MIM🌀SA

MultI-recycling strategies of LWR SNF focusing on

Deliverable 4.1: Report on definition of tested salt mixtures and candidate structural materials

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Glossary

Abbreviation / acronym	Description
ASME	American Society of Mechanical Engineers
ASTM	American Society of Testing of Materials
SEM	Scanning Electron Microscopy
MSR	Molten Salt Reactor
XRD	X-Ray Diffraction
DSC	Differential Scanning Calorimetry
WPX	Work package #
SPT	Small Punch Test

1 Executive Summary

The main objective of the present task is to provide a structured testing program for WP4 to evaluate the performance and the corrosion behavior of selected materials for key components in MSR. A test matrix detailing the reference chloride salt mixtures, candidate structural materials and the testing environmental parameters was constructed and will serve as input for Task 4.3.

The materials of interest are selected based on the identified material requirements and will include ceramic as well as metallic materials. Samples of commercially available alloys will be used for corrosion tests while ceramics and composites will be manufactured by Schunk (Associated Partner) and other subcontractors in Task 4.2.

The corrosion and deterioration of such materials in a molten salt environment will be investigated in Task 4.3.

2 Introduction

The Molten Salt Reactor (MSR) is one of the six nuclear reactor designs retained by the Generation IV International Forum as a promising concept for the next generation of reactors. It is a reactor class with notable safety and operational advantages, including low vapor pressures, passive safety features, high volumetric heat capacity of the fuel and stability under irradiation [2012BEN, 2012LUZ]. Despite these advantages, high radiation and temperatures, and corrosive salts are harsh environments for structural materials. Even if thermodynamic considerations permit selecting initial fuel compositions such that the salt will not attack the structural materials, in practice there are other corrosion mechanisms which could become active, including impurity-driven, thermal gradient-driven, and dissimilar materials corrosion [2009DEL, 2018FRE, 2013SRI]. A special point deserving attention is the susceptibility of Cr, a common alloying element, to attack by chloride salts, thereby forming salt-soluble chromium chlorides. The dissolution of the chromium chlorides excludes the formation of a corrosion layer which can protect the alloy from further attack (passivation), leading instead to chromium depletion and void formation [2022KEL], which in turn may degrade the mechanical properties of an alloy.

An alternative class of materials which could be considered for service in an MSR are ceramics. Silicon carbide (SiC), for example, is one such material with a long history of use in nuclear environments. Its primary use is in TRISO fuels, in which it has to be strong and inert enough to withstand: i) high pressures resulting from the buildup of gaseous fission products ii) chemical attack from metallic fission products and iii) mechanical loads due to the dimensional changes in pyrolytic graphite (another component of TRISO fuels) with irradiation [2020SNE]. The performance of SiC in contact with molten chlorides, however, is yet to be comprehensively evaluated. Free Si in the SiC matrix is susceptible to attack [2019DIN], which could lead to structural damage and a deterioration of mechanical properties, analogously to metal dissolution in alloys.

To study these effects, the purpose of this document is to describe a corrosion testing program for MIMOSA that will :

(a) Select potential structural materials for chloride-based MSRs.

(b) Select salt compositions which could be representative of fresh MSR fuel, from a set of compositions selected in MIMOSA WP2 (Milestone MS2).

(c) Determine detailed experimental conditions for out-of-pile static corrosion tests, including different testing phases, temperature, duration, roughness of surface, volume of salt, salt volume to coupon surface ratio, crucible configuration, and atmosphere.

(d) Establish a salt purification protocol.

(e) Determine general experimental conditions for out-of-pile dynamic corrosion, neutron irradiation, and simultaneous corrosion-irradiation tests.

This document will provide guidance to the testing activities and the individual technical work plans carried out in Task 4.2, Task 4.3,Task 4.4 and Task 4.5. It should be noted that those testing activities and work plans might still evolve during the course of the project in view of the results obtained progressively.

3 Purpose of the tests and general conditions

3.1 Investigation program strategy

WP4 will tackle the key aspects for the technical feasibility of chloride MSRs related to the interaction between salt mixtures and structural materials in the harsh environment of a nuclear reactor (high temperatures, corrosive environment and radiation). Contact between the structural materials and the molten salts at elevated temperatures (i.e. in the range from 500-800 °C) and under severe neutron flux for extended periods of time will lead to changes in the microstructure due to corrosion and diffusion phenomena as well as swelling, phase changes, segregation, hardening, and other mechanical effects due to irradiation. This will in turn induce changes in properties and performance (e.g. mechanical behaviour) that need to be determined to be used for design and safety analyses and evaluated for appropriateness.

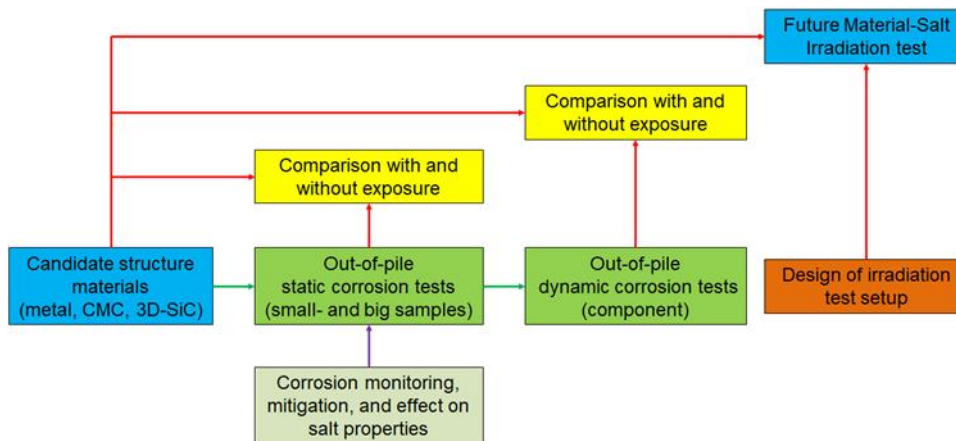A flow diagram of the planned work is shown in Figure 1.

