Ref. Ares(2024)8382167 - 25/11/2024

HEATERNAL

Deliverable D3.3

Novel Refractory materials

Due date of deliverable: 31/10/2024
Submission date: 25/11/2024

Responsible WP3: CIC energiGUNE
Task Leader: TORRECID
Lead Beneficiary : TORRECID

Revision: v5

Funded by the European Union

Document Control Sheet

PROJECT INFORMATION

Project Number	101103921		
Project Acronym	HEATERNAL		
Project Full title	innovative High tEmperAture ThErmal stoRage for iNdustrial AppLications		
Project Start Date	01/05/2023		
Project Duration	42 months		
Funding Instrument	Horizon Europe	Funding Scheme	
Topic	Development of high temperature thermal storage for industrial applications		
Coordinator	CEA		

DELIVERABLE INFORMATION

Deliverable No	**3.3**
Deliverable Title	**Novel Refractory materials**
Work-Package No	3
Work-Package Title	Storage materials development
WP-Leader (Name and Short Org. Name)	CIC energiGuNE (CICe)
Task No	3.2
Task Title	Development and Full characterization of refractort bricks
Task Leader (Name and Short Org. Name)	TCID
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Status	Draft ☐ Final ☒
Deliverable Type	Report ☒ Data ☐ Demonstration ☐ Other ☐
Dissemination Level	Public (PU) ☒ Sensitive (SEN) Classified ☐ PU: Public, fully open SEN: Sensitive, limited under the conditions of the Grant Agreement Classified R-UE/EU-R – EU RESTRICTED under the Commission Decision No2015/444 Classified C-UE/EU-C – EU CONFIDENTIAL under the Commission Decision No2015/444 Classified S-UE/EU-S – EU SECRET under the Commission Decision No2015/444
Date Approved by Coordinator	14/11/2024

DOCUMENT VERSION HISTORY

Version	Date	Author	Description of Change
1	1-9-2024	Carlos Concepcion (TCID)	Draft
2	3-10-2024	Kyran Williamson (CiCE)	Revision
3	8-10 2024	Grégory Largiller (CEA) Laura Teodorescu (CEA)	Revision
4	10-10-2024	Ángel Serrano (CICe)	Review
5	23-10-24	Claire Houzé (CEA) Sylvie Douard (CEA)	Final revision

DOCUMENT REVIEW

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Legal disclaimer

This project has received funding from the European Union's Horizon Europe research and innovation program under grant agreement No. 101103921

ABBREVIATIONS

Abbreviation	Definition
TES	Thermal energy store system
TESS	Thermal energy storage system
PCM	Phase change material
FFF	Fused filament fabrication
3D	Three-dimensional
AM	Additive Manufacturing
ABS	Acrylonitrile-butadiene-styrene copolymer
SA	Stearic acid
BYK	BYK MAX P4102
TGA	Thermogravimetric analysis

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Executive Summary

HEATERNAL develops a Thermal Energy Storage (TES) System (TESS) conceived to meet industry needs of constant high temperature heat in the face of climate and geopolitical urgencies.

HEATERNAL CONCEPT lies in refractory bricks containing phase change materials (PCMs). The TESS features three distinct zones, each utilizing a different PCM embedded in refractory bricks, with phase changes occurring at different temperatures.

In terms of refractory materials, HEATERNAL introduces innovation in TES technology through two key approaches. The first focuses on novel refractory formulations, leveraging traditional state-of-the-art manufacturing processes. The second explores complex geometries enabled by Fused Filament Fabrication (FFF) 3D printing of ceramic-based compositions.

CALD, UGENT CEA, and CICe have collaborated in the design of the solution based on state of art approach, whereas TCID, LEITAT and CICe have developed the 3D printing approach. This deliverable outlines the advancements made in refractory material development for both conventional manufacturing and 3D printing techniques, as well as the innovative geometries required for the TESS.

In order to design novel TESS Unit and to validate small-scale prototypes, FFF 3D printing technology using ceramic composites is being investigated by LEITAT and TCID.

1. Introduction

HEATERNAL aims to establish composite ceramic materials, for state of art technologies in ceramic refractory materials and FFF 3D printing, and study their performance for TES pioneering applications. To address the concept, HEATERNAL relies on the development of a solution using state of art technology for refractory processing and novel system by 3D printing. Current deliverable will summarize:

- Novel refractory systems based on state of art manufacturing. Their properties and manufacturing process.
- Novel refractory compositions tested for 3D printing.
- Performance of materials with PCM used in the project.

2. Novel refractory materials

2.1 Novel refractory materials by traditional processing

Within HEATERNAL, diverse refractory compositions were tested, based on compositions supplied by Calderys. Among them, two were initially selected, as being shown in Table 1.

		Thermal conductivity 800 ºC W /mK	Density 800 ºC	Reversible thermal expansion (20-1000 ºC)	Cold crushing strength MPa 800 ºC
ALKON CAST MT90	High Al2O3 composition 90%	3.26	3.03	0.88	80
AlKON CHEM PB85	High AL2O3 composition 85 % , 5 % P2O5	2.78	2.90	0.84	105

Table 1 Compositions of refractory materials by traditional processing

Based on preliminary PCM-refractory compatibility tests, WP3 proposes Alkon Cast MT90 for the prototypes.

In collaboration with WP4, a suitable geometry was developed for the TESS, encompassing both the overall structure of the unit and the design of the individual refractory bricks. Figure 1 illustrates the detailed layout of these bricks, as well as the final assembly of the complete TESS system. .

