strategic Research Agenda development

Development of the SRA is a crucial strategic activity within the project. The SRA/roadmap will be vital for identifying future work programme priorities (RD&D, strategic studies and knowledge management). The Baseline Strategic Research Agenda has been published in August 2021. This initial stage has focussed on the consolidation of the existing published SRAs of major European and worldwide stakeholder groups (where available) and describes the scientific and technical domains and sub-domains and needs of common interest in Predisposal. In addition to technical considerations, it is recognised that the different member states have differing political, legislative and socio-economic arrangements, and these need to be taken into account in the development of a strategic research programme. The final PREDIS predisposal SRA will be published in spring 2024, however an earlier version will be integrated to the EURAD SRA (predisposal section) in late 2022 so as to be ready for a future programme.

Conclusions

- **PREDIS develops technological innovations for predisposal management with focus on metallic, organic and cemented waste, and digital solutions.**
- **PREDIS has strong EU and international cooperation to avoid duplication and accelerate results.**
- **The diverse End User Group ensures high impact of the project.**
- **Please check https://predis-h2020.eu/ for more information.**

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

VTT

NATIONAL NUCLEAR LABORATORY

sck cen

Contact
Erika Holt, VTT
Tel. +358 40 593 1986
e-mail: erika.holt@vtt.fi

Innovations in liquid organic waste treatment and conditioning

- *PREDIS WP5* -

K. HAMADACHE[1], D. LAMBERTIN[1], M. FOURNIER[1], C. BUCUR[2], F. PANCOTTI[3], M. GUERRA[3], C. DAVY[4], R. LO FRANO[5], J. PROVIS[6], S. WICKHAM[7]

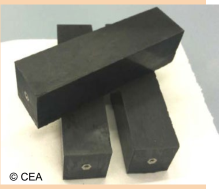
[1]CEA, DES, ISEC, DE2D, Marcoule, France (david.lambertin@cea.fr)
[2]Institute for Nuclear Research Pitesti (RATEN ICN), Campului no. 1, 115400 Mioveni, Arges, Romania (crina.bucur@nuclear.ro)
[3]SOGINSpA, via Marsala 51/C – 00185 Rome, Italy (pancotti@sogin.it)
[4]ECL, Ecole Centrale Lille, Cité Scientifique, 59650 Villeneuve-d'Ascq, France (catherine.davy@centralelille.fr)
[5]DICI- University of Pisa, Lg L. Lazzarino, 1- 56126 Pisa (IT)
[6]University of Sheffield (USFD), Department of Materials Science & Engineering, Sheffield S1 3JD, UK (j.provis@sheffield.ac.uk)
[7]GSL, Galson Science Ltd, Grosvenor House, Melton Rd, Oakham LE15 6AX, United Kingdom (smw@galson-sciences.co.uk)

Context

The PREDIS project targets the **development and implementation of activities for pre-disposal treatment of radioactive waste streams** (metallic, solid organic, liquid organic and cemented) other than nuclear fuel and high-level radioactive waste.

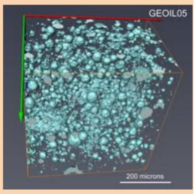
A significant amount of Radioactive Liquid Organic Waste **(RLOW) needs to be processed prior to storage and disposal**. PREDIS WP5 will develop and implement geopolymers and related alkali-activated materials as innovative RLOW **direct conditioning solution**.

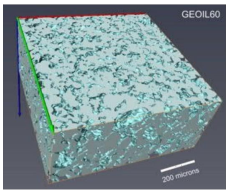
For 4 years, WP5 involves the collaboration of 19 partners from 8 countries all over Europe.



Objectives

- Study **innovative geopolymers** and their interactions with RLOW,
- Develop **direct conditioning solutions** for RLOW from TRL3 to TRL6 including **validation tests** (real waste) and feasibility **scale-up** tests,
- Optimize geopolymers and formulations for RLOW encapsulation, especially **waste loading** and **matrix performance**,
- Process **robustness** regarding waste, raw materials and process variability including study of the **stability** and **durability** of the final waste form,
- Realize a **disposability assessment** related to Waste Acceptance Criteria and scientific approaches for deeper physico-chemical understanding.





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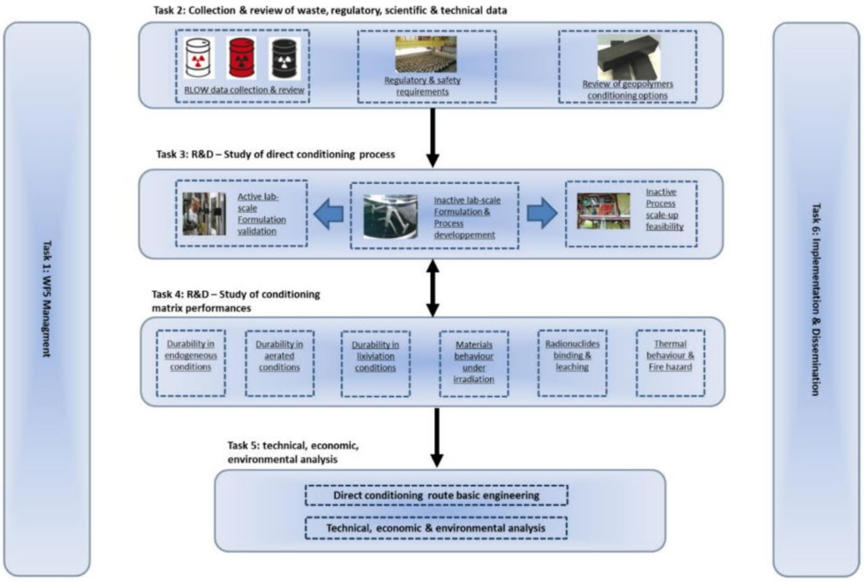
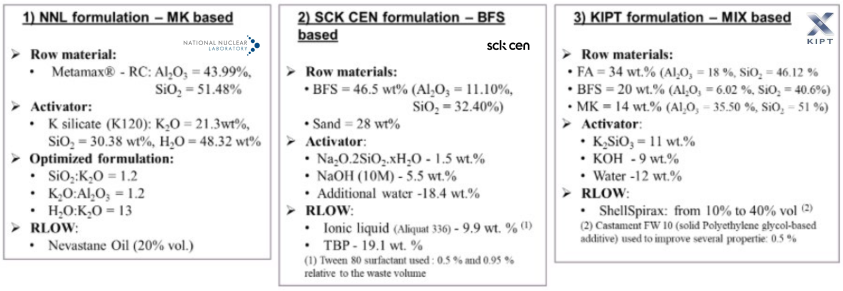


