Milestone 48
Final report in short-term leaching experiments

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Abstract

MS 48 (MS6.10) summarizes most relevant results obtained from the short-term leaching tests conducted in the framework of task 6.6.2 according to WP6 leaching protocol, including leachate analyses and the post-mortem characterization of the solids.

Additional leaching tests were carried out according to national requirements. Accelerated ageing of selected specimens was also performed by several partners. Complementarily to these tests, immersion tests were conducted in order to assess non-diffusive chemical and physical phenomena.

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1 Milestone Description

Milestone MS 48, associated with Work package 6, Task 6.6. has been completed on 30.06.2024.

The justification for the readiness is described below and complies with the Grant Agreement Description of Action noting verification by Report M.6.10. *(Verification is in Milestones table - right column, within Grant Agreement Part A starting on page 50).*

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

2 Short-term leaching tests in PREDIS WP6

Chemical reactivity of the wasteforms in aqueous environments and radionuclide release are critical issues to assess wasteform performance under relevant disposal conditions. Therefore, leaching is a phenomenon of fundamental interest in waste disposal. Degradation of wasteforms due to water infiltration can result in radionuclide release and could lead to the premature desintegration of the conditioning matrices. Though, minimization of contact of waste by water is one of the key issues considered in the design of disposal facilities, leachability assessment of wasteforms is also needed in order to prevent the migration of radionuclides off-site.

In subtask 6.6.2, resistance to leachability of the different types of wasteforms prepared in tasks 6.4 and 6.5 was evaluated by means of short-term leaching tests Milestone MS48 falls within the scope of this subtask.

This milestone has two main objectives. On one hand, it aims to give a brief description of the experimental conditions under which short-term leaching tests were performed in subtask 6.6.2. On the other hand, MS48 intends to summarize the most relevant results obtained from leachate analyses and post-mortem characterization of the specimens.

2.1 Methodology and harmonization of results

Short-term leaching tests carried out in subtask 6.6.2. intended to address two key issues for disposability assessment of the candidate wasteforms:

- Evaluation of radionuclides leachability in the different types of candidate wasteforms
- Identification of matrix degradation mechanisms and estimation of the extension of alteration under disposal conditions

For that purpose, post-mortem characterization of the solid specimens and chemical analyses of the leachates were performed by all partners. In order to harmonize results and allow direct comparison of the leached fractions, a common leaching protocol was agreed by all task contributors. WP6 leaching protocol is described in detail in Milestone 39 [1]. As leachant, a Synthetic Cementitious Waster was chosen, as suggested by EUG group to evaluate novel matrices behaviour in the most realistic conditions possible. Chemical composition of the solution was defined in the framework of WP ACED – EURAD and can be found in [2].

In order to assess the conditioning matrices stability and allow the direct comparison between partners, results of main elements in matrices were given as Normalized Elemental Mass Loss (NL in [g/m^2]). ANSI/ANS 16.1-2019 [3] was used as a screening method to directly compare the effectiveness of the different types of conditioning matrix. Leachability was expressed in terms of Leachability Indexes (LI) and according to this standard, LIs should be greater than 6.0. SCK CEN prepared an Excel template that was delivered to partners, so that same methodology was used by all contributors.

Several partners conducted additional short-term leaching tests under their national interests. These studies included:

- CEA: glass monoliths leached according ASTM Standard Test Method MCC-1 [4]
- CSIC-UAM-CIEMAT: cement- and geopolymer-based wasteforms in national conditions (protocol based on ISO 6961:1982 and as leachants, ultrapure water and water sampled in the disposal platforms in the ILW-LLW facility)

- VTT & UH: geopolymer-based wasteform in nationally relevant conditions (Synthetic disposal site groundwater)

Table 1 summarizes experimental conditions of short-term leaching tests conducted in the framework of subtask 6.6.2.

