Milestone 49
Final report on long term durability of conditioned waste form

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Abstract

Sub-task 6.6.3 "Long-term durability of reconditioned waste form" of WP6 aims at the determination of long-term stability and durability of the treated and reconditioned waste. To simulate the long-term damage and investigate the long-term durability, the samples ageing has been accelerated by means of freeze-thaw cycles, immersions in water (for more than 1 year) or in chemically aggressive solutions (e.g. salted water, ammonia-rich solutions). The investigations involved both analysis of the leachates to assess the release of contaminants and characterization of the solid to determine if recrystallization or secondary phase formation have occurred. The requirements of the WAC have been considered whenever possible.

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1 Milestone Description

Milestone 49, associated with Work package 6 “Innovations in solid organic waste treatment and conditioning”, Task 6.6 “Physico-chemical characterisation of reconditioned waste form and stability testing” has been completed on 28.06.2024, while the experimental work is going to continue until the end of the project (31/08/2024).

The justification for the readiness is described below and complies with the Grant Agreement Description of Action noting verification by memorandum.

The readiness of the milestone was reviewed and agreed upon by WP6 leader Thierry Mennecart, SCK CEN.

2 Introduction

Long-term durability of the waste forms is a fundamental issue to be assessed to prove their long-term performances under relevant disposal conditions. In fact, the waste forms are intended to be safely disposed of for a long period, at least some decades up to hundreds of years. Sub-task 6.6.3 aims at the determination of long-term stability and durability of the treated waste (produced in Task 6.3) stabilized (in Task 6.4 and 6.5) in a conditioning matrix, e.g. in cements, geopolymers, molten glass coated waste and HIPped waste. Since the experiments cannot last for decades or hundreds of years, the long-term damage was simulated by accelerating the samples ageing, e.g. by means of freeze-thaw cycles, immersions in water (for more than 1 year) or in chemically aggressive solutions (e.g. salted water, ammonia-rich solutions). The effects of ageing have been investigated, e.g. by means of characterization of the solids to determine possible modifications of physico-chemical properties, e.g porosity, phase composition, microstructure, resistance to compression, etc. Moreover, the leaching stability of the aged samples has been assessed to determine the performance of the waste form and the release of contaminants. In fact, leaching is a critical phenomenon which may occur during disposal by causing the premature degradation of the waste forms due to water infiltrations or repository flooding. The requirements of the WAC have to be considered whenever possible.

This milestone falls within the scope of sub-task 6.6.3. The milestone text is complemented by supplementary materials describing in detail the experimental conditions and the results obtained by the contributing organizations.

3 Data collection and harmonization

In conjunction with Task 6.6.2 “Short-term leaching experiments under different exposed conditions”, two template files, one preparatory document (*.docx* file) and one data document (*.xlsx* file), were sent to the partners involved in Task 6.6.3 to collect the data they have produced. The collected data have served as supplementary material for the drafting of the milestones “Final report on short term leaching experiments” and “Final report on long term durability of conditioned waste form” and of the deliverable “Final report on the Physico – chemical characterization of reconditioned waste form and stability testing”.

3.1 Preparatory document (.docx file)

The preparatory document is a *.docx* file. It was aimed at collecting synthetic descriptions of the work done by each partner, including the protocols for preparation and ageing of the samples and the main characteristics of both treated waste and conditioning matrix, as well as the methods used for characterizations and analysis and the main results on short term leaching and long-term durability.

In a first section named “*sample preparation*”, each organization was asked to describe the waste (origin, chemical composition, other characterizations), the matrix (materials, preparation and curing protocols, chemical composition, other characterizations…) and the waste encapsulation protocol (including loading factors, added contaminants…).

In a second section named “*Ageing protocols (if any)*”, each organization was asked to describe the samples ageing protocols (e.g. total dose/dose rate/radionuclide/atmosphere/etc. for irradiations, duration/ composition/

temperature/etc. for immersions in water or in chemically aggressive solutions, duration/temperatures/etc. for freeze-thaw cycles…).

In a third section named "*Leaching protocols*", each organization was asked to describe the samples leaching protocols (e.g. duration/intervals/leachant/temperature/etc. …) and the performed characterizations (post-mortem analyses: porosity, µ-CT, XRD, SEM/EDS, compression tests… leachates analyses: pH, conductivity, ICP-OES/MS for constituents and stable contaminants, radiometric analyses for radioactive contaminants). Each organization was warmly recommended to perform the experiments following the protocol commonly agreed by WP6 partners and available here: PREDIS_M39_WP6 Leaching Test Protocol_2021-08-31.pdf [1].