Results

In 2021, collection and review of waste, regulatory, scientific and technical data (Task 2) involving PREDIS stakeholders permitted to describe **RLOW inventories at the European level**. High priority and large volume RLOW streams were identified to be the focus of the PREDIS experimental work. The four references surrogates are: **oils, decontamination solvents, TBP/dodecane and scintillation cocktails**.

Three **reference geopolymers matrix formulations** based on **metakaolin**, **slags** and **mixes** of raw materials have been identified as eligible RLOW direct conditioning solutions (Task 3). They have shown very promising results improving waste loadings and wasteform properties in comparison with traditional cementitious waste forms.



1) NNL formulation – MK based

- **Row material:**
  - Metamax® - RC: $Al_2O_3 = 43.99\%$, $SiO_2 = 51.48\%$
- **Activator:**
  - K silicate (K120): $K_2O = 21.3wt\%$, $SiO_2 = 30.38$ wt%, $H_2O = 48.32$ wt%
- **Optimized formulation:**
  - $SiO_2:K_2O = 1.2$
  - $K_2O:Al_2O_3 = 1.2$
  - $H_2O:K_2O = 13$
- **RLOW**:
  - Nevastane Oil (20% vol.)

2) SCK CEN formulation – BFS based

- **Row materials:**
  - BFS = 46.5 wt% ($Al_2O_3 = 11.10\%$, $SiO_2 = 32.40\%$)
  - Sand = 28 wt%
- **Activator**:
  - $Na_2O.2SiO_2.xH_2O$ - 1.5 wt.%
  - NaOH (10M) - 5.5 wt.%
  - Additional water -18.4 wt.%
- **RLOW**:
  - Ionic liquid (Aliquat 336) - 9.9 wt. % (1)
  - TBP - 19.1 wt. %

(1) Tween 80 surfactant used : 0.5 % and 0.95 % relative to the waste volume

3) KIPT formulation – MIX based

- **Row materials:**
  - FA = 34 wt.% (Al_2O_3 = 18 %, SiO_2 = 46.12 %
  - BFS = 20 wt.% (Al_2O_3 = 6.02 %, SiO_2 = 40.6%)
  - MK = 14 wt.% (Al_2O_3 = 35.50 %, SiO_2 = 51 %)
- **Activator**:
  - K_2SiO_3 = 11 wt.%
  - KOH - 9 wt.%
  - Water -12 wt.%
- **RLOW**:
  - ShellSpirax: from 10% to 40% vol (2)

(2) Castament FW 10 (solid Polyethylene glycol-based additive) used to improve several propertie: 0.5 %

Conclusion

Next steps on the project will permit to:

- Evaluate the **matrix performances** including their durability under endogeneous, aerated or leaching conditions as well as their behavior under irradiation and fire (Task 4),
- Perform a **technical, economic and environmental analysis** (Task 5) providing a holistic evaluation of geopolymers matrices.

PREDIS WP5 will lead to develop innovation and to provide a **reliable solution for the direct conditioning of RLOW**, allowing access to storage, transportation or disposal of this waste stream, while complying with technical, economic and safety requirements.

10th European Commission Conference on EURATOM Research and Training in Radioactive Waste Management
30 May – 3 June 2022 | Lyon, France

EURADWASTE'22

Development of formulations for direct conditioning of Radioactive Liquid Organic Wastes – PREDIS WP5

F. PANCOTTI[1], M. GUERRA[1], R. SCIACQUA[1], C. BUCUR[2], C. MANOLESCU[2], E. LARA ROBUSTILLO[3], M. RODRIGUEZ ALCALA[3], G. PIÑA LUCAS[3], V. SHKUROPATENKO[4], Y. SVITLYCHNYI[4], S. SAYENKO[4], M. HAYES[5], D. CORI[6], A. FAUSTI[6], E. MOSSINI[7], A. SANTI[7], I. MOSCHETTI[7], G. MAGUGLIANI[7], E. MACERATA[7], M. MARIANI[7], Q. T. PHUNG[8], T. N. NGUYEN[8], L. FREDERICKX[8], J. PROVIS[9], D. LAMBERTIN[10], M. FOURNIER[10]

[1] SOGIN SpA, via Marsala 51/C – 00185 Rome, Italy (pancotti@sogin.it)
[2] Institute for Nuclear Research Pitesti (RATEN ICN), Campului no. 1, 115400 Mioveni, Arges, Romania (crina.bucur@nuclear.ro)
[3] CIEMAT, Avda Complutense 40, Madrid, Spain (esperanza.lara@ciemat.es)
[4] KIPT, Akademichna 1, Kharkiv, 61108, Ukraine (sayenko@kipt.kharkov.ua)
[5] National Nuclear Laboratory (NNL), Immobilisation Science & Technology Team, Risley, WA3 6AE, UK (martin.hayes@uknnl.com)
[6] NUCLECO, via Anguillarese 301 – 00123 Rome, Italy (Cori@nucleco.it)
[7] Politecnico di Milano (POLIMI), Department of Energy, Piazza Leonardo da Vinci 32, 20133 Milano, Italy (eros.mossini@polimi.it)
[8] Belgian Nuclear Research Centre (SCK CEN), Boeretang 200, 2400 Mol, Belgium (quoc.tri.phung@sckcen.be)
[9] University of Sheffield (USFD), Department of Materials Science & Engineering, Sheffield S1 3JD, UK, (j.provis@sheffield.ac.uk)
[10] CEA, DES, ISEC, DE2D, Univ. Montpellier, Marcoule, France (david.lambertin@cea.fr)

Introduction

Work Package 5 (WP5) of the H2020-PREDIS project aims at addressing the key issue of Radioactive Liquid Organic Waste (RLOW), which is the lack of a disposal or treatment route, by investigating, developing and assessing (especially regarding disposability) direct conditioning solutions based on alkali-activated materials (AAM).