Figure 1 : Flow diagram of the investigation plan of WP4 from MIMOSA proposal

It includes:

- **Out-of-pile static corrosion tests.** These are mainly static testing (capsule and crucible experiments) which are a very useful and economic way to conduct initial screening experiments and compare alloys, and for conducting targeted corrosion studies to investigate specific phenomena in salt mixtures and alloys. The experimental plan is organised into two main phases:
    - **Phase 1,** in which immersion tests are carried out on "small" samples for 500-1000 hours
    - **Phase 2,** in which immersion tests are carried out on "larger" samples, suitable for mechanical tests, for at least 1000 hours

    In addition, as support to the material selection for Phase 1, a Phase 0 is proposed at TU Delft, in which a larger variety of materials could be tested. The setup proposed allows for a high-throughput and faster (96 hours) screening (see Annex A).

- **Out-of-pile dynamic corrosion tests.** In order to evaluate the effect of thermal gradient and salt flow on corrosion, dynamic tests (natural convection) will be performed in WP4. Based on the results of the previous phase, a circulation loop or dynamic set-up will be purchased or designed by the partners of the project, and later tested.
- **Simultaneous corrosion-irradiation test.** At DIFFER, a chamber to perform simultaneous irradiation and corrosion experiments on materials relevant to MSRs will be designed to be

installed on one of the available beamlines. The design will be adapted to allow dynamic corrosion tests, i.e. allowing salt circulation, and to use Th-containing salts.

- **Irradiation tests.** This work will be carried out at NRG, and the design work includes: establishing requirements on irradiation conditions, sample matrix and post-irradiation examinations, preparing technical drawings, performing Monte Carlo analysis to obtain salt composition and fuel power, CFD analysis to obtain salt flow patterns, thermo-mechanical analysis for temperature distributions and facility safety assessment; and writing an Irradiation Proposal to be submitted to HFR for reactor operations.

3.2 Test conditions

3.2.1 Requirements for corrosion tests

Corrosion is the degradation of a refined material into a more stable chemical form in a given environment. It is a complex phenomenon depending on several factors and manifesting itself in different forms (e.g. uniform vs. pitting corrosion). Hence, it is highly context-specific and difficult to standardize: conditions as close to those in the real-world application must ultimately be sought after. Still, there are best practices that the experimentalist may take as a guide, related among other things to specimen preparation, apparatuses, test conditions, and reporting corrosion rates.

The American Society of Testing of Materials (ASTM) has compiled collections of such best practices, which have been taken into account when designing the different phases of the corrosion tests. They will also be considered during subsequent data analysis. Two guides which particularly informed the proposed experimental procedures are *ASTM G31-21: Standard Guide for Laboratory Immersion Corrosion Testing of Metals*, and *ASTM G1 : Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.*

3.2.2 Static corrosion tests

3.2.2.1 *Phase 1*

3.2.2.1.1 Experimental procedure

For Phase 1, small coupons of the selected materials will be completely submerged in the selected chloride mixtures contained in a closed crucible for a total exposure time of 500-1000 hours.

All coupons will be cut to the specified dimensions and abraded to the correct roughness (see Table 1), preferably by one single laboratory. Each coupon type should be abraded with a different paper, so as to avoid introducing contaminations. Afterwards, the coupons will be cleansed with deionized alcohol and water and left in a drying oven until ready for experimental use. The surface of the coupons should then be characterized with the relevant techniques (see Table 2) prior to exposure to the salt.

The coupons will be loaded in the crucibles –one coupon per crucible– inside a glovebox with an Ar atmosphere (H_2O and O_2 content < 5 ppm). The salt will then be added and the crucibles will be closed tight within said atmosphere. The filled crucibles will then be transferred to a furnace, also with an Ar atmosphere, and be exposed to the experimental temperature (e. g. T = 923 or T = 1023 K).

At TU Delft, there will be one to four coupons (depending on the experiment) per tested material. In case four coupons are envisaged, they will all be subjected to their thermal cycles simultaneously, with the first coupon being taken out after 250 h and the subsequent ones taken out sequentially every 250 h, such that the last coupon will be taken out after 1000 h. In case only 1 coupon is tested, it will be extracted after 500 or 1000 h depending on the set conditions. The coupons will be extracted from the

salt while it is still molten to avoid the use of solvents and mechanical stresses that would have to be applied to extract the coupon otherwise. The corrosion behaviour of a given material and concurrent evolution of salt composition will be thus studied over time for some selected (most interesting) combinations of salt and coupon.

At JRC, two coupons per material will be tested according to the following procedure:

- Step 1: The first coupon is exposed to salt for 500 hours, following which a full destructive analysis of the coupon surface is performed as well as ICP-MS analysis of the salt.
- Step 2: A second coupon is introduced in the same (500h treated) salt for additional 500 hours
- Step 3: The coupon is extracted and the salt is analysed by ICP-MS to check the concentration of corrosion products dissolved in the salt
- Step 4: The second coupon is re-inserted in the same salt and treated for another 500 hours
- Step 5: A full analysis of the second coupon,that accounts for 1000 total hours,) is performed as well as the ICP-MS analysis of salt

This procedure would allow minimizing the amount of $PuCl_3$ needed.