Complementarily to short-term leaching tests, immersion tests were performed by CIEMAT-CSIC-UAM, SIIEG and POLIMI. Early leaching rates observed in solidified waste forms are mostly explained by diffusion. However, other mechanisms, such as erosion, dissolution or corrosion cannot generally be assessed by standardized leaching tests but can be evaluated by the use of immersion testing. In performed tests, specimens were immersed in ultrapure water for 90 days and post-immersion mean compressive strengths were determined.

Accessorily, accelerated ageing tests were conducted by SCK CEN and POLIMI, in order to assess the influence of carbonation and thermal cycling effects on the release rate. Table 2 lists the characteristics of these tests.

Table 1. Description of short-term leaching tests performed in the framework of subtask 6.6.2.

Partner	Composition of matrix	Type of waste /contaminants of interest	Waste load %w/w	WP6 leaching protocol (Yes/No)	Duration	Data available from short-term leaching tests	
						Monitoring/analysis of leachant	*Post-mortem analysis of the solid*
Geopolymer							
VTT - UH	MK+Na_2SiO_3/KOH	Surrogates SIERs ashes: Fe, Ce, Cs and Eu.	0, 15 & 50	**Yes**	3 months	Monitoring and analysis	XRD; SEM; Al/Si MAS NMR; combined micron scale –XRF, -XRD and -XAS.
SIIEG·NASU	MK+BFS+KOH+Na_2SiO_3	Surrogates SIERs ashes: Cs,Sr, Ce	20	**Yes** Additionally: leachant NaOH 0.1M	3 months	Monitoring and analysis	Compressive strength, density, SEM/EDX
CSIC	MK+BFS+ Na_2SiO_3	Surrogates SIERs ashes: B, Cs, Sr and activation products (Fe,Co, Cr, Mn, Ni, Zn, Ag.)	0 & 20	**Yes**	3 months 6 months	Monitoring and analysis	Compressive strength, XRD, MIP, BSEM/EDX and FTIR
UAM				Additionally: leachant ultrapure water	3 months 6 months	Monitoring and analysis	Compressive strength, XRD, BSEM/EDX
CIEMAT				Additionally:leachant disposal site water	6 months	Monitoring and analysis (+ TIC/TOC & Eh)	Compressive strength, XRD, BET, MIP, BSEM/EDX and FTIR
POLIMI	Volcanic tuff, BFS, FA, NaOH	IRIS ashes (CEA) doped with Cs, Sr, Co, Ni, Ag, Ce, Nd, Eu, Th, U	0, 10 & 20	No: Standard ANSI/ANS 16.1-2003	2 weeks	Monitoring and chemical analysis	Compressive strength
	Volcanic tuff, BFS, steel slag, NaOH	IRIS ashes (CEA) doped with Cs, Sr, Co, Ni, Ag, Ce, Nd, Eu, Th, U	0, 20 &30	No: Standard ANSI/ANS 16.1-2003	1 week	Monitoring and chemical analysis	XRD
		IRIS ashes (CEA) + Molten salts (CVRèz)	16/20	No: Standard ANSI/ANS 16.1-2003	1 week	Available monitoring and chemical analysis	N.A
		Wet oxidation sludge	12	No: Standard ANSI/ANS 16.1-2003	1 week	Available monitoring and	N.A.