The main goal of the preliminary R&D stage was to select three optimised reference formulations for RLOW encapsulation with the target to achieve an incorporation rate of at least 30% by volume.

Table 1. *Raw materials used by the different Partners for laboratory trials*

Partners	Raw Materials	Partners	Raw Materials
NUCLECO / SOGIN	BFS: Fos-sur-Mer (France) - Specific Surface Blaine: 4450±250 cm^2 - Average diameter: 11 µm Activator solution: NaOH or KOH Oil: Shellsprirax and Nevastane EP 100 Solvent: TBP and Dodecane	POLIMI	VT: Salerno (Italy) NOCHAR N910 (USA) Recycled PU (Italy) Scintillation cocktail: Ultima Gold (PerkinElmer) Solvent: TBP and Kerosene
NNL / USFD	MetaMax Rotary Calcined MK: SSA Rigden: 3851 m^2/kg, D_{50} 3 µm Argicem Flash Calcined MK: SSA Rigden: 605 m^2/kg, D_{50} 41 µm Activator solution: K_2SiO_3/KOH Oil: Nevastane EP 100 Solvent: TBP	CIEMAT	Commercial MK Activator solution: Na_2SiO_3/NaOH Oil: Repsol Super Tauro Grade ISO 100
KIPT	MK: from Ukrainian deposit BFS: ground granulated, from Ukrainian metallurgical plants FA: from Ukrainian power stations All raw materials sieved (≤500 µm) Activator solution: K_2SiO_3/KOH Oil : Nevastane EP 100, Shellsprirax Surfactant: Castament FW-10 (BASF)	SCK-CEN	BFS: Ecocem Benelux MK: BASF (Metamax) TBP (Merck) Ionic liquid: Sigma-Aldrich
		RATEN	BFS: Liberty Steel Galati, dried, grounded and sieved (<125 µm) VT from Barsana, calcined (80°C) and sieved (<125 µm) Sand: certified CEN, EN 196-1 Oil: Shellsprirax Scintillator: Ultima Gold AB

Description of work and main findings

NUCLECO/SOGIN

Formulation based on BFS + KOH was the most promising. It was tested for the incorporation of different surrogated wastes. Good results were obtained with Shellspirax oil and further investigations are needed to find suitable additive/surfactant/emulsifier mainly with solvent waste.

NNL/USFD

Small-scale laboratory work (~160 mL) studies have been undertaken. 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. Good results have been obtained for Nevastane EP 100, in that 50 vol% has been incorporated into both geopolymer systems. 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.

CIEMAT

The laboratory work consisted 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.

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 it was not possible to obtain a matrix with good workability for waste loading higher than 10% (wt.%). Regardless of the order of addition, the GP matrix with oil/scintillator is not homogeneous and after a short time, the waste is separated. Additional tests are needed to find the most appropriate surfactants or emulsifiers to be used.

POLIMI

Two different approaches have been followed:

1. RLOW direct encapsulation in volcanic tuff (VT) geopolymer (GP)

The pozzolanic reactivity 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 tested with some surrogate RLOW, with addition of surfactants when needed.

2. 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 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. Good results (homogeneous structure, accepted setting time as well as compressive strength) were obtained with Shellspirax oil and Nevastane oil up to 30-40% of waste loading.

Conclusions

The work performed by all the Partners allowed to arrive to the selection of following three reference formulations to be further studied within PREDIS Task 5.3 (Robustness study) and Task 5.4 (Durability study).

Table 2. *Reference Formulations to be further studied*

1) NNL formulation – MK based

- **Row material:**
  - Metamax® - RC: Al_2O_3 = 43.99%, SiO_2 = 51.48%
- **Activator:**
  - K silicate (K120): K_2O = 21.3wt%, SiO_2 = 30.38 wt%, H_2O = 48.32 wt%
- **Optimized formulation:**
  - $SiO_2:K_2O = 1.2$
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- **RLOW**:
  - Nevastane Oil (20% vol.)

2) SCK CEN formulation – BFS based

- **Row materials:**
  - BFS = 46.5 wt% (Al_2O_3 = 11.10%, SiO_2 = 32.40%)
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PREDIS

Pre-disposal management of radioactive waste

The Immobilisation of Radioactive Liquid Organic Wastes (RLOW) in Geopolymers

Authors **S. Irving, M. Hayes, National Nuclear Laboratory, UK**

Introduction

The H2020-PREDIS (Pre-disposal management of radioactive waste) Work Package 5 is focused on investigating the use of alkali activated binders for the treatment of Radioactive Liquid Organic Wastes (RLOW). Geopolymers (GP) offer a potentially alternative encapsulant to Portland cement (PC) based grouts for the treatment of RLOW, in which loadings may be restricted due to the retardation of cement set and poor emulsification of RLOW in PC grouts. In addition, long-term retention of RLOW is also a significant issue when immobilising such species in PC based grouts. Preliminary results from a study of two GP systems, incorporating different metakaolin (MK) powders are presented, which were used to immobilise Nevastane EP 100, representing an inactive RLOW surrogate via a direct solidification process.