The targeted temperature for the corrosion tests is the reactor outlet temperature, which is expected to be the most challenging one for the materials with respect to corrosion. Although the exact temperature need still needs to be confirmed (output from WP3 calculations), the following temperature are taken as reference for the two reactor designs:

- Composition 1 - Medium size core 2 m^3- Pu MOX : 650 °C
- Composition 2 - Thorizon design: 750°C.

Table 1: Experimental conditions for corrosion tests in Phase 1

	TU Delft	JRC
# samples	9	4 (2 coupons x 1 material x 2 compositions)
Size of specimens	2x2x1 mm^3 to 10X5x1 mm^3	$\emptyset$ = 2 mm x 0.5 mm
Roughness	Mirror surface roughness < 0.8 µm	Mirror surface roughness < 0.8 µm
Surface/Volume ratio	$3·10^{-4}$<ratio<0.02 ml:mm^2	0.6 ml:mm^2
Salt volume	0.03 < V < 0.2 ml	~ 6 ml (TBC)
Duration	1000 hours (sampling every 250 h for selected samples)	500 hours & 1000 hours
Atmosphere	Ar	Ar
Configuration (open/ close crucible, sample holder material)	Closed crucible Boron nitride liner within a stainless-steel body	Closed crucible BN liner
Temperature	923, 1023 K	923 K

3.2.2.1.2 Material selection and test matrix

Materials selection is discussed at greater length in Section 3.5. Overall, for Phase 1, the following materials will be considered:

- One ceramic material (selection supported by the preliminary results of Phase 0 – Annex A)
- Pure Nickel
- SS-316L
- Two alloys: one qualified for use in the nuclear industry (e.g. 800H, 9Cr-1-Mo-V) and one Ni-based alloy (selection supported by the preliminary results of Phase 0 – Annex A).

The corrosion tests on SS-316L will be performed with and without a corrosion mitigation strategy (to be developed in Task 4.3) in place. Finally, one material will be selected for testing at JRC-Karlsruhe with Pu-containing salts.

The final test matrix for Phase 1 is given in Figure 2.

Laboratory	TUD	TUD	JRC	JRC	JRC
Salt Mixture	Sim-Comp. 1: Medium size core 2 m3 - Pu MOX (NdCl$_3$/CeCl$_3$)	Sim-Comp.2: Thorizon design (NdCl$_3$/CeCl$_3$)	Sim-Comp. 1: Medium size core 2 m3 - Pu MOX (NdCl$_3$/CeCl$_3$)	Comp. 1: Medium size core 2 m3 - Pu MOX (PuCl$_3$)	Comp. 2: Thorizon design (PuCl$_3$)
Liquidus	447 °C		447 °C	440 °C	394.6 °C
Temperature	Tout ~ 650 °C (TBC)	750 °C (TBC)	Tout ~ 650 °C (TBC)	Tout ~ 650 °C (TBC)	750 °C (TBC)
Duration	250 - 1000 hours	250 - 1000 hours	500 hours	500 hours & 1000 hours (2 points)	500 hours & 1000 hours (2 points)
# samples per material	1 to 4	1 to 4	1	1	1
BEST PERFORMING CERAMIC (SiC$_f$/SiC vs SiC)	x	x			
Ni-201	x		x		
SS-316L (N)	x	x	x		
Selected material 1: qualified (low Cr content, 800H)	x	?			
Selected material 2: Ni-based (e.g. Hastelloy N, Haynes-244, Inconel-625?)	x	?			
SS-316L (N) corrosion mitigation	x	x			
SINGLE SELECTED MATERIAL based on Phase 1 (TUD)				x	x
# materials tested	# experiments TUD			# experiments JRC	
7	9			4	

Figure 2. Test matrix – Phase 1

3.2.2.1.3 Interlaboratory comparison

Two laboratories will be involved in the static corrosion testing: (1) TU Delft focusing on Ce (or Nd)-containing simulant mixtures and (2) JRC-Karlsruhe focusing on Pu-containing mixtures. To help ensure the reproducibility of the results obtained and assess their reliability, the following actions will be put in place:

- A benchmark campaign performed in both laboratories using the same salt mixture (Composition 1, with $CeCl_3$/$NdCl_3$ as surrogate for $PuCl_3$, see Table 5)*, same conditions (temperature and duration) and same standard materials (Ni-201 and SS316L).
- Salt mixtures will be characterized following the procedure described in 3.3.1.1
- Coupons will be prepared and polished by one laboratory to ensure the same finishing or, if not possible, both labs will need to comply the defined standards (e.g. roughness)
- In case one lab can afford to run experiments with a longer duration than another, the specimens will be compared up to the highest common duration.

*Note that prior to the testing, the suitability of $CeCl_3$ and $NdCl_3$ as simulant for $PuCl_3$ will be compared at TU Delft and the best surrogate material will be selected.

As one lab (JRC-Karlsruhe) will be using $PuCl_3$ as one of the salt constituents, while the other (TU Delft) will be using a non-actinide surrogate ($NdCl_3$ or $CeCl_3$) in its place, working within conditions with which reproducibility can be compared will allow to evaluate the choice of $NdCl_3$/$CeCl_3$ as surrogate for $PuCl_3$ (in terms of similar chemical behaviour).

3.2.2.1.4 Post-corrosion examinations

Both laboratories will use similar characterization strategies for the salt and the coupons, namely:

Table 2: Experimental techniques to be applied to the salt mixtures and coupons at both laboratories.