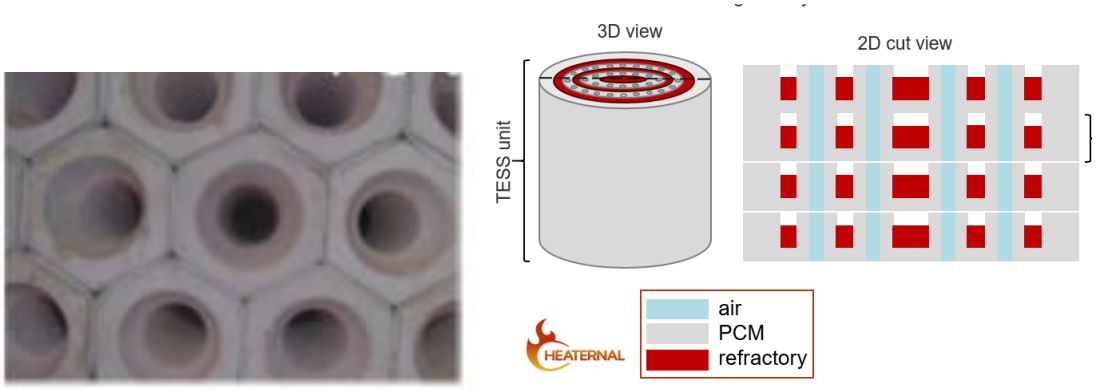


Figure 1 Refractory design

The production process for the ceramic samples is based on casting. The process consists of four steps:

- Step 1: Preparation of a metallic mould

The mould can be disposable or reusable. The outer part of the piece should be constructed in steel, in order to hold the pressure during the casting. The holes and boreholes (or blind holes) can also be made with metallic parts but, in this case, it is preferable to consider carton pipes (lost during dry out process) or a silicon insert (easy to remove).

There are several options to make a shape but it is important to keep in mind that the difficult step is the demoulding. The moulds have therefore conicity and a good ratio between length/diameter has to be respected to ensure the design can be manufactured. Typically, an angle between 2 and 3 ° is targeted.

Figure 2: Mold with pins to make the holes

- Step 2: Casting a refractory castable into the mold

The higher technology refractory castable materials require particular attention given to the equipment and the installation environment in order to reach optimum installation quality. Castable materials are to be stored between 5 and 25°C, at least 48 hrs before the materials are to be used. As the castable will be mixed with water, we consider the optimum water temperature to be between 15-25°C. The water must be of potable quality, which means a pH close to 7 (>6 and <8). Lower pH tends to increase the setting time while higher pH tends to decrease the setting time, which has an effect on the development of the strength of the final product.

Use of an efficient horizontal paddle mixer for dense castable materials is required. The mixer should preferably be equipped with a planetary blade turning counter current, in addition to the main mixer blade. Figure 3 shows an example of such a planetary mixer.

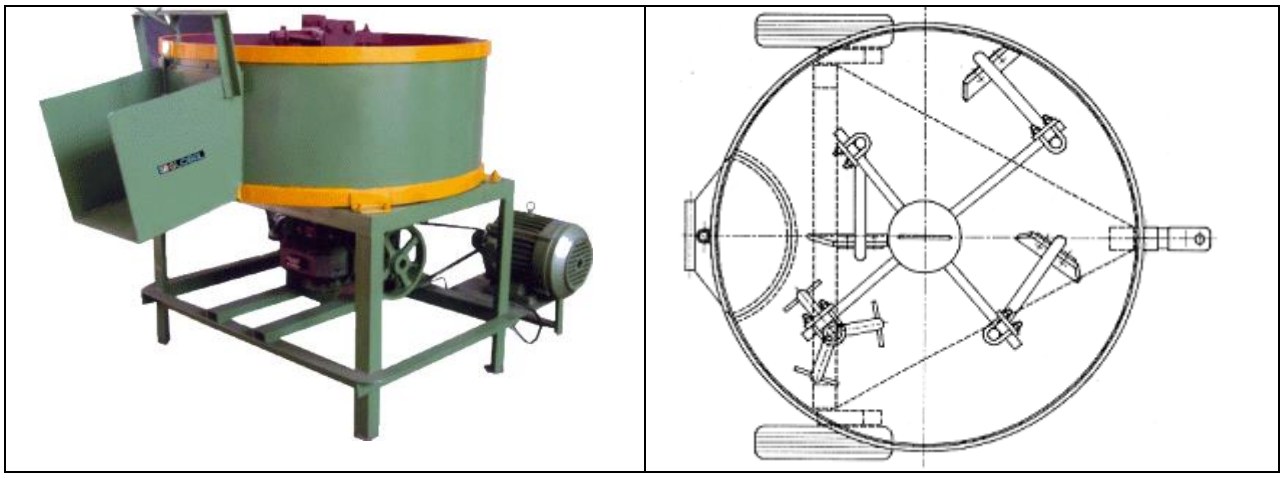


Figure 3: Example of planetary mixer

It is paramount to use a mixer strong enough to provide an as efficient mixing as possible.

We recommend not using more than 80% total mixer capacity to ensure good mixing efficiency.

The size of the mixer has to be adapted to the amount of castable material to ensure proper casting and avoid layering, especially with low/no cement (low water) castables.

Depending on the size of the pieces, Calderys will use:

- Starring mixer: 400 – 600 kg – Engine with minimum 15 kW output
- Eirich type mixers: 200 – 500 kg – Engine with minimum 10 kW output.

Figure 4: Mixing equipment - left: discharging area / right: mixing area

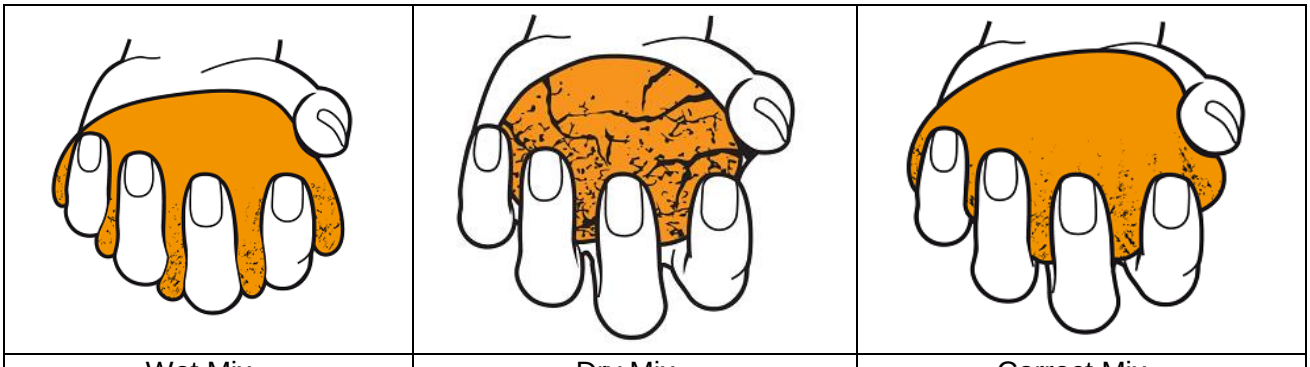
The mixing is performed in two steps:

- Dry mixing: The dry mixing is important to homogenize the different aggregates. It is necessary in case there is segregation in the (big) bag.
- Wet mixing.