Geopolymer

Potassium activated silicate based geopolymers incorporating MK powders have been identified as an alternative cement system for the encapsulation of RLOW. GP are formed through the reaction of an alkaline ‘activating solution’ with an aluminosilicate pre-cursor, to form a 3-D amorphous aluminosilicate product:

$$AS_y + RS_z(aq) + nH \longrightarrow RAS_{(y+z)}H_n$$

Where: A = Al_2O_3, S = SiO_2, H = H_2O and R = alkali metal e.g. Na, K.

MK Type	Fineness (m²/kg)	Practical Size Distribution (µm)			Particle Density (g/cm³)	X-Ray Fluorescence Analysis (wt%)					Molar SiO_2/Al_2O_3
		D_y10	D_y50	D_y90		Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	
MetaMax®	3843	1.1	3.0	9.5	2.62	44.0	51.5	0.4	<0.05	<0.05	1.99
Argicem®	670	4.3	41.0	139.0	2.65	20.0	73.8	2.2	0.9	0.1	6.28

Scope

4 L scale mixes covering GP systems incorporating both MK powders.

Oil volume loading range: 10 – 50 vol%
Shear regimes assessed: “High” and “Low”

Molar ratios investigated were:
SiO_2:K_2O= (1.0 – 1.4) K_2O:Al_2O_3= (1.0 – 1.35/1.5) H_2O:K_2O= (11 – 14/15)

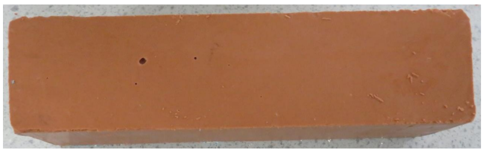
Two MK powders were investigated:

- BASF MetaMax® (a high purity MK manufactured via a rotary calcination process)
- Argeco Developpement Argicem® (MK containing a high quartz fraction manufactured via a flash calcination technique)

Results

MetaMax®

Argicem®



Mid-point formulations containing 40 vol % Nevastane EP 100 Oil

MetaMax®

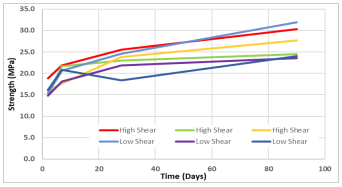
- All the mixes set within 24 h
- Bleed volumes of between 0.25 – 1.25 vol % for high and low shear regimes and loadings up to 50 vol %
- High fluidity grouts (380 mm - >1020 mm)
- Low viscosities of <1 Pa·s
- Increasing viscosity with increasing oil loading
- Shear had little effect on mix viscosities for mid-point formulations at 20 vol % RLOW

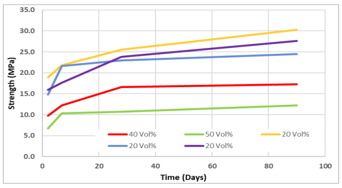
Argicem®

- All mixes set within 48 h
- Bleed volumes of 0 – 0.5 vol % for high and low shear regimes and loadings up to 50 vol %
- High fluidity grouts (540 mm - >1020 mm)
- Low viscosities of <1 Pa·s, although higher than MetaMax® formulations
- Low shear produced a slight increase in viscosity for mid-point formulations at 20 vol % RLOW

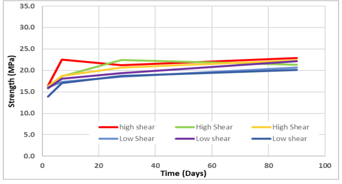
Compressive Strength

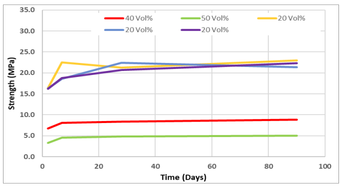
MetaMax®





Argicem®

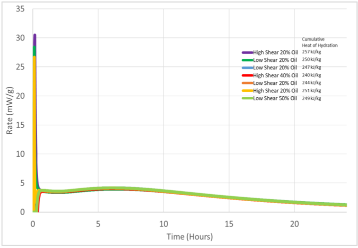




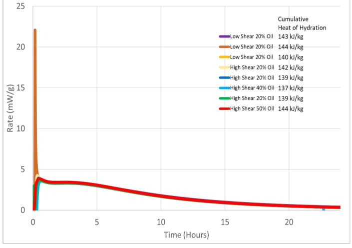
- Rapid strength gain by 7 d curing
- Oil loadings of 10 – 50 vol % could be satisfactorily incorporated in both GP systems
- Acceptable strengths ranging from 5 MPa – 37.5 MPa at 90 d
- Strengths decreased as oil volume loading increased
- Minimal effect of shear (at 20 vol % loading)

Isothermal Conduction Calorimetry

MetaMax®



Argicem®



$$\text{Reactive material} = \frac{Water\ mass + Silicate\ water + Oil\ mass}{KOH\ mass + MK\ mass + Silicate\ solids}$$

- High heats of MK dissolution resulting in high cumulative heats of reaction after 24 h
- Small second polymerisation peak
- Lower heat output for Argicem® than MetaMax® mixes due to MK being coarser and high SiO_2 content
- Effect of shear and oil loading negligible

Conclusions

- Successful encapsulation of up 10 – 50 vol% RLOW
- Both MK GP systems offer a potentially viable method of encapsulation

Future work

- Development of formulations in order to reduce bleed volumes and potentially increase waste loadings

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

NATIONAL NUCLEAR LABORATORY

Sellafield Ltd

The University Of Sheffield.

