

**Coordinated Research Project Proposal**

T21029

**Benchmarking waste form testing protocols to facilitate the use of geopolymers as a matrix for the immobilization of radioactive waste.**

# Summary

The International Atomic Energy Agency (IAEA) promotes the safe and peaceful use of nuclear energy including the management of radioactive waste according to nationally and internationally agreed principles and standards; with safe disposal as endpoint for all waste types.

Many low-level waste (LLW) streams require immobilization to meet the waste acceptance criteria (WAC) for storage and disposal. There are many technologies, including both thermal and non-thermal processes, that are operational world-wide to produce a variety of stable waste forms. To ensure that the waste form produced will conform to the relevant WAC, it is necessary to perform a number of tests to establish the long-term durability and overall performance of the waste form in storage and simulated disposal conditions. These tests are referred to as waste form performance tests.

Geopolymers, or alkali-activated aluminosilicate cements or binders, were first discovered in early 20th century, and since have gradually been developed into usable applications in different areas of industry, including construction, nuclear waste immobilisation and encapsulation, ceramics, fireproofing and patching materials. A geopolymer undertakes a very similar process to that of a standard Portland cement binder but has the added benefit of using readily available aluminosilicate materials with different activators.

Geopolymer immobilisation and encapsulation has receiving increasing attention globally as an alternative waste form to standard Portland cement blends because of their high strength, adaptable and tailorable gel network and overall low environmental impact. Formulation development in this field has extensively been researched in recent years and a series of potential formulations for waste immobilization has been developed. These formulations, usually consisting of metakaolin or slag-based systems, have shown real promise in the stabilization of different waste streams. However, in order to ensure that the waste form produced will conform with the relevant WAC, which is usually based around a cementitious matrix, it is necessary to perform a number of tests to establish the performance of the waste form over long time periods, in conditions representative of storage and disposal. Due to the unavailability of any international standards for geopolymers, in either the construction or nuclear sector, waste form testing has been performed using many different protocols by researchers from different Member States. These testing protocols, usually based around cementitious materials, have produced different results depending on implementation of the test procedures. The ability to compare the results from different Member States for geopolymers has become increasingly difficult.

The IAEA has initiated this CRP to investigate the benchmarking of selected cementitious protocols against new developing procedures investigated for geopolymer matrix testing in order to facilitate the establishment of future waste form testing protocols for geopolymers as a matrix for the immobilization of radioactive waste.

# Background : Scientific and problems to be researched

Geopolymers, were first discovered in early 20th century, and since then have gradually been developed into usable applications in different areas of industry, mainly as construction, ceramic, fireproof materials.

Despite geopolymeric materials having been utilized for ~100 years, it is only within the last 20 years that efforts having been made toward deployment of geopolymers within the nuclear industry. The applications to date are predominantly oriented towards the immobilization, stabilisation and encapsulation of radioactive waste. To date the usage of geopolymers as construction or shielding materials for substitution of Ordinary Portland Cement (OPC) concrete in nuclear industry (resistant to extreme conditions of radiation fields) is considered, but relevant information has not been explicitly published. Investigation in the waste immobilisation using geopolymer matrix has been gained in a number of Member States and networks (PREDIS, EURAD 2), but only few of Member States have approved the application for waste processing. A variety of geopolymer matrices have shown high waste loading for the immobilization of radioactive waste including “challenging” waste streams. The main advantage of the geopolymers arises from fundamental mineralogical differences between geopolymers and cementitious materials. In contrast to cementitious materials, based on hydrated calcium silicate (C3S and C2S) products, the geopolymer matrices represent mainly amorphous aluminosilicate structures linked into three-dimensional networks. The structural differences partly explain the higher chemical and thermal stabilities of geopolymer materials and contribute to the retention of radionuclides and other elements in geopolymer matrices and are closely related to the potential applications in the nuclear industry.

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PREDIS network [PREDIS Deliverable D2.6\_Gap Analysis\_v2021\_0531] indicated that: “Cement-based materials remain the most common option for the immobilisation of the treated waste. The gap is to compare the performance of the two types of binder (cement and geopolymer). The gap is also to define a need for common protocol and experimental conditions that will allow the evaluation of the performance of the end products. Additionally, defining reference protocols and experimental conditions is required”.