						chemical analysis	
SCK CEN	MK+BFS+$Na_2Si_2O_5$	Molten Salts (MSO) (CV Rez): *no contaminants*	10 & 20	**Yes**	3 months	Monitoring and analysis (additional: TIC/TOC)	XRD, SEM-EDX
Cement							
VTT - UH	CEM I 42,5 N – SR3	Surrogates SIERs ashes: Fe, Ce, Cs and Eu	0, 15 & 50	**Yes**	3 months	Monitoring and analysis	XRD; SEM; Al/Si MAS NMR; combined micron scale –XRF, -XRD and -XAS.
SIIEG·NASU	CEM II/A-LL 42,5-R	Surrogates SIERs ashes: Cs,Sr, Ce	20 & 30	**Yes** Additionally: leachant NaOH 0.1M	3 months	Monitoring and analysis	
CSIC				**Yes**	3months 6 months	Monitoring and analysis	Compressive strength, XRD, MIP, BSEM/EDX and FTIR
UAM	CEM I/42.5 SR CEM III/B32.5	Surrogates SIERs ashes: B, Cs, Sr and activation products (Co, Cr, Mn, Ni, Zn, Ag.)	0 & 20	Additionally: leachant: deionized water	3months 6 months	Monitoring and analysis	Compressive strength, XRD, BSEM/EDX
CIEMAT				Addtionally: leachant: disposal site	6 months	Monitoring and analysis (+ TIC/TOC & Eh)	Compressive strength, XRD, MIP, BET BSEM/EDX and FTIR
SCK CEN	CEM III+BFS+FA+ Lime+limestone	Molten Salts (MSO) (CV Rez): *no contaminants*	10 & 14	**Yes**	3 months	Monitoring and chemical analysis	XRD, SEM/EDX
Glass/ceramic							
USFD	HIPed		95 & 100	**Yes**	3 months	Monitoring and chemical analysis	SEM/EDX
SCK CEN	HIPed	IRIS ashes (CEA): *no contaminants*	95	**Yes**	3 months 6 months	Monitoring and chemical analysis	XRD, SEM/EDX
CEA	HIPed		95	**Yes** Additionally MCC-1 standard [4]	3 months	Monitoring and chemical analysis	SEM/EDX
CEA	Molten glass		30				

Table 2. Experimental conditions for the accelerated ageing of geopolymer and cement wasteforms

Organization	Accelerated degradation tests	Post-mortem characterization
SCK CEN	Accelerated carbonation: 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)

3 Main results

As an overall conclusion, glass-ceramic wasteforms exhibited the greatest resistance to leachability in cementitious water of the three types of conditioning matrices studied. Al and Si- Normalized Losses measured for geopolymer wasteforms were significantly higher than OPC-based samples in alkaline medium.

Immobilisation of ashes from thermal treatments (gasification, pyrolysis, incineration…) in geopolymer and cement produced wasteforms with an improved leaching behaviour compared to MSO wasteforms (lower $NL_{Si, Al}$ and higher LIs for contaminants). For OPC and geopolymer wasteforms where surrogate SIERs ashes were immobilised, LIs were significantly above 6.0 for all dopants (>8 in all cases). In the case of Cs and Sr, LIs were in the range of 11-13 for both, OPC- and geopolymer wasteforms.

In general, hyperalkaline medium (pH>12) enhances Si and Al leaching in geopolymer-based wasteforms. Normalized Elemental Mass Losses (NLs) calculated for Si and Al were significantly greater in the case of geopolymer specimens compared to OPC-wasteforms This alkaline-induced dissolution seems to result in a decrease of the retention capacity of the matrix (lower LIs), especially in the case of Cs.

Regarding immersion tests carried out in cement and geopolymer wasteforms, post-immersion compressive strength exceeded 3MPa or the 75 percent of the "*as-cured"* compressive strength in all cases. No erosion or spalling was reported for any wasteform.

4 Additional information

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

CEA
CIEMAT
CSIC
POLIMI
SCK·CEN AAC & OPC
SCK CEN HIPed
SIIEG NASU
UAM
USFD
VTT-UH

References

[1] MS39 PREDIS WP6 milestone "Definition of the leaching procedure for the short-term experiments and the long-term durability experiments". Emmi Myllykylä

[2] Reference document for properties of cementitious materials in ACED with GEM-Selektor and based on CEMDATA V18.1. ILW waste and container backfill mortar. G. Kosakowski

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

[4] MCC-1: Standard. test method for static leaching of monolithic waste forms for disposal of radioactive waste. ASTM Standard.
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