Contact
Name: Samantha Irving
e-mail: samantha.irving@uknnl.com

Pre-disposal management of radioactive waste

Stability, Physico-Chemical Characterisation, and Leaching of Reconditioned Waste Forms Relevant to Radioactive Wastes

Gianni F. Vettese[1]*, Joyce W. L. Ang[1], Taavi Vierinen[1], Tandré Oey[2] , Laura Stefanini[2], Suvi Lamminmäki[2], Matti Nieminen[2], Jaana Laatikainen-Luntama[2], Jukka Maunumäki[2], Jaakko Sippola[2], Jaana Rantanen[2], Emmi Myllykylä[2] & Gareth T. W. Law[1]
[1]The University of Helsinki, Radiochemistry Unit, Espoo, Finland, [2]VTT Technical Research Centre of Finland, Helsinki, Finland

1. Introduction

Low and Intermediate Level radioactive Waste (LILW) typically includes operational wastes and spent ion-exchange resins (IXR). Although LILW represents only ~1% of the total activity of waste, it represents >95% of the total volume. Finland alone generates over 300 m^3 of LILW annually. **Finnish IXR waste is generally immobilised in a solid matrix** (e.g., bitumen or cement). It is held in interim storage until final disposal in rock caverns ~100 m below surface. During final disposal, the space surrounding the solidified waste packages will likely be backfilled with cement, and any passing waters will therefore be in equilibrium with this, resulting in **a high pH** (~12), Ca rich solution that could **act as a leachate,** potentially **mobilising radionuclides**.

Instead of direct immobilisation IXR waste can be thermally treated. VTT have developed a new thermal treatment method to (1) reduce volume significantly and, (2) remove organic matter, prior to final disposal. IXRs (named PR3 and PR4) have been thermally treated and immobilised in novel metakaolin geopolymers as an alternative immobilisation matrix at VTT. We share early (6 months) results that follow the geochemical behaviour of key geopolymer components and assess the potential for radionuclide mobilization compared to ordinary Portland cement (OPC).

2. Material Characterisation

- The ash contains stable isotopes of Cs, Sr, Cr, Co, and Ni, representative of nuclear fission and activation products. Ce and Eu were also added as analogues for transuranic elements.
- Two IXRs were thermally treated: PR3, without added Fe; and PR4, with added Fe and loaded into the geopolymer matrix with ash loadings of 15% or 50% (Table 1). Varying ash loadings assess the potential range for waste loading using thermal treatment. Fe may be present in ash as a corrosion product from the nuclear reactor.
- Ash particles are heterogeneously concentrated as dense agglomerations observable in back-scatter electron (BSE) imaging (Figure 1). These are retained after encapsulation into the geopolymer matrix (data not shown).

Table 1 (left): Geopolymer / cement descriptions.
Table 2 (right): Leachant recipe.

	Geopolymer Description				
	PR3 15%	**PR3 50%**	**PR4 15%**	**PR4 50%**	**OPC PR4 15%**
Ash (%$_{wt}$)	15	50	15	50	15
Precursor	Argical	Argical	Argical	Argical	Cement paste
Fe (%$_{wt}$)	0	0	8	8	8
Cs, Eu, Ce in ash (ppm)	300, 50, 50	300, 50, 50	250, 50, 75	250, 50, 75	250, 50, 75

Leachant recipe	
Ca^{2+} (ppm)	18
K^+ (ppm)	2801
SO_4^{2-} (ppm)	650
OH^-	850
pH	12.5
Conductivity (mS/cm)	12.9

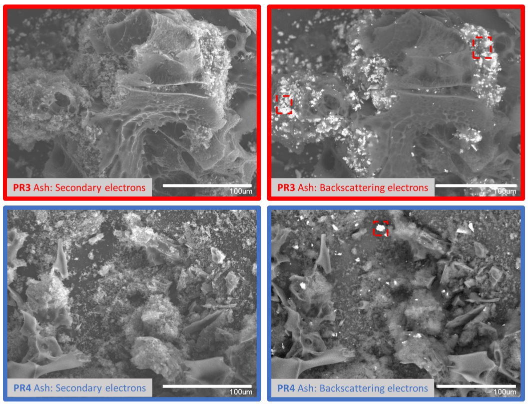


Figure 1: SEM imaging of ion-exchange resin ashes for PR3 (top, red) and PR4 (bottom, blue). Red squares highlight where EDX analyses were completed.

3. Geopolymer Leachability

Ongoing, semi-dynamic leaching experiments assess the short-term (≤ 6 month) behaviour of the matrix and contaminants (Figure 2) using a representative leachant (Table 2).

- pH reaches steady-state in all experiments within 60 days at 12.6. Experiments with PR4 ash are more reducing (Eh ~ -350 mV), vs. experiments with PR3 ash (Eh ~ -70 mV) (data not shown).
- Bulk geopolymer components Si & Al leach into the solution (Figure 2), Ca precipitates from leachant into the solids (data not shown).
- Trace analogues Cs, Ce & Eu leach into the solution at comparable rates to OPC (Figure 3). Sr, Ni, Co, Cr also (data not shown).
- No colloids were observed in leachate using dynamic light scattering / zetapotential analyses.

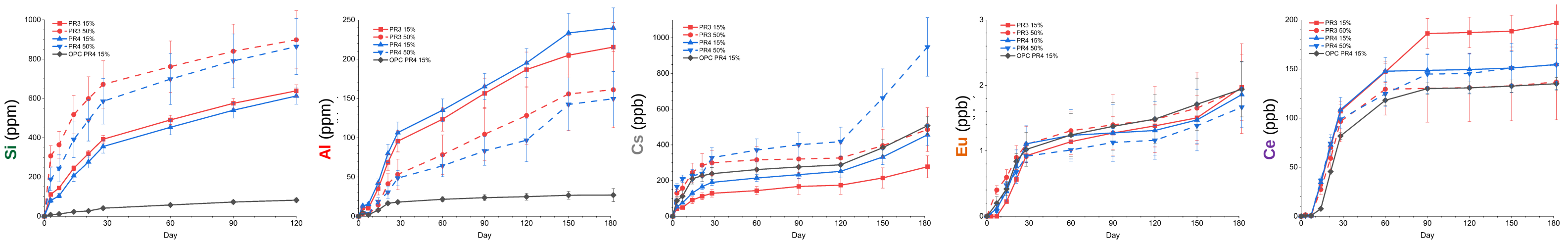


Figure 2: (From left to right) cumulative leaching of Si, Al, Cs, Eu, and Ce. 60 mL leachant was refreshed after 7, 14, 21, 28, 60, 90, 120, 150, and 180 days.