	TU Delft	JRC-Karlsruhe
Salt	X-ray diffraction (XRD) Differential Scanning Calorimetry (DSC) ICP Mass spectrometry (ICP-MS) XANES (X-ray Absorption Near Edge Structure Spectroscopy)	X-ray diffraction (XRD) Differential Scanning Calorimetry (DSC) ICP Mass spectrometry (ICP-MS)
Coupon	Mass loss Scanning Kelvin Force Microscope (SKPFM) Optical Miscroscopy (OM)	Mass loss Scanning Electron Miscroscopy/X-ray spectroscopy (SEM/EDX)

	Scanning Electron Miscroscopy/X-ray spectroscopy (SEM/EDS)	

3.2.2.2   Phase 2

3.2.2.2.1   Experimental procedure

Following Phase 1, two selected materials, one alloy and one ceramic, will undergo mechanical testing without any exposure to molten salt. Identical specimens will be prepared for full immersion in Composition 1 (with $NdCl_3/CeCl_3$ as surrogate for $PuCl_3$), under Ar atmosphere for a duration of 1000 h. Corrosion may affect crack initiation which could then influence the ductility and fracture toughness of the material. Mechanical testing of the salt-exposed specimens will then be carried out, and results will be compared between exposed and unexposed specimens.

Moreover, the microstructural changes of the exposed samples will be investigated at TU Delft to interpret the changes in the mechanical properties. The samples will be observed with Optical Microscopy as a first approximation and assessment of the extent of corrosion produced by the molten salt. Later, a deeper analysis by Scanning Electron Microscopy (SEM) will be performed to study the microstructural changes on the surface, focusing mainly on the formation of voids; and by Energy Dispersive X-ray Spectroscopy (EDS) to observe the elemental distribution of alloying elements in depletion or enrichment zones. If needed, further analysis to evaluate the grain orientations and grain boundaries with Electron Backscatter Diffraction (EBSD) is proposed, in order to analyse preferential pathways for corrosion processes and gain a better understanding of the corrosion mechanisms.

The mechanical testing will include, but not be strictly limited to, the Small Punch Test (SPT). The main outcomes and sample geometries required for the SPT and other potential mechanical tests to be carried out are summarized in Table 3.

Table 3: Listing of potential post-mechanical tests with the associated specimen dimensions.

Test type	Mechanical Properties	sample geometry	Dimension 1	Dimension 2	Dimension 3	Notes
Small Punch Test	strength Rp0.2; ultimate tensile strength Rm; ductile to brittle transition temperature (DBTT) and creep properties (only in creep tests)	Disc	diameter 8mm	thickness 0.5mm	NA	+0.1mm in the thickness has to be considered if polishing is performed in house before the corrosion test

Small Punch Test	strength Rp0.2; ultimate tensile strength Rm; ductile to brittle transition temperature (DBTT) and creep properties (only in creep tests)	Disc	diameter 3mm	thickness 0.25mm	NA	+0.1mm in the thickness has to be considered if polishing is performed in house before the corrosion test
Bending Test	Bending modulus, flexural stress, flexural strain	Beam	Length 20mm	Height 5mm	Thickness 6mm	Validation for Dynamic Young's modulus (DYM) is needed
Compression Test	Compressive modulus of elasticity, compressive yield stress, compressive ultimate tensile stress	Rod	Length 16mm	Diameter 5mm	NA	Validation for DYM is needed

3.2.2.2.2 Material selection & test matrix

The final test matrix for Phase 2 is given in Figure 3.

Laboratory	TUD
Salt Mixture	Sim-Comp. 1: Medium size core 2 m3 - Pu MOX (NdCl3/CeCl3)
Temperature	Tout ~ 650 °C (TBC)
Duration	1000 hours
# samples per material	?
SINGLE SELECTED alloy based on Phase 1 (TUD)	x
SINGLE SELECTED Ceramic based on Phase 1 (TUD)	x
# materials tested	# experiments TUD
2	2

Figure 3: Test matrix -Phase 2

3.2.3   Dynamic corrosion tests

The dynamic corrosion behaviour of the selected materials will be investigated through a loop test setup that will be installed at TU Delft. The experimental setup, which will be acquired in Task 4.3, will be tested at TU Delft and optimised. Several options for the supply of the loop test setup are being currently explored, therefore at this stage the exact characteristics of the setup and the experimental conditions are not yet defined. However, a number of requirements have been identified:

- **Flow conditions:** natural convection, salt velocity of few cm/s
- **Temperature conditions:** presence of thermal gradient between two sections of the loop/set-up, temperature on the hot leg around 650 °C - 700°C
- **Material:** selected based on the static corrosion tests
- **Size:** should minimize the amount of salt in the loop, order of magnitude for the salt volume: 300-500 ml of salt.
- **Salt loading and handling:** the salt mixture must be loaded under protected Ar atmosphere and air tightness must be ensured for the complete duration of the test; the set-up shall be rinsed with a sacrificial salt before the actual testing.
- **Instrumentation required:** thermocouples to monitor temperature distribution throughout the circuit.

Experimental procedures for the dynamic measurements will be designed with the support of JRC. The microstructure of samples before and after dynamic exposure will be investigated by TU Delft using the same techniques as mentioned previously.

3.2.4   Corrosion-irradiation tests (protons)

The simultaneous corrosion-irradiation tests will be performed at the DIFFER 3.5 MeV accelerator, namely at a custom-built instrument called DICE (DIFFER Irradiation Corrosion Experiment). DICE is meant to i) demonstrate that ion irradiation is representative of the damage obtained via neutron irradiation in a molten salt environment, and ii) deliver corrosion data under irradiation at a faster rate than a neutron irradiation experiment.

Within the instrument, the salt will be contained in a 1 cm^3 chamber which will be exposed to a high energy proton beam. One of the windows of the chamber will be made of a thin plate of the ceramic (60 μm) or alloy (30 μm) of interest, such that the incoming 3 MeV protons will pass through the plate creating defects but the implanted hydrogen will be deposited in the salt. Thus, the back-side of the plate will be under the simultaneous effects of corrosion and irradiation whereas the front side of the plate will experience irradiation only. With DICE, a considerable radiation damage of 5 dpa (displacements per atom) will be achieved within 96 hours. Moreover, it will have the capability of handling Th-bearing salts, such that both salt compositions 1 and 2 (see Table 5 below) will be tested. Experimental conditions are given in Table 4.