The smallest mixing quantity possible will always result in the best final product.

Material	Dry mixing	Wet mixing	Mixer types
Low cement	10 – 30 sec	Up to 5 – 7 min	Pan/ paddle mixer, counter current

The handball test is used to check the consistency of the mix:



Wet Mix	Dry Mix	Correct Mix

Figure 5: Consistency test

Dense hydraulic bonded castables are mixed with a very low percentage of water, to achieve high strength with minimum porosity. In such a situation, it is necessary to vibrate the castable to achieve the proper densification. In case of a precast shape, it will be done on a vibrating table.

After mixing, the castable has to put in the mold within 20 minutes to ensure the best flow features and the minimum vibration. A too long vibration period can cause segregation in the final products.

Dense chemically bonded castables are mixed with the binder in the same way as hydraulic bonded castable and then, cast and vibrated.

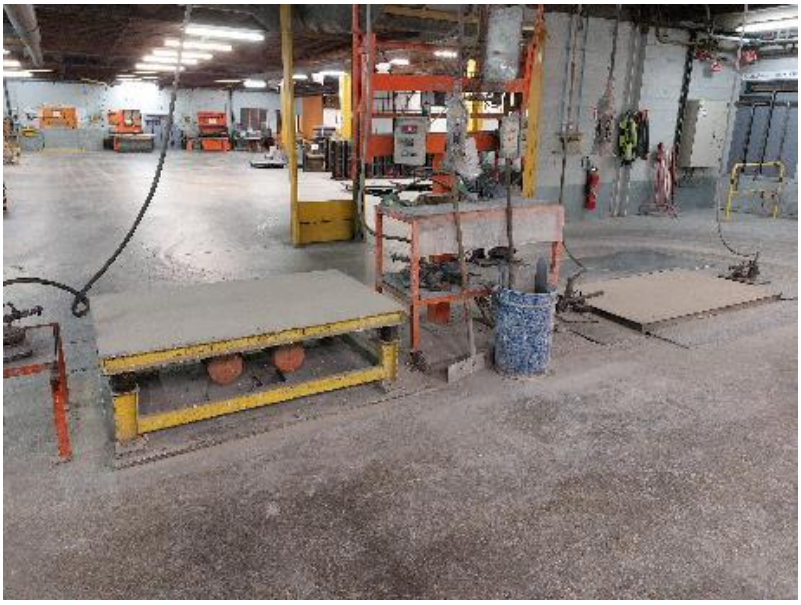


Figure 6: Vibrating tables

- Step 3: Demoulding the refractory piece

The product, after casting is left for 24 hours minimum for setting and curing until it is demoulded for the hydraulic bonded material. For chemically bonded material, this period is shorter since is a setting but no curing.

The demoulding is a manual operation, which requires care since the freshly cast castable has a low strength at green state. Green state is the state of the castable just after setting and before firing in the stove.

NB: the low strength comes from the fact that we use low cement products while the strength development is initiated a higher temperature.

- Step 4: Drying the refractory piece in a stove

The pieces are charged with the help of a forklift or crane according to the weight and dimensions and the stove. After closing the stove, the firing system is ignited and the piece follow a heating cycle. Figure 1Figure 7 shows the temperature program in the stove (Figure 8 image of a stove). The short curve can be used for small pieces, depending on pieces thickness the preferable curve will be selected. However, minimum drying time will be 130h, ie ~5,5 days.

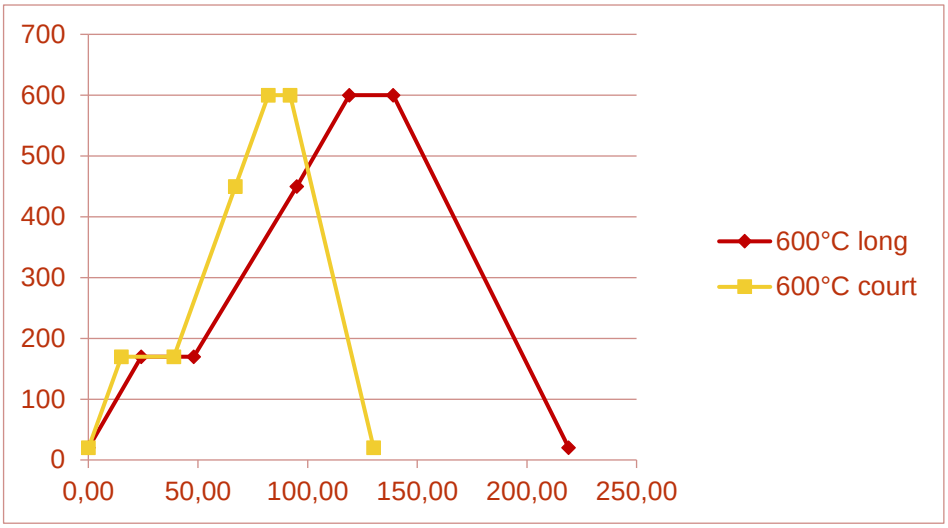


Figure 7: Drying curve in DegC/h

Figure 8: Stove

2.2 Novel refractory materials for 3D printing. Ceramic powder compositions

TCID has prepared ceramic powder corresponding to ceramic compositions to be mixed with suitable binder for 3D printing. Compositions were prepared to be used for the printing of ceramic like and/or full ceramic samples. The different solutions cover use in ceramic like systems or ceramic systems. For ceramic like, the ceramic powder and polymer are mixed and printed, while for ceramic type, the ceramic -polymer material is sintered after printing after a debinding stage. Full ceramic needs a higher ceramic content in the 3D filament.

For the temperature use between 600 and 800 ºC, suitable ceramic compositions were developed with melting points above 800 ºC. Three types of materials were developed showing in Table 2.