4. Post-Mortem Analyses (ongoing):

- Leached geopolymers are sacrificed, preserved, and dissected after 1 month, 6 months, 1 year, and 2 years of leaching.
- The evolution of the bulk geopolymer components will be assessed via XRD, ESEM-EDX, Raman / IR & ^{29}Si / ^{27}Al MAS NMR.
- Trace contaminant speciation & distribution will be assessed via EMPA, µ-XANES / XRF / XRD.
- Preliminary results suggest a change in morphology, weakening of structural integrity, and growth of secondary, calcium-containing phases.

5. Conclusions & Future Work:

- Current, short-term leaching studies suggest that geopolymers retain a range of radionuclides relevant to LILW disposal equally as well as Portland cement.
- The initial rate of trace analogue release is most significant in the first 30 days, suggesting multiple mechanisms for radionuclide retention, linked to matrix dissolution.
- The rate of radionuclide leaching does not increase linearly with ash loading, suggesting that the added ash% may be optimized. Fe content has a slight effect on Cs retention, but not on other radionuclides, suggesting that mobilisation of the other nuclides is not driven by redox processes.
- Experiments will continue for up to 24 months, and the elevated concentrations of radionuclides will permit microscale analysis of local structure and bonding environments, which will be used to clarify retention mechanism(s).

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

Always happy for a chat!

Email: gianni.vettese@helsinki.fi

Pre-disposal management of radioactive waste

Innovations in liquid organic waste treatment and conditioning

PREDIS Work Package 5 Management Team: I. Giboire[1], K. Hamadache[1], M. Fournier[1], C. Bucur[2], F. Pancotti[3], M. Guerra[3], M. Briffaut[4], R. Lo Frano[5], J. Provis[6], S. Wickham[7]

[1]CEA, DES, ISEC, DPME, Marcoule, France
[2]Institute for Nuclear Research Pitesti, Campului no. 1, 115400 Mioveni, Arges, Romania
[3]SOGIN SpA, via Marsala 51/C, 00185 Rome, Italy
[4]Ecole Centrale Lille, Cité Scientifique, 59650 Villeneuve-d’Ascq, France
[5]Università di Pisa, Lg L. Lazzarino, 1- 56126 Pisa, Italy
[6]University of Sheffield, Department of Materials Science & Engineering, Sheffield S1 3JD, UK
[7]Galson Science Ltd, Grosvenor House, Melton Rd, Oakham LE15 6AX, UK

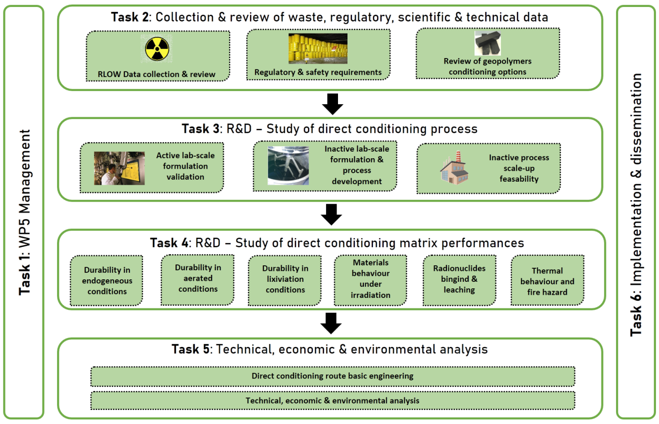
The EU-project PREDIS targets the development and implementation of activities for pre-disposal treatment of radioactive waste streams (metallic, solid organic, liquid organic and cemented) other than nuclear fuel and high-level radioactive waste

A significant amount of radioactive liquid organic waste (RLOW) needs to be processed prior to storage and disposal: Work Package 5 develops and implements geopolymers and related alkali-activated materials as innovative direct conditioning solutions

Work Package 5 involves the collaboration of 19 partners from 8 countries all over Europe

Objectives

- **Implement geopolymers as mineral binders for RLOW**, from TRL 3 to TRL 6, including validation tests with real waste and feasibility scale-up tests
- Consider **process robustness** regarding waste, raw materials and process variability
- Lead to **final waste forms** showing properties and performances **compatible with safety and technical requirements** related to transport, storage, and disposal



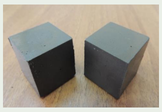
PREDIS Work Package 5 structure and tasks

Relevance

- **Societal issue**: contribution to the sustainable management of radioactive waste
- **Environmental and nuclear safety issues**: limitation of long-time storage of RLOW volumes awaiting treatment
- **Technical issue**: development of flexible and versatile innovative conditioning solutions
- **Economic issue**: development of industrially robust and economically viable solutions (LCA and LCC analyses)

Results and ongoing work

- **Task 2** identified and categorised 1200 m^3 of RLOW divided between **oils** (35%), **solvents** (25%), **scintillation cocktails** (20%) and **decontamination liquids** (20%)
- **Task 3** selected, and is currently optimizing, **three geopolymer matrices** based on metakaolin, blast furnace slags (BFS), and mixes of raw materials. They have shown very promising results with RLOW loadings up to **50 vol.%**

Formulation	Metakaolin-based	BFS-based	Materials mix
Raw materials	Metamax®	BFS and sand	fly ashes, BFS, and metakaolin
Activators	K-silicate	Na_2O and NaOH	K-silicate and KOH
RLOW	Nevastane oil 20 vol.%	TBP, ionic liquid 30 vol.%	Shell Spirax oil up to 40 vol.%
Samples			