Table 4: Experimental conditions for the corrosion-irradiation tests at DIFFER.

# samples	9
Size of specimens	1 cm in diameter, 30-60 μm thick

Roughness	Mirror surface for alloys[1]
	Ceramics as received
Surface/Volume ratio	0.01 ml:mm^2
Salt volume	1 ml
Duration	96 hours
Atmosphere	Ar
Configuration (open/ close crucible, sample holder material)	Closed crucible: Ni liner with a window from the material of interest

The planned tests are as follows:

- corrosion only on materials selected from phase 0 (see Annex A) – 96 hours to see if corrosion of thin samples is the same as for thick samples from phase 0 done by TU Delft, and to have a reference for test 2
- Simultaneous corrosion-irradiation: 5 dpa and static salt for 96 hours.
- Simultaneous corrosion-irradiation: 5 dpa and dynamic salt for 96 hours.

The samples will be characterized post-mortem with the following techniques:

a) SEM to evaluate corrosion attack on the surface by observation of changes in surface texture and roughness
b) Energy Dispersive X-ray Spectroscopy (EDS) to observe element enrichment/depletion
c) ICPMS to analyse corrosion products in the salt
d) Secondary Ion Mass Spectrometry[2] to analyze the surface composition
e) Focused Ion Beam (FIB) to get cross-sections and depth of attack.
f) Positron Annihilation Lifetime Spectroscopy (PALS) to quantify defect size and density

3.2.5   Neutron irradiation tests

A decision on the material will be made based on the outcome of Phase 1. It will be used as a crucible containing actinide-bearing chloride salt (Th and Pu) and irradiated at the High Flux Reactor (HFR) in Petten. With this test, the combined effects of irradiation and corrosion will be observed, with the added effect of fission products shifting the redox potential of the salt. Mechanical tests such as SPT for the alloy and bending for the ceramic could be done to get an understanding for the impact of irradiation damage on the ductility and bending strength. Ultimately, the mechanical characterization of in-pile corroded specimen will be dependent on the final capsule design.

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[1] If 30 μm alloys can be polished.
[2] Subject to instrument availability.

3.3 Salt mixtures

3.3.1 Salt compositions

The salt compositions to be considered in WP4 were selected in WP2 and are reported in Table 5. For further details, we refer to: *Technical note regarding the selection of salt composition in WP2 (Milestone MS2).*

Table 5: Selected mixtures from WP2

Reference compositions	Fuel salt (JRC)	Surrogate salt (TU Delft)
Composition 1 Medium size core 2 m^3- Pu MOX	Including PuCl$_3$	Including NdCl$_3$ or CeCl$_3$
Composition 2 Thorizon design	Including PuCl$_3$	Including NdCl$_3$ or CeCl$_3$

3.3.1.1 Salt purity

The importance of salt purification for molten salt corrosion studies as well as for use in molten salt systems is a glaring fact as extensively discussed in literature. Salt purity is strongly correlated with corrosion rate but the large variability in purification methods/handling procedures and the lack of salt impurities quantification in most studies, makes the "salt purity" definition rather arbitrarily.

Halide salts in the as-received state generally contain significant levels of moisture and metallic impurities and need to be purified before use. Moreover, salts must be handled and kept constantly under protected atmosphere, typically in an Ar glove-box, with O$_2$ and H$_2$O level below 5 ppm.

As the salt mixtures for the experiments will be prepared in three different labs, namely TU Delft, JRC and ICJLab, a protocol needs to be put in place to ensure that results are reproducible and comparable with each other. The strategy proposed consists of the following steps:

- Purity check of the end-members by XRD to identify additional phases (e.g. oxide and/or oxychloride).
  - ➢ **Acceptance criteria:** below detection limit of the technique
- Purity check of the end-members by DSC to determine the melting point of the compounds
  - ➢ **Acceptance criteria:** single peak on heat flow, temperature in agreement with the literature within ± 10 K
- Quantitative analysis of all the elements except the main constituents by ICPMS
  - ➢ **Acceptance criteria:** > 99.9% metal base for commercial salts
- Salt composition check by DSC (comparison with thermodynamic model)
  - ➢ **Acceptance criteria:** in agreement with the literature within ± 10 K

In addition, to further characterize the salt mixture prepared, the following analyses will be performed:

- At JRC-Karlsruhe: determination of the residual oxide content by complete salt vaporization in KEMS
- At ICJLab: Determination of residual oxygen in the salt mixture by electrochemical methods (SWV)

3.4 Material selection

The structural materials required for a molten chloride reactor need to show corrosion resistance at high temperatures, mechanical strength and ductility, irradiation stability, adequate heat transfer properties, and low neutron absorption. For the reactor designs considered herein, operating temperatures as high as 1023 K and gradients up to 300 K need to be withstood. These properties could be fulfilled by certain ceramics, metals, and ceramic-metal composites known as cermets. Due to technological maturity, the focus in MIMOSA is on ceramics and metals, discussed below.

3.4.1 Ceramic materials

Ceramic materials are very attractive high-temperature structural materials as they have shown excellent material properties as listed above.

Despite the benefits in terms of low neutron absorption cross-section and high temperature resistance and chemical inertness, the issues with carbon-based ceramics (carbon fiber composite, graphite, or other carbon forms) are large dimensional change, anisotropy, and significant property changes that continue as function of flux and temperature. Graphite even shows a change from initial shrinkage to swelling as flux increase, which can create large complications in a nuclear reactor.