The IAEA recognizes that geopolymer waste forms have an important role in waste conditioning and as such the Waste Technology Section (WTS) at the IAEA has initiated the CRP to investigate the application of cementitious testing standards to geopolymer matrixes in order facilitate the establishment of future Waste Form Testing Protocols for Geopolymers as a Matrix for the Immobilization of Radioactive Waste.

Where did the proposal originate from:

• Initial Hybrid TM (12-23 April 2021) on “Waste form testing protocols” provided an indication of the current state of knowledge on waste form testing protocols including geopolymer matrixes and provided a platform to discuss with experts from industry the application of waste form testing standards. Several of the attending participants expressed interest to further confirming/developing/adjusting cement protocols for geopolymer applications.

• During the Hybrid TM (4-8 April 2022) on “The status and use of geopolymers to immobilize radioactive waste”, experts from industry presented the application of geopolymer for the immobilization of different waste streams and highlighted the limited waste form testing protocols for the manufactured geopolymer matrixes. Several of the attending participants expressed interest in exchanging/receiving protocols/information regarding the developed of geopolymer testing standards.

• The 2nd TM was followed with another Workshop ( 24-28 June 2023) on durability of waste forms, including geopolymers, hosted by IAEA that provided an indication of the current state of knowledge on waste form testing protocols required to perform safety assessment for disposal. It provided a platform to discuss with experts (mostly regulators) a minimum waste form testing required for evaluating waste form durability for disposal considerations. Several of the attending participants expressed an interest in confirming/developing protocols for geopolymer waste form durability.

• A CM was held at the IAEA (August 2023) was held with invited experts (currently implementing durability protocols) to identify the absence of geopolymer protocols waste form testing needed to determine durability and if a CRP could facilitate modification of cementitious durability protocols for geopolymer testing.

# Overall Objective

The overall objective of the proposed CRP is to benchmark waste form testing protocols for geopolymers waste forms in order to:

* Enhance the international knowledge basis on geopolymer waste form durability testing;
* Support Member States strategic decision on whether to pursue waste immobilization into geopolymers;
* Support EURAD II;
* Support future discussions (i.e., TM, conferences and network meetings) on testing protocols for geopolymers waste forms.

**Specific Research Objectives defined as Work Packages (WP)**

To address the overall objectives of the CRP a series of sample production and testing methodologies will need to be performed by the CRP members. When potential CRP members are applying for work packages 2-5, a detailed list of equipment/experimental capabilities to perform the testing requirements should be added as well. The following work packages (WP) have been produced to comprehensively test the test associated with geopolymer samples.

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*FIG. 1. Waste form properties influencing durability during disposal.*

**WP 1: Proposal to define the geopolymer systems and the testing protocols to be analyzed during this CRP.**

This work package will define and develop the geopolymer formulation envelope that will be used during this CRP. This will be outlined during the first CRP technical meeting. CRP members can use their own formulations and designs, including commercial products, however the laboratory grade products outlined below are for comparison testing.

Consideration and chemical analysis of the precursors under research

* Metakaolin/Calcined Clays
* Blast Furnace Slag
* Fly Ash
* Additives (inc. superplasticizers, silica fume, etc.)
* Other aluminosilicates

Activating Solutions

* Sodium Hydroxide/Silicate
* Potassium Hydroxide/Silicate
* Carbonates (Sodium Carbonate, Potassium Bicarbonate, …)
* Acids (Phosphoric Acid etc.)
* Other alkalis from the nuclear cycle – Sr/Cs hydroxides

Standardizing Testing Protocols across institutions

* Physical Testing
* Chemical Degradation and Durability Testing
* Chemical Stability Testing
* Chemical Characterization
* Transportation Protocols (in WP 2)

Commercial products will be accepted within this CRP, providing they can be classified as a geopolymer product, with limited knowledge of the chemical composition.