Reference geopolymer formulations for direct RLOW conditioning

- **Task 4** is evaluating the **performances** the three reference geopolymer matrices, including their **durability** under endogeneous, aerated and leaching conditions, as well as their behavior under **irradiation and fire hazard**
- **Task 5** is performing the **Life Cycle Assessment** of gepolymer matrices from overall process schemes and data

PREDIS WP5 will lead to develop innovation and to provide a reliable solution for the direct conditioning of RLOW, compatible with storage, transportation, and disposal of this waste stream, while complying with technical, economic and safety requirements

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

Contacts

Isabelle Giboire and **Maxime Fournier**
isabelle.giboire@cea.fr
maxime.fournier@cea.fr

CONDITIONING OF LIQUID ORGANIC WASTE INTO A GEOPOLYMER MATRIX

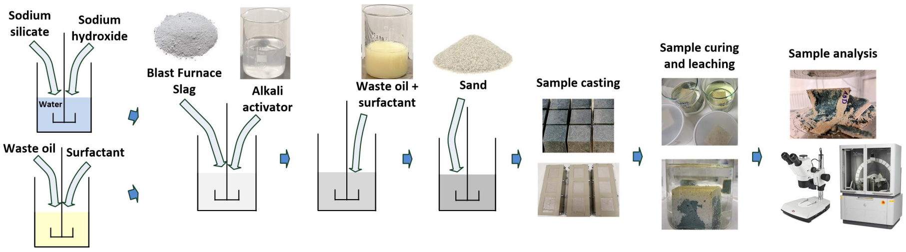
www.cvrez.cz

Anna Sears[1], Vojtěch Galek[1], Thi Nhan Nguyen[2,3], Quoc Tri Phung[2]
anna.sears@cvrez.cz
1 Research Centre Řež, Czech Republic, 2 Belgian Nuclear Research Centre (SCK CEN), Belgium,
3 Department of Materials Engineering, KU Leuven, Belgium

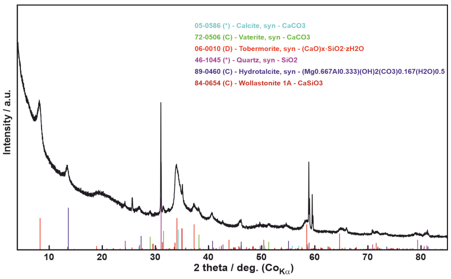
Introduction

This study addresses challenges in managing and disposing of liquid organic radioactive waste (LORW) by exploring a novel approach of directly incorporating organic waste into geopolymer matrices. Motor oil Mogul was used as a surrogate for LORW, along with a combination of blast furnace slag, alkali activator, and surfactant to produce geopolymer matrices. Multiple characterisation techniques were employed to assess the physical, chemical, and mechanical properties of the geopolymer waste forms. Further, leaching experiments were conducted to assess the leachability of oil and selected elements from the geopolymer samples.

Material and Methods

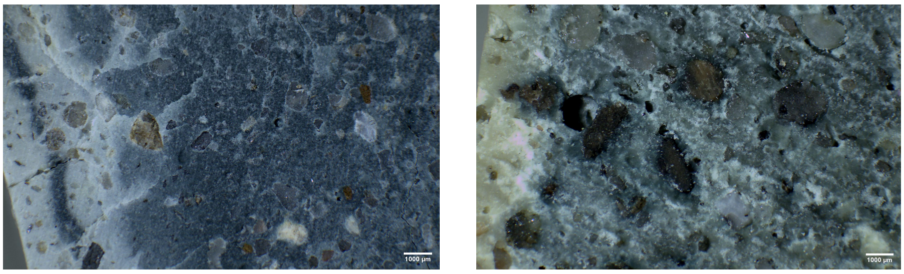


XRD analysis



The XRD analysis of the sample with added waste oil and surfactant Tween® 80.

Stereoscopic microscope analysis



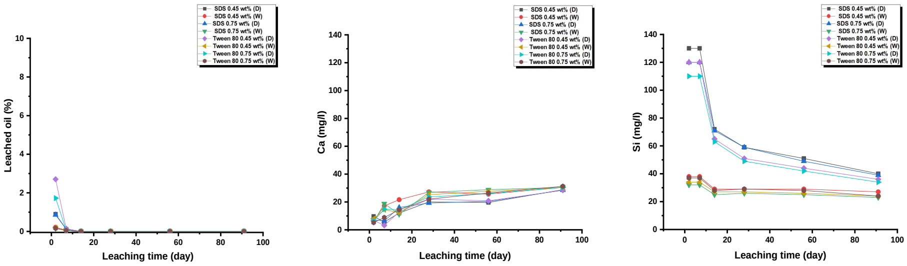
The stereoscopic microscope images of the sample without added waste oil (left) and with waste oil and surfactant mixture (right).

Compressive strength

Surfactant addition (wt%)		Compressive strength before leaching (MPa)	Compressive strength after leaching (MPa)
Tween 80 (D)	0.45	17.03	31.37
	0.75	20.42	29.75
Tween 80 (W)	0.45	19.72	28.59
	0.75	20.71	24.96
SDS (D)	0.45	26.41	34.55
	0.75	23.32	29.37
SDS (W)	0.45	29.73	29.97
	0.75	22.30	27.56

The compressive strength analysis of the samples before and after leaching.

Leaching of oil, calcium and silica



The evaluation of oil, calcium and silica leaching behaviour in geopolymer samples during a 91-day experiment for long-term durability assessment.

Conclusion

In our investigation, we assessed the suitability of an innovative approach for managing LORW, which due to its hazardous nature and long-term environmental impact, poses a significant challenge. Compressive strength tests indicated acceptable mechanical performance, but adding waste oil with surfactants reduced strength compared to the samples without added waste oil, with higher surfactant concentrations showing weaker results. Leaching experiments revealed minimal oil release, promising high immobilisation efficiency. Additionally, leaching studies on calcium and silica showed initial release followed by stabilization. XRD analysis demonstrated variations in mineral composition, while microscopy revealed structural changes influenced by added oil. In conclusion, this approach offers potential for LORW immobilisation and disposal.