Silicon carbide has similar benefits and has therefore been considered for nuclear applications (fission and fusion) already for a very long time. In general, SiC shows very high DPA resilience, and dimensional and material property changes that stabilize (saturation point), and remain similar up to very high DPA levels. An issue is that SiC-materials are difficult to produce. In particular, monolithic SiC can be produced by (1) sintering a pre-formed shape; (2) printing and sintering with Si-infiltration; and (3) Si-free printing and sintering.

Another interesting option are the silicon carbide fiber reinforced silicon carbide (SiC_f-/SiC) composites which show very similar behavior to (monolithic) SiC, but have higher bending and fracture strength. This can be very beneficial for use in a reactor considering that bending can be induced by dimensional change and thermal expansion. SiC_f/SiC has been manufactured in the past and also irradiated, but it still needs extensive development for upscaled mass-production of SiC_f/SiC components. SiC_f/SiC is therefore quite expensive (especially the SiC-fibers) but will most likely become more economical with increasing demand, especially from aviation industry, but, hopefully, also the nuclear industry. Currently, the main SiC_f/SiC production methods are with (1) SiC_f with SiC-CVD followed by Si-infiltration; (2) SiC_f with SiC CVI (Si-free); and (3) hot isostatic pressing of SiC_f/SiC and sintering (high density SiC_f-SiC, Si-free), but developments are ongoing. A third class of materials considered, as alternative to SiC-fibers composites, was the carbon fiber reinforced SiC (C_f/SiC) material, which from performance, cost and manufacturing maturity would be preferable. However, it is expected that the differences between dimensional and property changes between the C-fiber and SiC-matrix under irradiation, will generate a lot of unmanageable material issues. This option has therefore been dismissed.

Several suppliers have been contacted as part of the activities in Task 4.1 to discuss material characteristics and production methods. A summary of the potentially available SiC materials including suppliers is given in Table 6. Particular attention was given to the presence of residual free Si in the SiC matrix as it will be corroded preferentially in terms of thermodynamics generating weak areas with worse corrosion resistance in liquid salts. Si in the microstructure can have additional effects like acting as diffusion pathways, and thus, enhancing corrosion even at grain boundaries.

Table 6: SiC materials, characteristics, and suppliers.

Supplier	SiC material	Agreed to supply ?	Considerations
Schunk	SiC$_f$/SiC	Yes	SiC$_f$/SiC with CVI, Si-free.
	printed SiC (with free Si)		Printed SiC, is open porosity sintered SiC, with Si-infiltration (free Si).
Mersen Boostec	Pre-formed SiC and sintered	Yes	Monolithic SiC, contains B$_4$C (<0.5%), no free Si
Nanoe	Printed SiC (no free Si)	Yes, possibly with payment	Nanoe is a filament supplier, who has developed a filament to allow SiC printing (contains two binders, that are removed in two sintering steps, leaving pure SiC (96% density, with <0.5% B$_4$C), no free Si
Admatec	Printed SiC (no free Si)	To be checked with partner	Admatec can also print pure SiC, similar to Nanoe. They do this together with a partner, which needs to agree and support sample delivery, no free Si
SGL	Can only deliver SiC coated materials, printed SiC (Si-infiltrated)	Not asked	Most likely not relevant

From these, the SiC$_f$/SiC composite would seem to be the most promising material, due to the aforementioned enhanced bending and fracture strengths. Moreover, an analogous C/C-SiC matrix was found to retain its mechanical properties even after exposed to the salt and subsequent corrosion of free Si [2019DIN]. However, it would still be of use to observe variations in corrosion resistance within Phase 0.

3.4.2 Alloys

From a practical perspective, it is desirable to focus on alloys which have been qualified according to international standards and codes. Outside this set, promising alloys would take many years to qualify for use in an industrial application. That being said, one Ni-based alloy would be interesting as a case study, to contrast with the established alloys and perhaps make a case for its qualification.

In the American Society of Mechanical Engineers (ASME) code, Section III Division 5: *Rules for Construction of Nuclear Facility Components – High Temperature Reactors*, there are only six qualified alloys: (i) Stainless steel 304; (ii) Stainless steel 316; (iii) 800H; (iv) 2.25Cr-1Mo; (v) 9Cr-1-Mo-V and (vi) Inconel 617. Their compositions are shown below in Table 7.

Table 7: ASME-qualified alloys for nuclear components at high temperatures. Composition in weight %. Reproduced from [2019WRI].

Material	Fe	Ni	Cr	Co	Mo	Al	C	Mn	Si	S	Ti	Cu	B	P	V	N	Nb
304/304H	Bal	8.0-10.5	18.0-20.0	-	-	-	0.04-0.08/0.10	2.0 max	0.75 max	0.03 max	-	-	-	0.045 max	-	0.10 max	-
316/316H	Bal	10.0-14.0	16.0-18.0	-	2.0-3.0	-	0.04-0.08/0.10	2.0 max/0.04-0.10	0.75 max	0.03 max	-	-	-	0.045 max	-	0.10 max	-
800H	39.5 min	30.0-35.0	19.0-23.0	-	-	0.15-0.60	0.05-0.10	-	-	-	0.15-0.60	-	-	-	-	-	-
2.25Cr-1Mo	Bal	-	2.0-2.5	-	0.90-1.1	-	0.07-0.15	0.30-0.60	0.50 max	0.025 max	-	-	-	0.025 max	-	-	-
9Cr-1Mo-V	Bal	0.40 max	8.0-9.5	-	0.85-1.05	0.04 max	0.08-0.12	0.30-0.60	0.20-0.50	0.010 max	-	-	-	0.020 max	0.18-0.25	0.30-0.70	0.06-0.10
617	3.0 max	44.5 min	20.0-24.0	10.0-15.0	8.0-10.0	0.8-1.5	0.05-0.15	1.0 max	1.0 max	0.015 max	0.6 max	0.5 max	0.006 max	-	-	-	-

To begin with, it should be noticed that Inconel 617 has a Co content which is too high for service under neutron irradiation [2019WRI], reducing the space of qualified alloys to 5.