*\*Samples containing Portland cement are out of scope for this CRP.*

**WP 2 Manufacturing and shipping of reference waste forms**

Based on the results of WP 1 candidate formulations will be elucidated and produced in accordance with a standard methodology. This standard methodology will be defined by the work package members but should include as a minimum the mixing equipment and characteristics, order of addition, curing conditions. Large numbers of samples produced to different geometries, both standard and non-standard will need to be produced and shipped to all the CRP members for testing. Once this has been decided the formulations due for testing can be produced to include, but not limited to, the following formulations:

* Geopolymer
* Geopolymer + Additive (e.g., superplasticizers, silica fume, etc.)
* Geopolymer + Surrogate Materials
* Geopolymer + Surrogate Materials + Additive

Once these formulations have been produced, shipment will need to be organized to the agency. These samples will then be anonymized and shipment to the testing institutions will be undertaken. This shipment will need to involve a standard test method to control issues, such as handling, storage, overheating/cooling, time in transit and onset of experimentation.

Active samples will be accepted into the study; however, it will be the CRP member’s responsibility to test these samples at their home institution.

**WP 3: Protocol testing of the degradation in geopolymer waste forms.**

Under this work package, analysis of the protocols for testing degradation within geopolymer samples will be investigated. International protocols selected in WP 1 will be used on supplied samples. Additionally individual CRP members are expected to perform additional degradation tests beyond this international protocol, so that data can be compared to the supplied samples.

* Leaching studies
	+ - Chemical Analysis
			* Requirement to be able to perform ICP OES/MS
			* TOC/TIC on leachate is desirable
		- Leached specimens will be analyzed in line with WP 5 and compared to non-leached samples.
* Alkali silica reaction (ASR)
* Carbonation
* Radiation stability:
	+ - Gamma Irradiation – Co60
		- Alpha/Ion Beam
		- Determination of G value for Radiolytic Hydrogen
* Temperature Studies
	+ - Cyclic
		- Low Temperature
		- High Temperature
* Biodegradation

**WP 4: Physical characterization studies of geopolymer waste forms**

Under this work package, physical characterization of the mechanical and microstructural analysis will be determined on supplied geopolymer samples and those that have undergone degradation in WP 3 as indicted below. Samples will be provided in accordance with a standard test method and CRP members are encouraged to perform additional physical characterization tests so comparison between the results can be provided. The following physical and microstructural tests will be performed:

Determination of testing standards

* Porosity – MIP, μCT, BET
* Water sorption, gas/water permeability and diffusion

Undertake combinations of the following tests on the samples produced in WP 3.

* Compressive Strength
* Flexural Strength
* Density
* Micro/Nano-Indentation
* Microstructural Imaging
* Thermal Conductivity

The results will be available as input into durability studies.

**WP 5: Chemical Stability of Geopolymer Systems**

In this work package, detailed chemical characterization of the samples produced in WP 2 and that have undertaken degradation and physical testing in WP 3 and 4. CRP members can perform additional chemical tests based on their laboratory capabilities which should be outlined initially.

* FTIR
* Raman
* Solid State Nuclear Magnetic Resonance
* Scanning Electron Microscopy
* TG-MS (inc. irradiated samples)
* TOC/TIC in the solid phase
* XRD
* XRF
* Synchrotron-based studies (inc. XAS, XAFS, μXRF, μFTIR, XANES, etc.)

CRP members will produce yearly reports and a final TEC DOC outlining the outcomes of these tests. This can reference CRP members published and unpublished work, comparing the testing protocols on commercial geopolymer products and laboratory produced samples. Commercially sensitive information will be respected throughout the reporting of this project.

# Expected Outcomes

The expected outcome of this CRP is that MS will have at their disposal a broader knowledge basis on testing protocols for geopolymer matrices to be used as:

* Construction materials for nuclear installations;
* Shielding materials;
* Matrices to encapsulate nuclear waste;
* Repairing of damaged cement nuclear constructions.

# Expected Outputs

The expected outputs of this CRP:

* IAEA course/workshop/TM to share information resulting from this CRP regarding the understanding on waste form testing protocols for geopolymers with a wider audience;
* IAEA workshop to engage with stakeholders (regulators) sharing an interest in this concept, for example to establish a WAC for disposal on associated regulatory framework;
* Attend international conferences and/or network meetings to share information resulting from this CRP;
* Produce a Technical IAEA document summarizing current state of knowledge on geopolymer waste form testing protocols to determine the durability of future disposed geopolymer waste packages.