			Sintering Tº C
HT01	Ceramic composition	clay based	1170 ºC
HT02-03-05-06-07-08	Ceramic refractory composition	Al_2O_3 based	1550-1450 ºC
HT04	Ceramic composition	clay based	1150 ºC

Table 2 Type of ceramic materials

2.2.1 Ceramic composition HT01

HT01 is a clay based ceramic composition modified from porcelanized ceramic. Material was prepared by weighing of raw materials, wet milling, spray drying of slurry and milling to achieve final powder below 63 microns. The wet milling step was optimized to reduce residue above 63 to cero. HT01 was selected initially based on high clay content to get a high plastic composition easily printed. Table 3 shows the composition.

	HT01
Quartz	10
Clay	55
Kaolinite	20
Feldspar	15

Table 3 HT01 composition

Figure 9 shows pressed discs of HT01 after sintering and with a whole drill for compatibility studies with Al alloys.

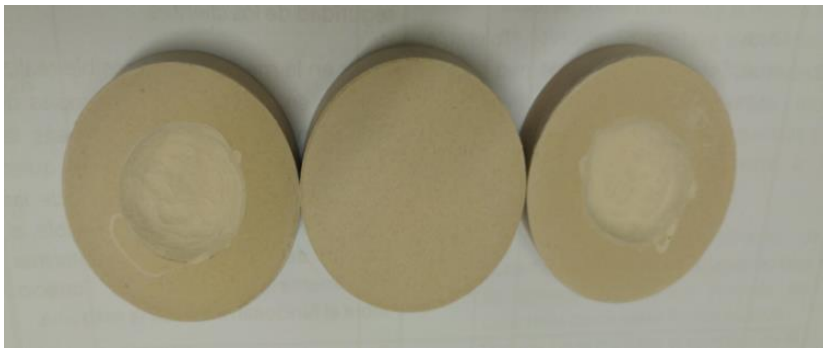


Figure 9 HT01 samples

HT01 was characterized in terms of sintering performance, measuring linear shrinkage and water absorption, as shown in Figure 10. Pressed samples as shown in Figure 9 were prepared and fired to different final temperatures. Shrinkage and water absorption were measured.

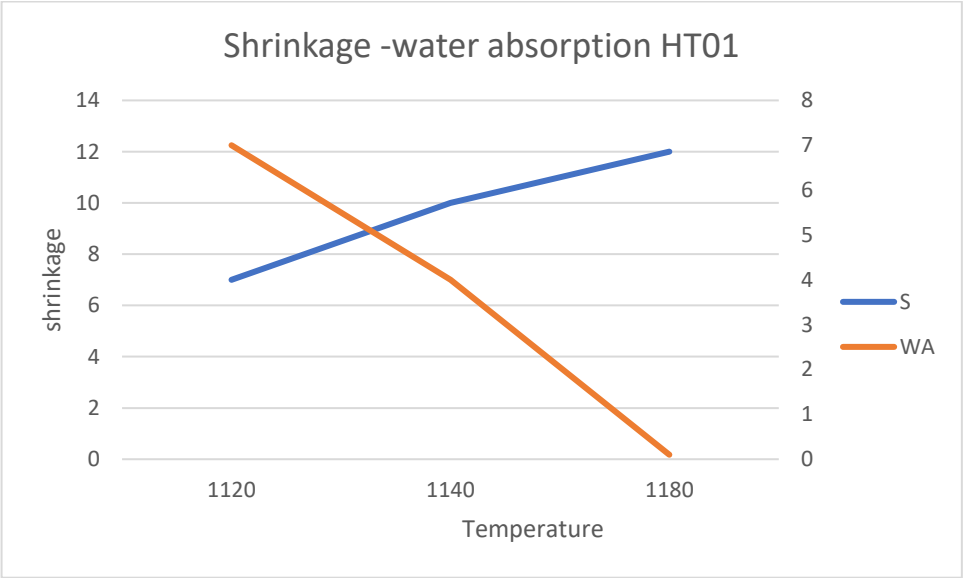


Figure 10 HT01 porosity -linear shrinkage

In Figure 11 shows the XRD pattern for HT01 before sintering while below is after sintering at 1170 ºC. It can be seen that at the beginning HT01 is a mixture of quartz, clay, albite (Na feldspar) and Kaolinite. After sintering, the main phase is quartz and mullite.