In the fourth section named "*Results*", each organization was asked to describe the main obtained results. It was requested to include only the most significant data (e.g. graphs/tables of compressive strength, leached fractions, normalized losses, leaching indices, relevant SEM/micro-CT pictures, XRD diffractograms, etc.). It was requested to compare the obtained results (e.g. compression and porosity values, leaching indices, normalized losses, etc.) with respect to different experimental conditions (such as different waste/matrix/loading factors/protocols, etc.) in order to give preliminary discussions and interpretations of the data.

The preparatory documents drafted by the partners are collected and stored on-line in the PREDIS sharepoint, available to PREDIS partners, here: Preparatory_documents_partners.

3.2 Data document (.xlsx file)

The data document is an *.xlsx* file. The template is available here: Data_collection_Task6_form.xlsx. It was aimed at collecting from each partner the detailed information on the samples, conditions and results of the leaching experiments (both short-term and long-term), characterizations before and after leaching/ageing.

In the first excel sheet named "*Reference_system_samples*" the reference ID and the information about the tested samples are collected: matrix (type of matrix and composition) and waste (type of waste and waste loading factor).

In the second excel sheet named "*Leaching_wasteforms*" additional and more detailed information about the matrix (preparation and curing protocols/conditions, techniques/parameters used for the characterization) and the waste (chemical compositions including the added contaminants, techniques used for the characterization, distribution of the waste) is collected.

In the excel sheet named "*Waste form_character_pre_leach*" the results of the characterizations performed before the leaching experiments are reported. According to the abovementioned leaching protocol of WP6, XRD, SEM-EDX, porosity, and compression strength are considered as basic characterizations. Additional characterizations are also collected (e.g. FT-IR, NMR, µ-CT, etc.).

In the excel sheet named "*Leachates_short-term*" the samples which have undergone short-term leaching are listed. As well, the type of the short-term leaching is described. In particular, it is specified if the samples have undergone leaching through the WP6 protocol or not. In that case, some experimental conditions are reported (leachant, temperature, and duration). Mostly important, the results of the short-term leaching experiments are reported: the normalized losses (NL, expressed in g/m^2) of the elements constituting the matrix (Si, Al, Na, K, Ca, B, etc.) and the leaching indices (Li, dimensionless) or the cumulative fraction leached (CFL, dimensionless) of the contaminants (Cs, Sr, Co, Ni, etc.). Both the NL and Li are calculated according to a common template available here: Template_WP6_Task 6.6.xlsx [2].

In the excel sheet named "*solid_charact_post_leach_short*" the *post-mortem* characterizations of the specimens which have undergone short-term leaching tests are reported. As abovementioned, XRD, SEM-EDX, porosity, and compression strength are considered as basic characterizations according to the WP6 leaching protocol. As well, additional characterizations are collected (e.g. FT-IR, NMR, µ-CT, etc.).

Analogously, in the excel sheets named "*Leachates_long-term*" and "*solid_charact_post_leach_long*", similar information is collected: samples which have undergone long-term leaching, types and conditions of the leaching experiments, results of the long-term leaching experiments (NL for the elements constituting the matrix, Li or CFL for the contaminants), basic (XRD, SEM-EDX, porosity, and compression strength) and

additional (e.g. FT-IR, NMR, µ-CT, etc.) *post-mortem* characterizations of the specimens after long-term leaching.

Finally, in the excel sheet named "*ageing methods*" the samples which have undergone accelerated ageing are reported along with the description of matrix (type of matrix and composition) and waste (type of waste and waste loading factor). The main part concerns the description of the ageing methods and especially the type of ageing (e.g. gamma irradiations, freeze-thaw cycles, long-lasting immersions in water or in chemically aggressive solutions) and the experimental conditions (e.g. total dose/dose rate/radionuclide/atmosphere/etc. for irradiations, duration/temperatures/etc. for freeze-thaw cycles, duration/temperature/etc. for immersions in water or composition of chemically aggressive solutions). Moreover, types, experimental conditions, and results of the long-term leaching experiments are reported: NL for the elements constituting the matrix, Li or CFL for the contaminants, basic (XRD, SEM-EDX, porosity, and compression strength) and additional (e.g. FT-IR, NMR, µ-CT, etc.) *post-mortem* characterizations of the specimens after long-term leaching.