# Action Plan

**Activity 1: Preparation of terms of reference**

A consultancy meeting to prepare the working materials and defining the scope for the CRP was held at the IAEA, Vienna, 14-18 August 2023.

**Activity 2: Receive, analyse and select applications**

It is anticipated that the CRP will involve 12-20 institutions from developed and developing MSs. The institutions that have participated in international networks, in particular working on development of geopolymers as waste forms, will be encouraged to participate in this CRP. Selection of institutions will be based on the relevance of their individual proposals according to the scope and objectives of the project, the qualifications of counterparts and availability of proper R&D facilities and available equipment. The balance between representatives from developed and developing MSs will be considered. A consultancy meeting will be organized at the Agency to make the final selection of participants based on realization of a balanced program.

**Activity 3: Perform research and collect data**

Research, collection and analysis of data will be undertaken by the participants under the aegis of up to 5 Contracts and up to 25 Agreements. Capabilities of individual institutions, availability of resources and facilities for implementation of all individual projects will be analyzed and used to allocate the work described in the specific work packages across the participants. It is expected that some participants will contribute to more than one specific research objective.

**Activity 4: Sharing results, coordination and plan**

Three RCMs will be held to share results and coordinate and plan the subsequent steps of the CRP. At the first RCM to be held in 2024 the objectives of the CRP and individual projects will be discussed together with any initial results. The working plan for CRP implementation will be discussed, including the establishment of bilateral and multilateral co-operation between participating institutions.

The 2nd Research Co-ordination Meeting in 2025 will discuss the status of the CRP, progress in the implementation of the individual R&D activities and results achieved, as well as recommendations for further development of the CRP. The program leading to the final Research Co-ordination Meeting will be discussed.

At the 3rd RCM to be held in 2026 summary reports of the outcomes of the individual projects will be presented and discussed. The structure and the scope of the final report of the CRP will be developed. The material to be included in the final report of the CRP will be prepared and discussed. The main achievements and general summary of the CRP will be identified and a small group convened to compile the final report.

In addition to the three RCMs suitable international meetings will be identified where sub-groups of the CRP can meet and update each other on progress. The outcomes of these meetings will be circulated to all CRP participants.

**Activity 5: Drafting /finalising TECDOC**

The CRP final report will take the form of an IAEA-TECDOC. The TECDOC will include the summary of the CRP implementation and individual reports of all participating institutions. The group identified will hold one consultancy meeting and will participate in two home-based assignments to finalize the draft TECDOC. In addition, appropriate publications in the technical literature will be encouraged.

#  CRP contracts

The duration of the CRP will be four years.

The Agency will provide financial support for the three RCMs, support for up to 5 Research Contracts, 2 Home Based Assignments as well as for financial support and staffing for the three Consultancy Meetings.

The participants in the CRP will be the Agreement and Contract holders (up to 25 Agreements and 5 Contracts), both from developed and developing countries. Technical supervision of the CRP will be implemented by the Technical Officer**.**

A Chief Scientific Investigator of the CRP will be appointed from one of the participants.

# Assumptions

It is assumed that national organisations with expertise in geopolymer activities will participate in the CRP. It is also assumed that within each nation support will be provided from appropriate institutions to participants during the duration of the CRP to enable them to undertake relevant research.

# Foreseen Participation

Participants in the CRP will be drawn from a selection of appropriate and qualified institutions from Member States, not limited to the following MS:

Argentina, Australia, Belgium, Brazil, Canada, China, Czech Republic, Egypt, Finland,

France, Germany, Hungary, India, Japan, Kazakhstan, Lithuania, Romania, Russian

Federation, Slovakia, South Africa, South Korea, Spain, Sweden, Switzerland, Ukraine,

UK, USA and Uzbekistan.

The number of institutes to be included in the CRP will be determined by the optimal number of participants that can be effectively supported by the Agency to ensure the attainment of research objectives within available budgetary resources. The number of participants in the CRP should not be less than ten and should not exceed thirty.