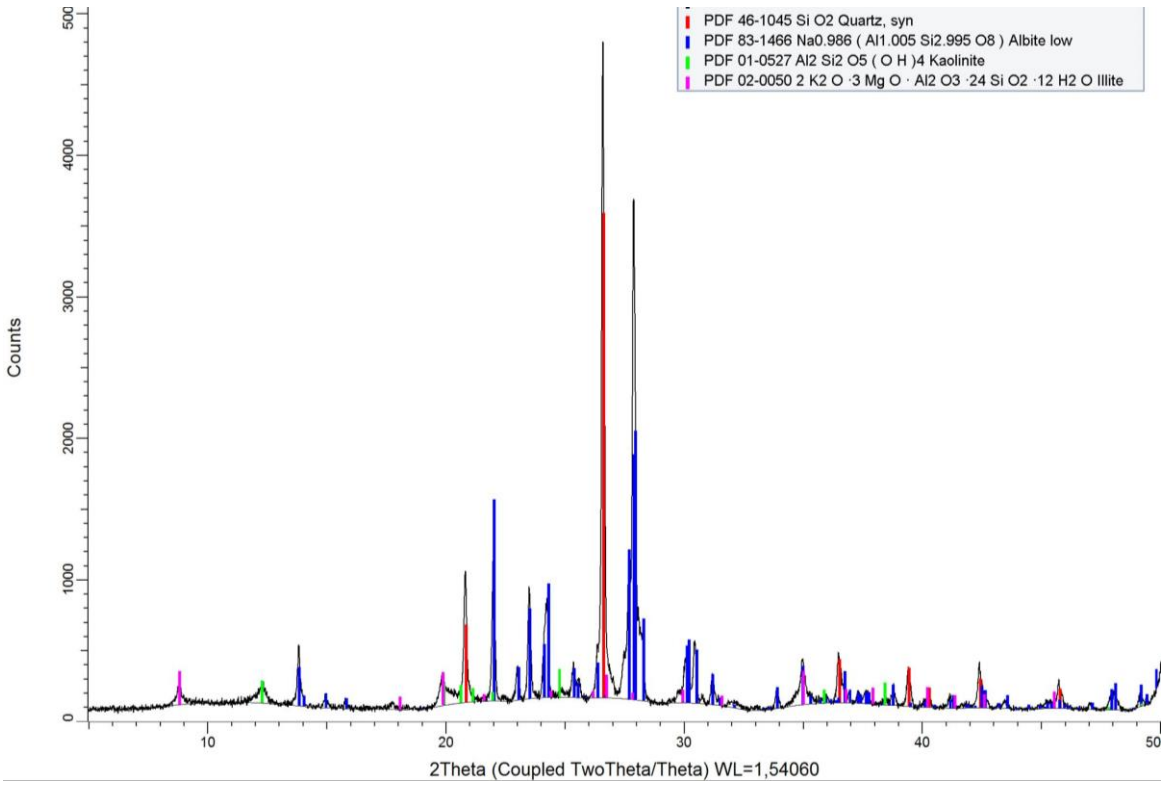


Figure 11 HT01 XRD

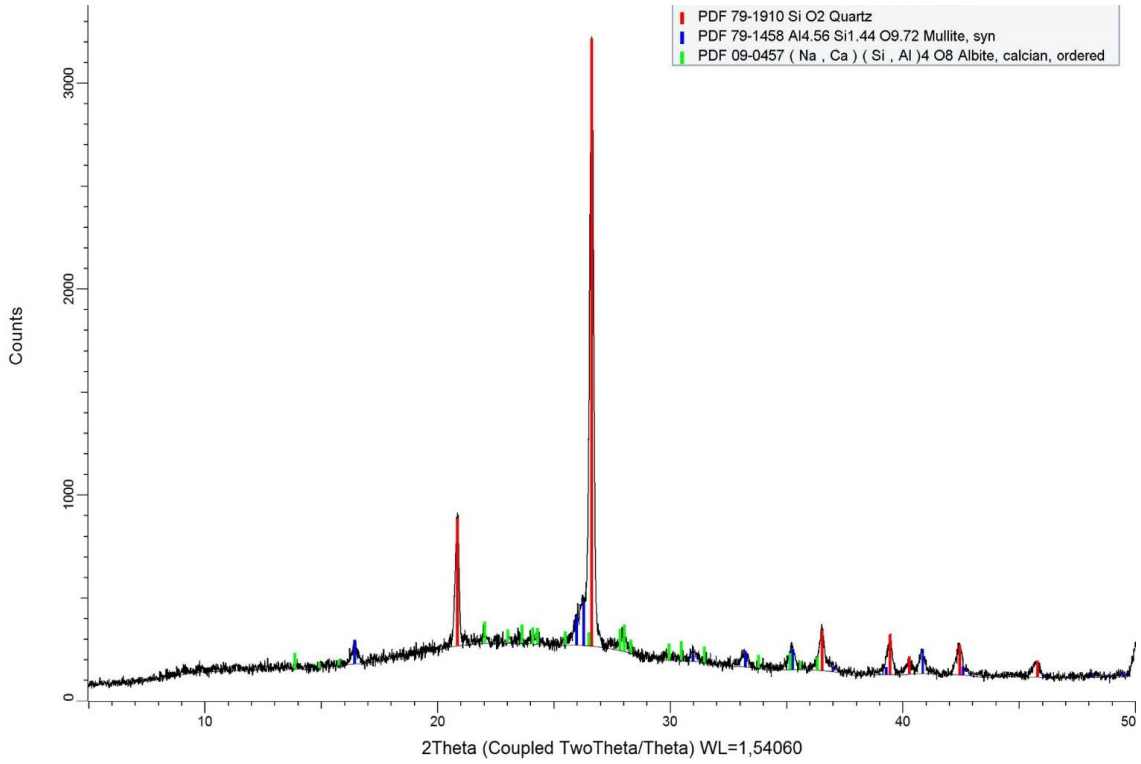


Figure 12 XRD of sintered HT01

Figure 13 shows surface microstructure of HT01 and SEM-EDAX analysis.

