Milestone 45
Intermediate report on characterization of the durability related properties of conditioned wasteform

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Abstract

Milestone MS45 consists of a status update report of subtasks 6.6.1 'Characterisation of reconditioned waste form' and 6.6.2 'Short term leaching experiments under different exposed conditions' in WP6 'Innovations in solid organic waste treatment and conditioning'.

This milestone summarizes the characterization methodology followed by contributing partners and the update status of leaching tests (both, short and long-term tests) performed in subtasks 6.6.2 and 6.6.3 'Long-term durability of reconditioned waste form'.

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1 Milestone Description

Milestone MS45, 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 28.02.2023.

The justification for the readiness is described below and complies with the Grant Agreement Description of Action noting verification by Report M.6.7.

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

2 Characterization of durability-related properties of the reconditioned wastes

Chemical and mechanical stability of the waste form is a relevant aspect for the overall integrity of the waste packages. Durability of conditioning materials is a key issue to assess long-term performance of waste forms under disposal conditions. Characterization of chemical, physical and mineralogical properties of conditioning matrices plays a major role in the understanding of the performance of such materials for storage, transportation and disposal.

Task 6.6. aims to assess the physic-chemical and mechanical durability of the different waste forms produced in tasks 6.4 'Immobilisation of the treat wastes by geopolymer or cement-based materials encapsulation or by molten glass coating' and 6.5. 'Densification'. Resistance to leachability is also evaluated according to the leaching protocol defined for WP6 in Milestone 39 'Definition of the leaching procedure for the short-term experiments and the long-term durability experiments' (confidential).

This milestone summarizes the characteristics of the reconditioned waste forms tested in Task 6.6, the techniques used for their chemical/physical/microstructural characterization and the update status of leaching tests (both, short and long-term tests) performed in subtasks 6.6.2 'Short term leaching experiments under different exposed conditions' and 6.6.3 'Long-term durability of reconditioned waste form'.

2.1 Characteristics of the waste forms

Composition and chemical characteristics of the reconditioned waste forms condition their stability and long-term durability. In task 6.6., waste forms of interest include: cementitious, geopolymer, molten glass-coated and HIPed waste forms.

Table 1 lists the characteristics of the waste forms prepared for Task 6.6., classified according to the type of conditioning matrix. Additionally, other relevant parameters for durability-related properties of the waste forms are listed in Table 2. These parameters include pre-treatment of wastes, use of adjuvants for HIPed samples, additives for cement/geopolymer-based waste forms.

2.2 Basic characterization of the waste forms

Characterization results are used as a guideline for waste form development and durability assessment. Guidelines for waste form characterization are provided in Milestone 39. However, contributing partners have performed the characterization of the reconditioned waste forms according to techniques available. Table 3 lists the analytical techniques used by partners participating in subtask 6.6.1. 'Characterisation of reconditioned waste form' to characterize the different type of matrices: geopolymer, OPC cements and glass/ceramic materials.

2.3 Leaching tests

Chemical reactivity of the waste forms in aqueous environments and the long-term radionuclide release are critical issues to assess their long-term performance under relevant disposal conditions.

To assess the durability of the waste forms, both, short-term and long-term tests have been performed in the framework of subtasks 6.6.2 and 6.6.3., according to the leaching protocol defined for WP6 in Milestone 39. Complementarily to these tests, CIEMAT, UAM, VTT and UH will also conduct leaching experiments based on their national requirements.

Table 4 and Table 5 summarize the update status of both, short-term and long-term leaching tests perform in WP6.

Additional accelerated leaching tests are planned by SCK CEN and POLIMI in order to assess the influence of chemical ageing and gamma irradiation effects on the release rate. Table 6 lists the characteristics of these tests.

Table 1. Overview of the characteristics of the waste forms prepared for Task 6.6. classified according to the type of conditioning matrix

Institute	Matrix composition	Type of waste	Waste loads tried (%w/w) in T6.6.	Problems 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
CVRez*	*Metakaolin-based*	*Molten salts*	*25 & 40*	*>30 wt.% poor mixability*	*Yes*	*Good, but efflorescence on surface*
				>20 wt.% bad stability in high moisture environment	*Yes*	*Good (low shrinkage)*
Cement						
VTT-UH	CEM I	IERs 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 pososity 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 pososity 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	

*** CVRez does not participate in task 6.6 but collaborates by delivering reconditioned geopolymer-based wasteforms to interested partners.

Table 2. Other key parameters relevant for durability-related performance of the waste forms: pre-treatment of wastes, use of adjuvants for HIP samples, additives for cement/geopolymer.