Examination of the Cr content in these alloys suggests that those showing the greatest corrosion resistance will be 2.25Cr-1Mo and 9Cr-1Mo-V, although a better indicator for this than concentration is the Cr activity [2021PIL], which need not follow the same trend as the concentration.

3.4.3 Alternative/replacement materials

3.4.3.1 Ceramics

Pertaining the ceramics, there are enough suppliers to find different variations of SiC (Table 6). Aside from the SiC$_f$-SiC composite, a corrosion performance comparison with either printed or monolithic SiC would be desirable given the potential difficulty of scaling the production of SiC$_f$/SiC to mass production.

3.4.3.2 Alloys

The following alternative alloys have been reviewed:

- **Hastelloy N.** The Molten Salt Reactor Experiment (MSRE) established Hastelloy N, a high Ni alloy, as a reference alloy with high corrosion resistance against molten fluorides. In chloride salts, Ni is still less susceptible to corrosion than chromium and iron [2018Guo], yet not as inert so as not to suffer attack. Still, in thermal convection loops in a NaCl-MgCl$_2$/NaCl-KCl-MgCl$_2$ environment, Hastelloy N displayed a relatively good corrosion rate (< 100 µmyr^{-1}) relative to other alloys, including 316/316L and 800H [2022KEL]. Thus, it would be of interest to include Hastelloy N and compare its performance to that of the qualified alloys in Table 7.

- **Advanced HASTELLOY N derivatives.** Although there are also advanced Hastelloy N-derivatives under development, commercial suppliers of these do not yet exist. However, personnel at Haynes International, the supplier of alloy N, suggested and supplied other alloys which might show corrosion resistance in a chloride environment according to their experience, namely:
  - HAYNES 230
  - HAYNES 242
  - HAYNES 244
  - HAYNES 282

Table 8: Composition of Haynes 244. Reproduced from [2022HAY].

Nominal Composition
Weight %

Nickel:	Balance
Aluminum:	0.5 max.
Carbon:	0.03 max.
Chromium:	8
Iron:	2 max.
Manganese:	0.8 max.
Molybdenum:	22.5
Tungsten:	6

From these, Haynes 282, 230, and perhaps 242 are problematic because of their cobalt content. The latter is otherwise interesting because of its low chromium content and its high Mo content, Mo displaying inertness even in chloride media with induced thermal gradients [2022KEL]. Similarly, and without any cobalt, alloy 244 has the benefit of reduced Cr content, high Mo content and additions of tungsten, yet another inert metal in chloride media [2022KEL]. To conclude, alloy N and Haynes 244 (Table 8) are decidedly interesting materials to benchmark the performance of the ASME-qualified alloys during Phase 1 (immersion tests), and the choice between them could be aided by Phase 0 (high throughput).

- **HASTELLOY C276** is a Nickel-chromium-molybdenum wrought alloy that is considered the most versatile corrosion resistant alloy available. Alloy C276, with a high-nickel contents, is immune to chloride-induced stress corrosion cracking. The high molybdenum and chromium contents allow the alloy to perform in oxidising, non-oxidising and mixed acids media, whilst exhibiting outstanding resistance to pitting and crevice corrosion attack. The addition of tungsten inhibits the development of pits.

Table 9: Composition of C-276 alloy

Limiting Chemical Composition, %

Nickel	Balance
Molybdenum	15.0-17.0
Chromium	14.5-16.5
Iron	4.0-7.0
Tungsten	3.0-4.5
Cobalt	2.5 max.
Manganese	1.0 max.
Carbon	0.01 max.
Vanadium	0.35 max.
Phosphorus	0.04 max.
Sulfur	0.03 max.
Silicon	0.08 max

- **INCONEL-625.** Alloy 625 is a Ni-based alloy with great manufacturability, high mechanical strength and corrosion resistance, strengthened by carbon, chromium, molybdenum and niobium. While it was originally designed for service in supercritical steam power plants, its high content of refractory elements makes it possible to be used in molten chloride environments as well [2022KEL]. Table 13 shows the composition of Inconel 625.

Table 10: Composition of Inconel 625. Reproduced from [2013SPE].

Nickel	58.0 min.
Chromium	20.0-23.0
Iron	5.0 max.
Molybdenum	8.0-10.0
Niobium (plus Tantalum)	3.15-4.15
Carbon	0.10 max.
Manganese	0.50 max.
Silicon	0.50 max.
Phosphorus	0.015 max.
Sulfur	0.015 max.
Aluminum	0.40 max.
Titanium	0.40 max.
Cobalt[a]	1.0 max.

[a]If determined

- **ALLOY-709.** Alloy 709 is derived from NF709 (Fe-20Cr-25Ni-1.5Mo-Nb,B,N), which was a commercial heat- and corrosion-resistant austenitic stainless steel developed by Nippon Steel Corporation in Japan for boiler tubing applications. The high strength of NF709 is achieved by controlling the carbon content to 0.07–0.10% and precipitation strengthening by Nb(C,N) (MX phase) and CrNbN (Z phase). NF709 also shows good fabricability properties and weldability. It was regarded as one of the best austenitic steels for elevated temperature applications among commercially-available austenitic alloy classes. The NF709 alloy provides time dependent strength nearly double that for conventional 304 and 316 stainless steels at sodium-cooled fast reactor relevant temperatures. Alloy 709 has the same chemical composition as NF709 but is intended for SFR applications that include reactor vessel, core supports, primary and secondary piping, and possibly intermediate heat exchanger and compact heat exchanger.