The data documents drafted by the partners are collected and stored on-line in the sharepoint, here: Data collection_Task 6_Form.

4 Summary of the experimental work

The research activity has been focused on the treated waste produced in Task 6.3:

- self-produces ion exchange resins (IER) ashes tested by VTT, SIIEG, POLIMI, UAM, CSIC, and CIEMAT;
- IRIS ashes produced by CEA and tested by SCK CEN, POLIMI, and USFD;
- MSO residues produced CVRez and tested by SCK CEN and POLIMI.

In addition, some partners have tested the behaviour of contaminants (Cs, Sr, Co, Ni, Ag, Ce, Nd, Eu, Th, U, B, Fe, Cr, Mn, Zn) that were previously loaded in the surrogate waste before treatment or doped on the treated residues.

Different matrices were used for the encapsulation of the waste:

- geopolymers or alkali activated materials based on metakaolin (MK), blast furnace slag (BFS) and fly ash (FA) tested by VTT, SIIEG, UAM, CSIC, CIEMAT, POLIMI, and SCK CEN;
- cements (CEM I, CEM II, CEM III) tested by VTT, SIIEG, SCK CEN, UAM, CSIC, and CIEMAT;
- glass and ceramic materials tested by USFD and SCK CEN.

After curing, the samples have been tested for long-term durability. Three main types of experiments have been performed:

- immersion in ultrapure water for more than 1 year tested by UAM and POLIMI;
- immersion in chemically aggressive solutions (e.g. salty water to mimic the disposal site water) for more than 1 year tested by VTT, SIIEG, UAM, CSIC, CIEMAT, POLIMI, SCK CEN, and USFD;
- acceleration of the samples' ageing by means of freeze-thaw cycles followed by water immersion (tested by POLIMI) or carbonation (tested by SCK CEN), see Table 1 for details.

Table 1. Experimental conditions for the accelerated ageing of geopolymer and cement wasteforms

Organization	Accelerated degradation tests	Post-mortem characterization
SCK CEN	Accelerated carbonation for 3 months: 20ºC, 60%RH, 1% atmospheric CO_2	Expansion measurement, mechanical strength, carbonation depth by phenolphthalein spray, XRD, FTIR, SEM/EDX
POLIMI	Thermal cycling: -40 to 40ºC, 1 month, 90%RH, ΔT>10ºC/hour	Mechanical strength (compression strength)
POLIMI	Thermal cycling: -20 to 60ºC, 5 days, 90%RH, instant temperature changes	Leaching following WP6 protocol and standard protocol [2]

The leachates obtained from immersion tests were analysed to monitor the release of matrix constituents and contaminants. As abovementioned, in order to ensure proper comparison between the results obtained by the partners with similar or different waste or matrix or protocols, the NL were calculated for the elements constituting the matrix and the Li or the CFL for the contaminants (Cs, Sr, Co, Ni, etc.) according to a common template. After the completion of the immersions, post-mortem characterization of the specimens was performed to investigate the compression resistance and mineralogical/microstructural properties (e.g. porosity, phase composition, morphology, carbonation depth, etc.).

The list of samples produced during the project and tested by the partners are summarized in **Table 2**. The experiments are organized according to few principles: 1) type of matrix used to encapsulate the treated waste; 2) name of the partner; 3) type of waste. In few cases, several leaching protocols have been investigated and are reported with different colours. If performed, the type of accelerated ageing is reported in red.

5 Main outcomes and future perspectives

In most of the cases, the degradation of the tested waste form was not significant after several months of immersion neither after accelerated ageing, as mechanical and physico-chemical properties seem to be almost unchanged. Moreover, the leaching resistance seems to be compliant with the requirements generally requested by the repositories. Nevertheless, it could be pointed out that glass-ceramic waste forms are endowed with the best leaching performances, while geopolymers seem to be less resistant, especially if immersed in alkaline solutions, resulting in higher dissolution rates of matrix constituents (e.g. Al and Si) and contaminants (above all B, Cs, and Sr).

The MSO seems to be most problematic treated waste to be encapsulated in a durable waste form and further efforts are still required. For the future, it would be necessary to complete some experiments, for example by monitoring more contaminants or by performing more post-mortem characterizations. As well, it could be useful to extend the timescale of the experiments to produce data which are more relevant for the disposability assessment. In the same direction, the execution of gamma irradiations or thermal cycling or the immersion in chemically aggressive solutions (e.g. containing sulphates or chlorides) to accelerate the materials ageing may ensure a more complete understanding of the long-term durability of the waste forms.