In planning the CRP the award of more than one contract in a single MS should be avoided. Should it be considered necessary within the CRP to award two or more contracts to institutes in one MS, justification must be provided in the proposal evaluations. Consortium membership from a MS is permitted.

It is the policy of the Agency to proactively cooperate with other national and international organisations sponsoring research in fields of common interest. Priority for participation in CRPs is given to institutes in developing MSs, insofar as they can complete the required programme of work and to qualified young and female researchers. In cases where a female and male researcher are equally qualified, preference will be given to the female researcher in order to contribute to the goal of a gender balance.

# Links to Technical Cooperation Projects

The CRP is providing valuable information for participants of TC Regional Project RER9143 “Enhancing Radioactive Waste Management Capabilities” and some of CRP activities could be synergetic this TCP. Although the CRP has not followed from a TCP request, it is expected that there will be a technology transfer from this CRP particularly in concern with potential waste management schemes to Member States that have small, medium and large inventories. It is also likely that some of MS representatives could be partly funded via this TCP and thus a TC funding component could be addressed.

# CRP Advisory Documents

The CRP advisory documents are provided in Annex 1, 2 and 3

# Annex 1. Format for Presentation of Progress Reports at RCMs

The standardized report format should be used for individual progress reporting during RCM meetings. Additionally, individual PowerPoint presentations should be prepared for distribution to all IAEA CRP participants during the meeting. An IAEA PowerPoint template will be provided and it is preferred that participants use this template to report their results at the RCM.

The PowerPoint presentations for progress reporting should include:

1. Title slide with research title, authors and institutional affiliation(s);
2. Introduction/ background demonstrating linkage to CRP research objectives (two to three slides);
3. Research methodology – methods and assumptions (two to three slides);
4. Description of the study approach and/ or the experimental techniques and equipment used/ proposed for use (two to three slides). As appropriate this should include data sources and methods of analysis used;
5. Presentation and discussion of results (may be broken into 2 sections - up to 15 slides, including tables and graphs);
6. Conclusions and suggestions for further work. In the final RCM this should recommend material for inclusion in the TECDOC (one to two slides).

# Annex 2. Format for Preparation of the Final Report of the CRP

Standardization will facilitate compilation and editing of the individual research contributions in the preparation of the final report of the CRP results for the publication. In order to speed up the publication process the following MUST be provided:

1. Electronic file in MS Word format that contains the final report of the individual research topic. The report should be submitted by e-mail by a date that will be specified by the final RCM.

2. The report should follow the format required for IAEA TECDOCs (an example file will be provided).

3. The report itself should typically be between 15-30 pages including references; additional information may be provided in separate files (*e.g.* relevant published papers), subject to copyright requirements.

4. Figures and/or tables generated in applications other than MS Word, shall be integrated in the text of the report, but also submitted separately as the "source" files (e.g. Excel sheets, JPG or other graphic files, etc.) to enable any required formatting/editing by the report compilers.

The report should be structured as follows:

1. Research title, authors and institutional affiliation(s);
2. Abstract;
3. Introduction/ background demonstrating linkage to CRP research objectives;
4. Research methodology – methods and assumptions;
5. Description of the study approach and/ or the experimental techniques and equipment used. As appropriate this should include data sources and methods of analysis used;
6. Presentation and discussion of results (may be broken into 2 sections);
7. Conclusions and suggestions for further work.
8. References.

# Annex 3. Content to be included in the Final Report of the CRP

The CRP Final report should consist of:

1. An introductory overview of the CRP
2. Geopolymer waste form characterization issues
3. Organisation of the CRP (WP 1)
4. Summary of the physical characterisation of geopolymers (WP 2)
5. Summary of the chemical characterisation of geopolymers (WP 3)
6. Summary of transportation characterisation of geopolymers (WP 4)
7. Recommended waste form testing for acceptance criteria for final disposal
8. Conclusions
9. Cooperation achieved
10. References
11. Abbreviations
12. Contributors to drafting and review
13. Annexes containing individual detailed research reports of participants (may be provided purely electronically)