Acknowledgement

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CENTRUM VÝZKUMU ŘEŽ S.R.O.

Hlavní 130, Řež, 250 68 Husinec, Czech Republic
T: +420 266 173 181, F: +420 266 172 398
E: cvrez@cvrez.cz, W: www.cvrez.cz

CVŘ Research Centre Řež

PREDIS

WP7: Innovations in Cemented Waste Handling and Pre-disposal Storage

Pre-disposal management of radioactive waste

WP7.5: Data handling, processing and fusion

Objectives

Task 7.5 of the PREDIS project was dedicated to data handling, processing, and fusion. Its goal was to produce

- A conceptual model for data handling and storage
- Database and software prototype

The work was strongly connected to Task 7.3 on innovative instrumentation and Task 7.4 on simulation and digital twins. The joint showcase of these three tasks, presented at UJV, demonstrated the advancements made. It exemplified the collaborative, iterative, and integrative approach of the project, weaving together various strands of research and development.

Data management framework

The Data Platform is the central data repository of the data management framework, interfacing with the various data input and output flows.

The Decision Framework is the user interface to the data management framework and aims to assist the decision-makers in various ways with information about the condition of the monitored packages and complementing that information with the prediction capabilities of the digital twin subsystem.

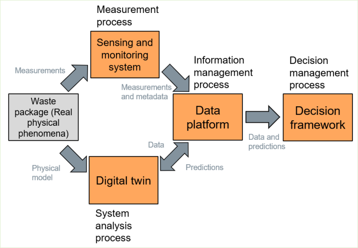

Figure 1: Data management framework high-level system architecture

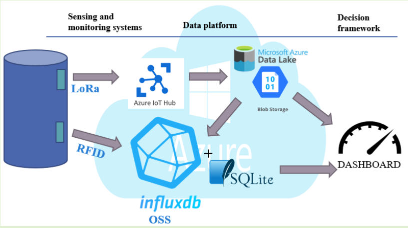

Figure 2: MS Azure scheme

Results

The Data Platform

A reference metadata model, accessible as a web service, was set up by using a Django Virtual Environment in a local server on a site. Four models (i.e., database tables) were associated (waste packages, sensors, nodes, images) with the possibility of managing data by the administrator and user groups with the necessary permissions. SQLite3 Database was preliminarily filled (by using Django syntax) with the relevant data of the project. Once the waste packages are defined as a master table, any changes associated with them are automatically traced in a change history. Data was visualized in three different ways: admin mode, public (webpage currently drafted in CSS according to Bootstrap 5.0 specification), and by other external open-source tools (i.e., HeidiSQL) to analyze the database structure and its consistency.

The Decision Framework

Utilizing a decision platform that integrates ML and digital twin-powered predictions and Online Analytical Processing (OLAP) analysis holds the potential to significantly support informed decision-making. Through the integration of sensor data and other monitoring systems, the PREDIS platform provides immediate insights facilitating improved performance and safety in waste management processes. The real-time monitoring capabilities facilitate the instant detection of deviations from normal conditions and automated alerts upon the detection of irregularities for prompt corrective actions. The OLAP analysis empowers users to selectively extract and query data, allowing for analysis from various perspectives. This proactive approach ensures timely interventions, thereby minimizing the likelihood of incidents/accidents or environmental impact.

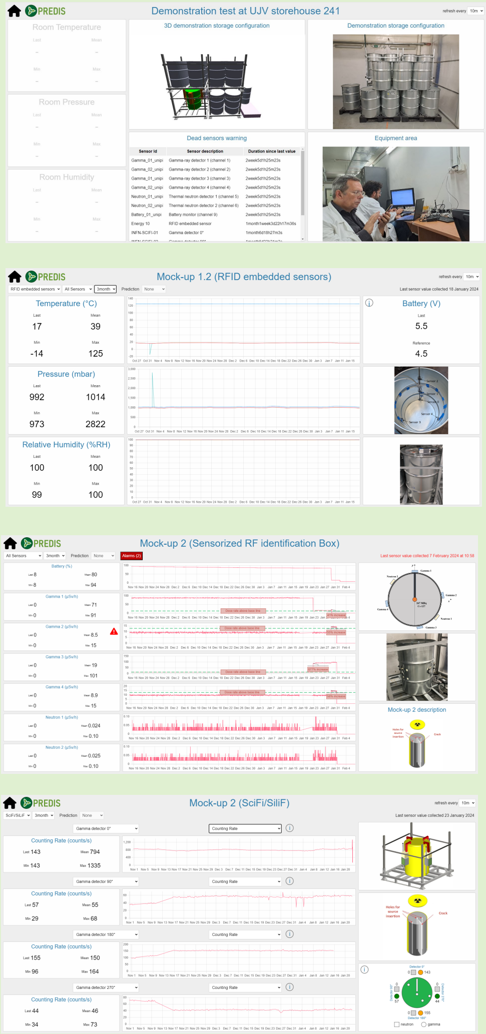

Figure 3: Dashboard examples

Conclusion

A conceptual model for data handling and storage was developed, and a practical implementation was performed. The demonstration test at UJV confirmed that monitoring data from sensors can be automatically uploaded to the Microsoft Azure cloud platform, and it can be visualized on the decision platform. A web-based decision platform with multiple dashboards was developed to present information from different perspectives customized to different users. The functionality of the decision platform has been proven in the UJV demonstration test. Predictive numerical models of the digital twin can be integrated into the platform to further support decision-making.

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

Contact
Tuula Hakkarainen
VTT, P.O. Box 1000, FI-02044 VTT
Tel +358 40 593 2542
e-mail: tuula.Hakkarainen@vtt.fi