6 Additional information

Additional information on partner's results is available upon request to data owner's in the links below:

VTT and UniHel

SCK•CEN

POLIMI

CIEMAT

CSIC

UAM

USFD

SIIEG

Table 2. Description of long-term durability tests performed in the framework of subtask 6.6.3.

Partner	Composition of matrix	Type of waste /contaminants of interest	Waste load %w/w	Ageing WP6 leaching protocol (Yes/No)	Leaching duration	Data available from short-term leaching tests	
						Monitoring/analysis of leachant	*Post-mortem analysis of the solid*
Geopolymer and alkali activated materials							
VTT - UH	MK+Na_2SiO_3/KOH	Surrogates SIERs ashes: Fe, Ce, Cs and Eu.	0, 15 & 50	Yes	24 months	Monitoring of constituents and contaminants	XRD; SEM/EDX; Al/Si MAS NMR; FTIR, combined micron scale – XRF, -XRD and -XAS.
CSIC	MK+BFS+ Na_2SiO_3	Surrogates SIERs ashes. Contaminants: B, Cs, Sr and activation products (Fe, Co, Cr, Mn, Ni, Zn, Ag)	0 & 20	YES	24 months	Monitoring of constituents and contaminants	Compressive strength, XRD, SEM/EDX, BET, MIP, and FTIR
UAM				YES, with ultrapure water			
CIEMAT				YES, with disposal site water			
POLIMI	Volcanic tuff, BFS, FA, NaOH and Na silicate	Surrogates SIERs ashes. Contaminants: Cs, Sr, Co, Ni, Ag, Ce, Nd, Eu, Th, U	0, 10 & 20	YES, with ultrapure water	18 months	Monitoring of constituents and contaminants	Not yet, leaching still on-going. XRD and MIP
	Volcanic tuff, BFS, steel slag, FA, NaOH and Na silicate	IRIS ashes (CEA) doped with contaminants: Cs, Sr, Co, Ni, Ag, Ce, Nd, Eu, Th, U	0, 20 &30	**Thermal ageing** YES No, with ultrapure water	3 months 1 week		No
		IRIS ashes (CEA) + Molten salts (MSO, CVRèz)	16/20 14/30	**Thermal ageing** YES No, with ultrapure water	3 months 1 week		No, samples did not withstand immersion
SCK CEN	MK+BFS+$Na_2Si_2O_5$	Treated Molten Salts (MSO) (CV Rez): *no contaminants*	10 & 20	**Carbonation** No	3 months	No	Monitoring of carbonation depth, Compressive strength, XRD, SEM-EDX
Cement							
VTT - UH	CEM I 42,5 N – SR3	Surrogates SIERs ashes: Fe, Ce, Cs and Eu	0, 15 & 50	Yes	24 months	Monitoring of constituents and contaminants	XRD; SEM/EDX; Al/Si MAS NMR; FTIR, combined micron scale – XRF, -XRD and -XAS.
CSIC	CEM I/42.5 SR	Surrogates SIERs ashes.	0 & 20	YES	24 months		

UAM	CEM III/B32.5	Contaminants: B, Cs, Sr and activation products (Fe, Co, Cr, Mn, Ni, Zn, Ag)		YES, with ultrapure water		Monitoring of constituents and contaminants	Compressive strength, XRD, SEM/EDX, BET, MIP, and FTIR
CIEMAT				YES, with disposal site water			
SCK CEN	CEM III+BFS+FA+ Lime+limestone	Treated Molten Salts (MSO) (CV Rez): *no contaminants*	10 & 14	**Carbonation** No	3 months	No	Monitoring of carbonation depth, Compressive strength, XRD, SEM-EDX
Glass/ceramic							
USFD	HIPed, no additives versus NaAlO2 and Na2B4O7	IRIS ashes (CEA): *no contaminants*	95 & 100	Yes	24 months	Monitoring of constituents	XRD, SEM/EDX
SCK CEN	HIPed		95	Yes	24 months	Monitoring of constituents and contaminants	XRD, SEM/EDX

7 References

[1] MS 39 PREDIS WP6 milestone “Definition of the leaching procedure for the short-term experiments and the long-term durability experiments”. Emmi Myllykylä

[2] ANSI/ANS-16.1-2019 (R2021): Measurement of the Leachability of Solidified Low Level Radioactive Wastes by a Short-Term Test Procedure