Institute	Matrix composition	Type of waste	Waste loads tried (%w/w)?	Use of adjuvants for HIP samples, additives for cement/geopolymer to improve conditioning/ performance, pre-treatment of waste…?	How performance / conditioning improves
Geopolymer					
SCK CEN	BFS, sodium disilicate	Molten salts	10 & 20	Pre-treatment of molten salt with $Ca(OH)_2$	No longer sensitive to variations in temperature orhumidity
Cement					
SCK CEN	CEM I (BFS, limestone filler and sand, lime & silica fume)	Molten salts	10 & 14	Pre-treatment of molten salt with $Ca(OH)_2$	No longer sensitive to variations in temperature or humidity
Glass/ceramics					
USFD	Glass/ Glass-ceramic	IRIS ashes	95 & 100	5wt.% $Na_2B_4O_7$ 5wt.% $NaAlO_2$	Lower porosity, reduced interaction with HIP cans during processing
SCK CEN	Glass-ceramic	IRIS ashes	95	5wt.% $Na_2B_4O_7$	N/A
CEA	Glass-ceramic	IRIS ashes	100	Adjuvant added for the pressing of the pellet	N/A

Table 3. *Basic characterization of the reconditioned waste forms (subtask 6.6.1.) used in short- and long- term leaching tests (subtasks 6.6.2 and 6.6.3, respectively)*

Organization	Type of waste	Waste load (%w/w) used for T.6.6.	Basic characterization of the solid	Additional characterization techniques /qualification protocol
Geopolymer				
VTT - UH	IERs ashes	15 & 50	On-going. XRD, SEM, porosity	N/A
SCK CEN	Molten Salt	10 & 20	XRD; Planned: SEM	Viscosity, setting Planned: FTIR**,** water porosity
CSIC/UAM/ CIEMAT	IERs ashes	20	XRD, SEM/EDX, MIP	FTIR, BET, NMR, µ-CT Qualification: mechanical resistance (compressive and flexural strength), water immersion, water accesible porosity, freeze-thaw (planned)
POLIMI	IRIS ashes	up to 50	XRD, SEM-EDX, MIP	Compressive strength, nanoindentation
	Ashes (dryox)	up to 20		
	Ashes (wetox)	up to 40		
	Molten salts	up to 35		
CVRez	Molten salts		XRD	XRF
Cement				
SCK CEN	Molten Salt	10 & 14	XRD; Planned: SEM	Viscosity, setting Planned: FTIR**,** water porosity
CSIC/UAM/ CIEMAT	IERs ashes	20	XRD, SEM/EDX, MIP	FTIR, BET, NMR, µ-CT Qualification: mechanical resistance (compressive and flexural strength), water immersion, water accesible porosity, freeze-thaw (planned)
Glass/Glass-ceramic				
USFD	IRIS ashes	95	XRD, SEM/EDX	N/A
		100	XRD, SEM/EDX	N/A
SCK CEN	IRIS ashes	95	XRD, SEM/EDX	N/A
CEA	IRIS ashes	30	SEM/EDX	N/A
CEA	IRIS ashes	100	SEM/EDX	N/A

Table 4. Update status of the short-term leaching tests on-going in subtask 6.6.2.

Finished On-going Not yet started

Partner	Composition of matrix	Type of waste	Waste load %w/w	WP6 leaching protocol (Yes/No)	*Status short-term leaching tests*		Data available from short-term leaching tests	
					Status	*Duration*	*Monitoring/analysis of leachant*	*Post-mortem analysis of the solid*
Geopolymer								
VTT - UH	MK-based	IERs ashes	0, 15 & 50	Yes	On-going	3 months	Available monitoring and analysis	On-going
SCK CEN	MK+BFS+$Na_2Si_2O_5$	Molten Salt	10 & 20	Yes	Finished	3 months	Available monitoring and analysis (additional: TIC/TOC)	Planned SEM
CSIC	MK+BFS+Na_2SiO_3	IERs ashes	0 & 20	Yes	Finished On-going	3 months 6 months	Available monitoring and analysis	On going: XRD, MIP, BSEM/EDX and FTIR
UAM				Modified (leachant: deionized water)	Finished On-going	3 months 6 months	Available monitoring and analysis	On going: XRD, MIP, BSEM/EDX and FTIR
CIEMAT				Modified (leachant: disposal site)	On-going	6 months	Available monitoring and analysis (additional: TIC/TOC & Eh)	
POLIMI	Volcanic tuff, BFS, FA, NaOH	IRIS ashes	20	No: Standard ANSI/ANS 16.1-2003	Finished	2 weeks	Available monitoring and chemical analysis	Compressive strength
			50	No: Standard ANSI/ANS 16.1-2003	Not yet started			
			50	Yes	Not yet started			
		Ashes-dryox Ashes-dryox	20	No: Standard ANSI/ANS 16.1-2003 Sample curing, then γ-irradiation	On-going	3 months	Available monitoring and chemical analysis	