  A code case for 709 is being prepared (with INL in the lead) and will be ready by the end of 2024. Although alloy 709 has greatly improved high-temperature (creep) strength over 316, it does not perform any better corrosion-wise. The latter is not so surprising given the same amount of Cr is present in both. No irradiation data is available, the code case is fully based on tests on non-irradiated 709.

  Taking into consideration the limited availability of alloy 709 and the similar corrosion behavior expected for the alloy 709 and the 316, only the latter will be tested in this project.

4 Conclusion

The present deliverable provides a testing program for WP4 to evaluate the performance and the corrosion behaviour of selected materials for key components in a chloride-based MSR. In particular, it delineates a clear test matrix for task 4.3 (out-of-pile static corrosion tests), drawing from two main groups of materials: SiC-based ceramics and alloys qualified for high temperature reactors according to the Section III Division 5 ASME Code. As for the salts, Compositions 1 and 2 with either $PuCl_3$ or $NdCl_3$/$CeCl_3$ surrogates (see Table 5) have been selected as representative fuels within the test matrix from task 4.3. Furthermore, this deliverable prescribes how the results from task 4.3 should be used in other tasks. The relationship between task 4.1 and the remaining tasks in WP4 is summarized in Table 14.

Table 11: Relationship between task 4.1 and the remaining tasks in WP4.

Task	Activity	Input from task 4.1
4.2	Manufacturing of ceramic materials (monolithic and composite) and investigation of material properties before salt exposure	Identification of several suppliers
		Hypothesized SiCf-SiC to be the most promising ceramic material *a priori*
4.3	Out-of-pile static and dynamic corrosion tests of candidate structural materials	Narrowed down the number of materials to be subjected to immersion corrosion tests in Phase 1 (**6**)
		Narrowed down the number of materials to be subjected to immersion corrosion tests in Phase 2 (**2**)
		Established salt purity criteria
		Identified the requirements for the dynamic corrosion tests (one material, flow conditions, temperature range, salt volume, instrumentation)
4.4	Development of corrosion mitigation methods in molten salt reactors and investigation of the effect of corrosion products on the salt thermochemical properties	Identified alloy for corrosion protection case-study (stainless steel 316)
4.5	Design of an integral irradiation and corrosion tests in the HFR Petten and at the 3.5 MeV ion accelerator at DFFR.	Identified basic experimental parameters
		Material selection in this task to be informed by results of task 4.3

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6 Annex A – Phase 0

The experimental space spanned by all the ceramics and alloys that could be considered make for a very intensive research program, such that it needs to be scaled down. One way to further refine the space would be through a high throughput assay as done by Wang et al. [2022WAN]. Therefore, a Phase 0 is proposed in support of material selection at TU Delft.

The proposed setup would consist of a matrix of rectangular coupons, each made from a given ceramic or alloy of interest, on which a pellet of salt would be placed and melted *in situ* at the same temperature as the immersion tests (see following section) under argon atmosphere (Fig. 4). In the study by Wang et al., the length of the corrosion test was 96 h, so the same timespan could presumably be used for this phase.
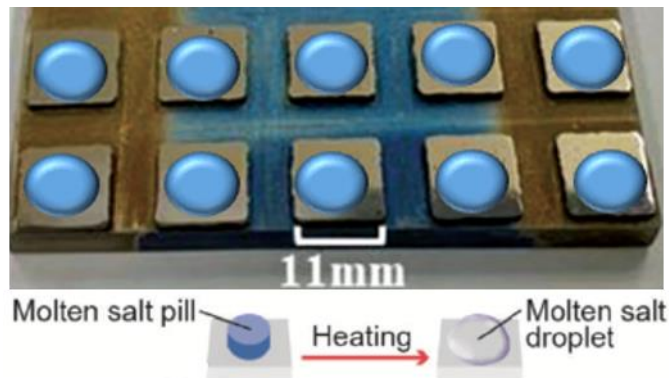

Figure 4 : Schematic of the pre-immersion corrosion test matrix, showing salt pellets placed horizontally on the test coupons, to be melted into droplets in situ. Adapted from [2022WAN].

An average temperature of 700°C would be used.

The final test matrix for Phase 0 is given below:

	Laboratory	TUD
	Salt Mixture	Sim-Composition 1: Medium size core 2 m^3 - Pu MOX (NdCl$_3$/CeCl$_3$ surrogate)
	Temperature	700 °C (TBC)
	Duration	96 hours
	# samples per material	1
CERAMIC	Monolithic SiC - Nanoe/ Mersen Boostec	x
	Infiltrated SiC (with free Si) - Schunk	x
	SiC fiber SiC (Schunk)	x
	C fiber SiC (Schunk)	?
ALLOY	Ni-201	x
	SS-316L (N)	x
	SS-304	x
	800H	x
	2.25Cr-1Mo	x
	9Cr-1Mo-V	x
	Hastelloy-N	x
	Haynes 244	x
	Hastelloy C-276	x
	Inconel-625	x
	GH35-35	?
	MoNiCR	?
	# materials tested	# experiments TUD
	10	13

Figure 5. Test Matrix – Phase 0

After exposure, the samples will be examined via SEM, to discard samples which present a high degree of corrosion. Additionally, those samples showing the least corrosion during the pre-immersion phase will be selected for the immersion tests in Phase 1.

Materials not discarded after the pre-immersion test and not selected for the first immersion tests could be saved for later if time allows.