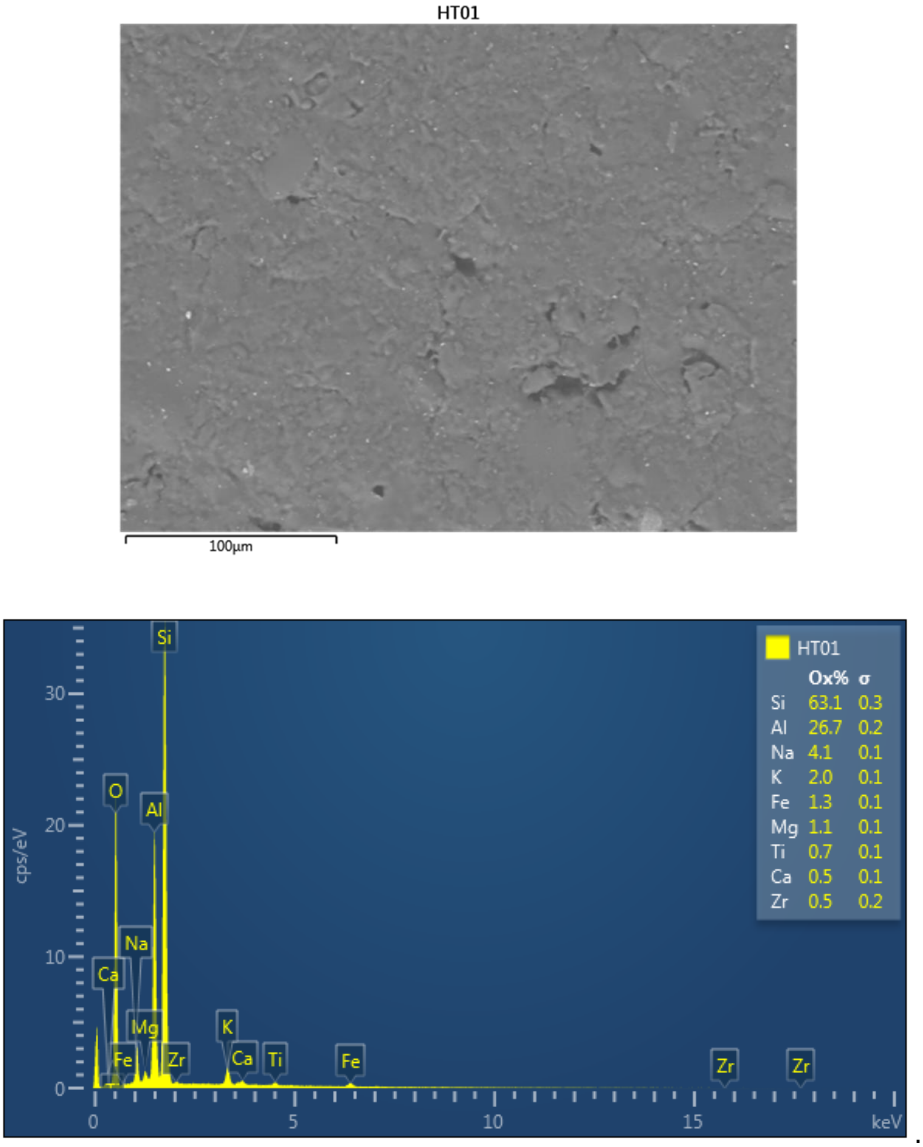


Figure 13SEM-EDAX HT01

2.2.2 Ceramic composition HT04

HT04 is a clay based ceramic composition with increased sinterability and reduced thermal expansion. Material was prepared by weighing of raw materials, wet milling, spray drying of slurry and milling to achieve final powder below 63 microns. Table 4 shows composition of raw materials during development of composition. HTO4 was finally developed to get a ceramic composition with high stability to thermal shock, based on lowering the thermal expansion material. Different compositions were tested to achieve low thermal expansion and low porosity at 1150 ºC.

				Final HT04
Clay	25	10	15	20
Feldspar	15	10	0	15
Ceramic Frit	15	50	20	20
ZrSiO4	10	10	5	10
Talc	5	4	12	8
Kaolinite	19	16	48	38
Water absorption 1150 ºC (%)	0.5	0.1	1.5	0.1
TEC 10^{-7} C^{-1}	35	35	30	25

Table 4 Compositions of HT04 intended for 3D printing

Figure 14 shows surface microstructure and SEM-EDAX of HT04. Figure 15 shows SEM-EDAX and Figure 16 XRD for sintered HT04