			30	Yes	Not yet started			Planned: Compressive strength, MIP, nanoindentation
		Residue (wetox)	40	No: Standard ANSI/ANS 16.1-2003	Not yet started		Available monitoring and chemical analysis	Planned: Compressive strength, MIP, nanoindentation
POLIMI		Residue (wetox)	40	Yes	Not yet started			Planned: Compressive strength, MIP, nanoindentation
		Molten salts (CV Rez)	35	No: Standard ANSI/ANS 16.1-2003 Sample curing, then γ-irradiation	On-going	3 months	Available monitoring and analysis	Compressive strength, MIP, nanoindentation
			45	Yes	Not yet started			Planned: Compressive strength, MIP, nanoindentation
Cement								
VTT - UH	CEM I	IERs ashes	0, 15 & 50	Yes	On-going	3 months	Available monitoring and analysis	On-going
SCK CEN	CEM I	Molten Salt	10 & 14	Yes	Starting in coming weeks		Planned: monitoring and chemical analysis	Planned SEM
CSIC	CEM I/42.5 SR	IERs ashes	0 & 20	Yes	Finished	3months 6 months	Available monitoring and analysis	On-going: compressive strength, XRD, MIP, BSEM/EDX and FTIR
UAM				Modified (leachant: deionized water)	Finished	3months 6 months	Available monitoring and analysis	On-going: compressive strength, XRD, MIP, BSEM/EDX
CIEMAT				Modified (leachant: disposal site)	Finished	6 months	Available monitoring and analysis (additional: TIC/TOC & Eh)	On-going. compressive strength, XRD, MIP, BET BSEM/EDX and FTIR
CSIC	CEM III/B32.5	IERs ashes	0 & 20	Yes	Finished	3months 6 months	Available monitoring and analysis	On-going: compressive strength, XRD, MIP, BSEM/EDX and FTIR

UAM				Modified (leachant: deionized water)	Finished	3months 6 months	Available monitoring and analysis	On-going: compressive strength, XRD, MIP, BSEM/EDX
CIEMAT				Modified (leachant: disposal site)	Finished	6 months	Available monitoring and chemical analysis (additional: TIC/TOC & Eh)	On-going. compressive strength, XRD, MIP, BET BSEM/EDX and FTIR
Glass/ceramic								
USFD	Glass/ Glass-ceramic	IRIS ashes	95 & 100	Yes	Finished	3 months	Available monitoring and chemical analysis	SEM/EDX
SCK CEN	Glass-ceramic	IRIS ashes	95	Yes	On-going	3 months 6 months	Available monitoring and chemical analysis	
CEA	Glass-ceramic	IRIS ashes	30	Yes	On-going (end March'23)	3 months	Available monitoring and chemical analysis	SEM/EDX

Finished On-going Not yet started

Table 5. Update status of the long-term leaching tests on-going in subtask 6.6.3.

Partner	Composition of matrix	Type of waste	Waste load %w/w	WP6 leaching protocol (Yes/No)	*Status long-term leaching tests*		Data available from leaching tests
					Date of dismantling	*Duration*	
Geopolymer							
VTT-UH	MK-based	IERs ashes	0, 10&50	Yes	On-going	*2 years*	Available monitoring and chemical analysis
CSIC	MK+BFS+ Na_2SiO_3	IERs ashes	0 & 20	Yes	October'24	2 years	Available monitoring and chemical analysis
UAM			20	Modified (leachant: deionized water)	October'24	2 years	Available monitoring and chemical analysis
CIEMAT			20	Modified (leachant: disposal site)	October'24	2 years	Available monitoring and chemical analysis (additional: TIC/TOC & Eh)
POLIMI	Volcanic tuff, BFS, FA, NaOH	IRIS ashes	50	Yes	Not yet started		
			50	No, ANSI/ANS-16.1-2019	Not yet started		
		Ashes (dryox)	20	No, ANSI/ANS-16.1-2019	On-going**		**γ-irradiation (Co-60) of the specimen previously to leaching test
			30	Yes	Not yet started		
		Residue (wetox)	40	No, ANSI/ANS 16.1-2019	Not yet started		
			40	Yes	Not yet started		
		Molten salts	35	No, ANSI/ANS 16.1-2019	On-going**		**γ-irradiation (Co-60) of the specimen previously to leaching test
			45	Yes	Not yet started		
Cement							
VTT-UH	CEM I	IERs ashes	0,15 & 50	Yes	On-going	2 years	Available monitoring and chemical analysis
CSIC	CEM I/42.5 SR	IERs ashes	0 &20	Yes	July'24	2 years	Available monitoring and chemical analysis

UAM				Modified (leachant: deionized water)	July'24	2 years	Available monitoring and chemical analysis
CIEMAT				Modified (leachant: disposal site)	July'24	2 years	Available monitoring and chemical analysis
CSIC	CEM III/B32.5	IERs ashes	0 &20	Yes	June'24	2 years	Available monitoring and chemical analysis
UAM				Modified (leachant: deionized water)	June'24	2 years	Available monitoring and chemical analysis
CIEMAT				Modified (leachant: disposal site)	June'24	2 years	Available monitoring and chemical analysis
Glass							
USFD	Glass/glass-ceramic	IRIS ashes	95 & 100	Yes	March-July'24	2 years	Available monitoring and chemical analysis
SCK CEN	Glass-ceramic	IRIS ashes	95	Yes	January'24	2 years	Available monitoring and chemical analysis

Table 6. Additional accelerated leaching tests

Organization	Accelerated degradation tests	Status
SCK CEN	Accelerated tests in NH_4NO_3 media	To be started in coming weeks
POLIMI	Gamma irradiation (Co-60) (sample curing and then, gamma irradiation)	Finished (short-term)/not yet started (long-term tests)