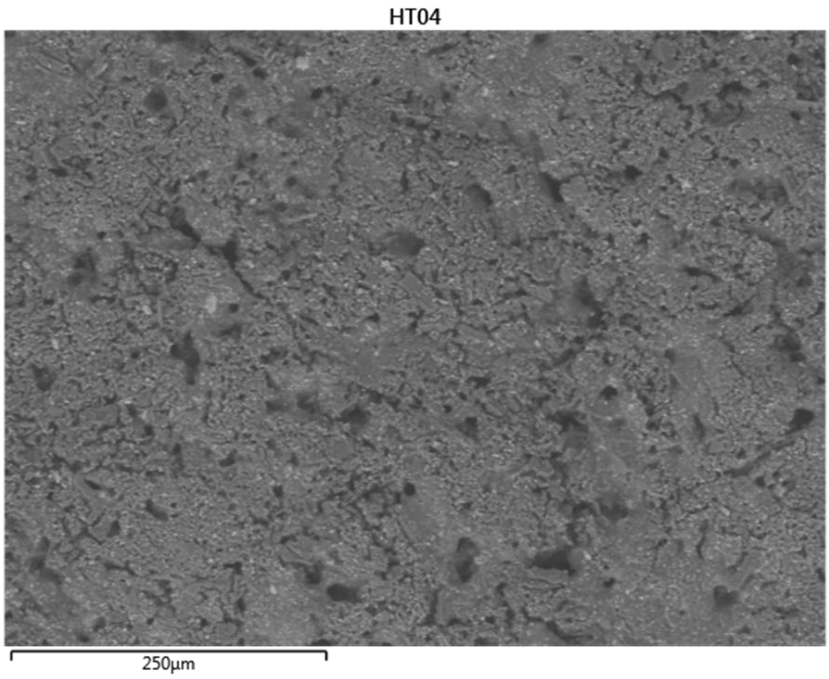


Figure 14 HT04 microstructure

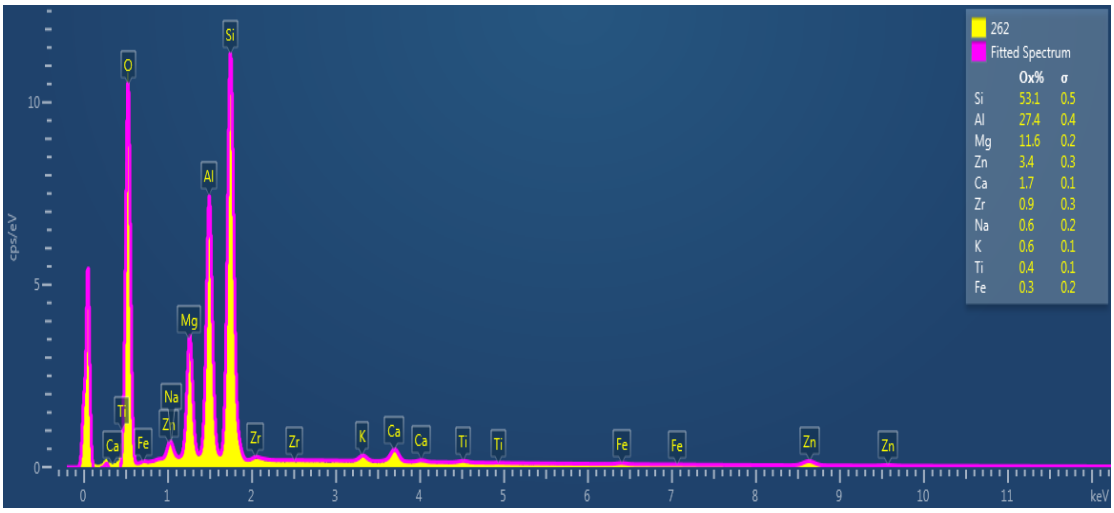


Figure 15 HT04 SEM EDAX

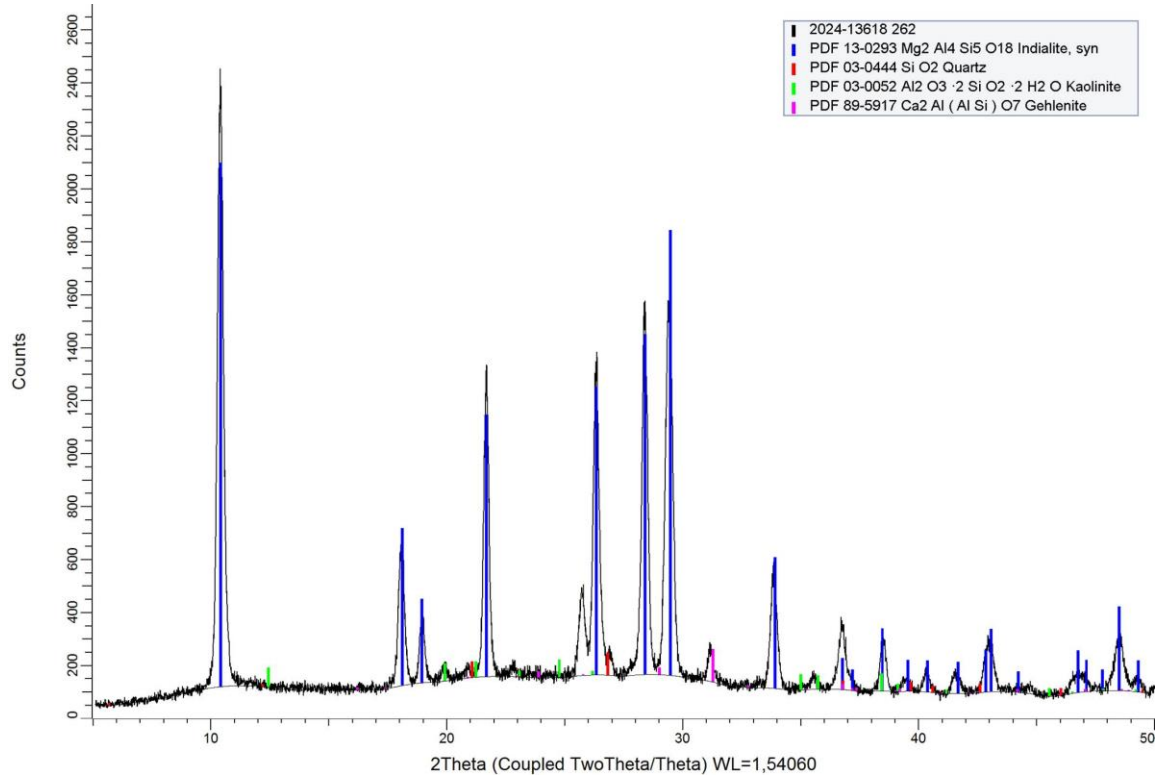


Figure 16 XRD of sintered HT04

2.2.3 Refractory compositions HT02-03-05-06-07-08

High-temperature refractory compositions are based on A_2O_3 with different additives. Within HEATERNAL initial refractory compositions were prepared HT02, HT03, HT05 following the procedure described above. Al_2O_3 has high melting point, inconsequence different approaches were followed to reduce the sintering

temperature. In parallel, FFF 3D printing trials resulted in compositions changes to increase plasticity modifying levels of bentonite and Kaolinite. Table 5 below shows the compositions developed.

	HT02	HT03	HT05
Al_2O_3	81	80	74
Alkaline earth Carbonates	15	10	10
Kaolinite	4	10	15
Bentonite			1
Sintering temperature T ºC	1550	1550	1550

Table 5 Refractory compositions HT02-HT03 HT05

These powders were sent to LEITAT for testing compatibility with 3D polymers. Powders and samples prepared were characterized by SEM and XRD. Figure 17 shows surface microstructure of HT03 and Figure 18 SEM-EDAX

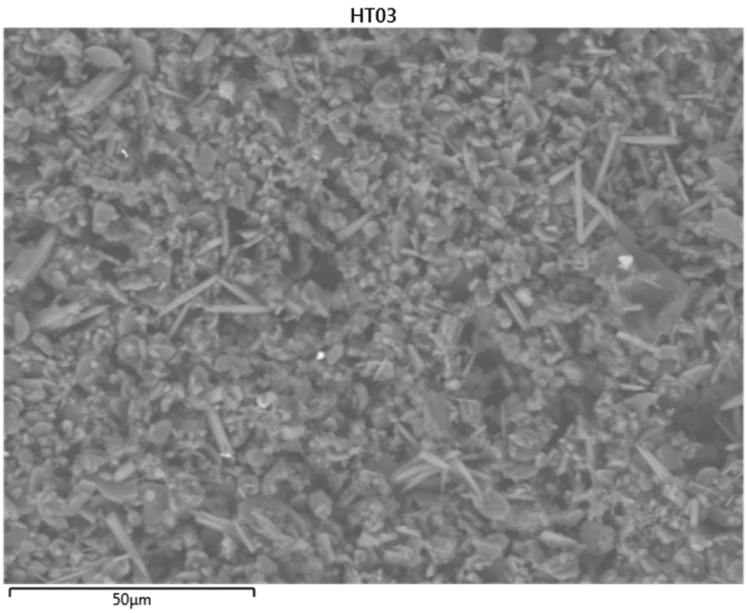


Figure 17HT03 microstructure

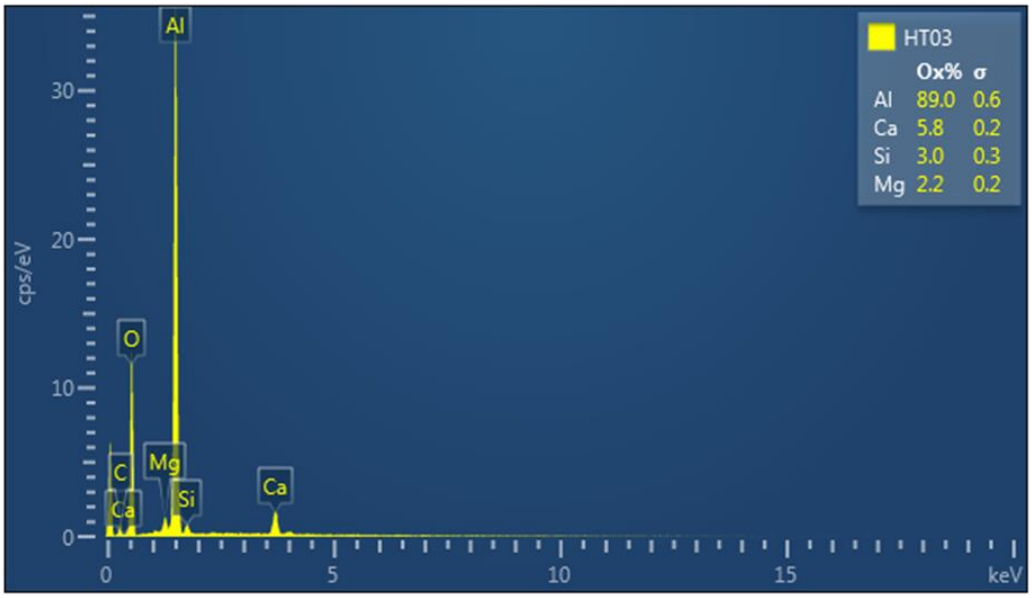


Figure 18 HT03 SEM EDAX

HT05 is the composition chosen initially for ceramic like compositions.

Table 6 describes novel compositions, starting from HT05 developed to reduce sintering temperature and improved densification, looking forward to improve materials performance for a full ceramic sample. Composition was modified adding different frits and fluxes like petalite.

	HT06	HT07	HT08
HT05	81	80	80
Frit -1	5		
Frit-2	4	20	10
Petalite	10		10
Sintering temperature	1500ºC	1450ºC	1450 ºC

Table 6 HT05-08 compositions

Figure 19 shows water absorption of samples HT03-HT06-HT07 versus temperature, showing improvement in HT07.HT08 showed presence of small pinholes.

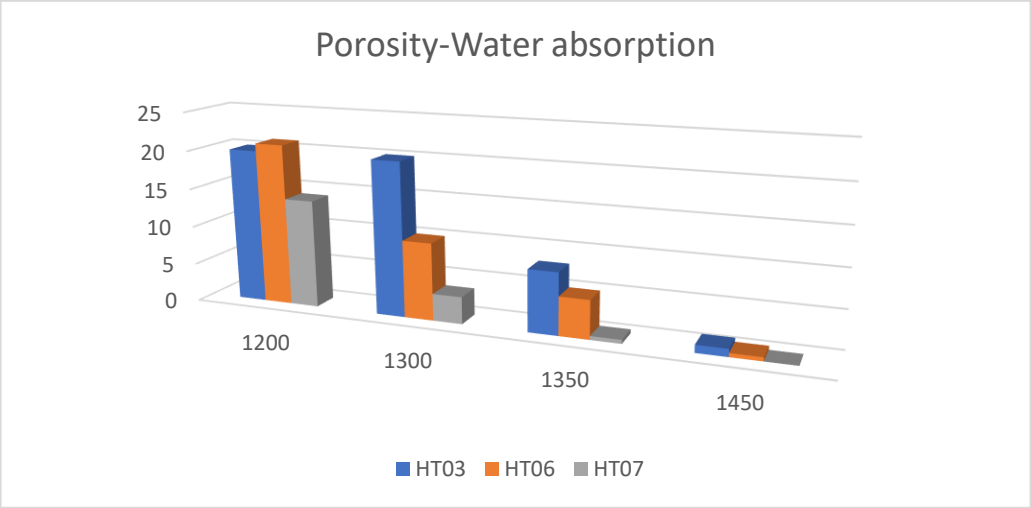


Figure 19 7HT03-6-7 water absorption

Figure 20 to Figure 21 show XRD of sintered HT06 and HT07.

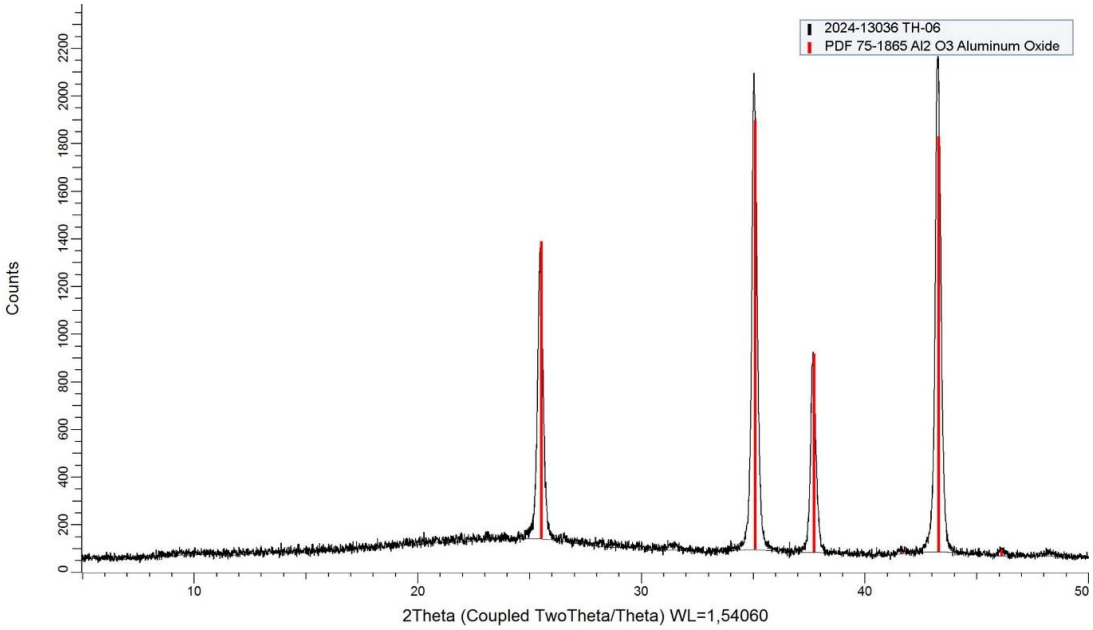


Figure 20 XRD for HT06

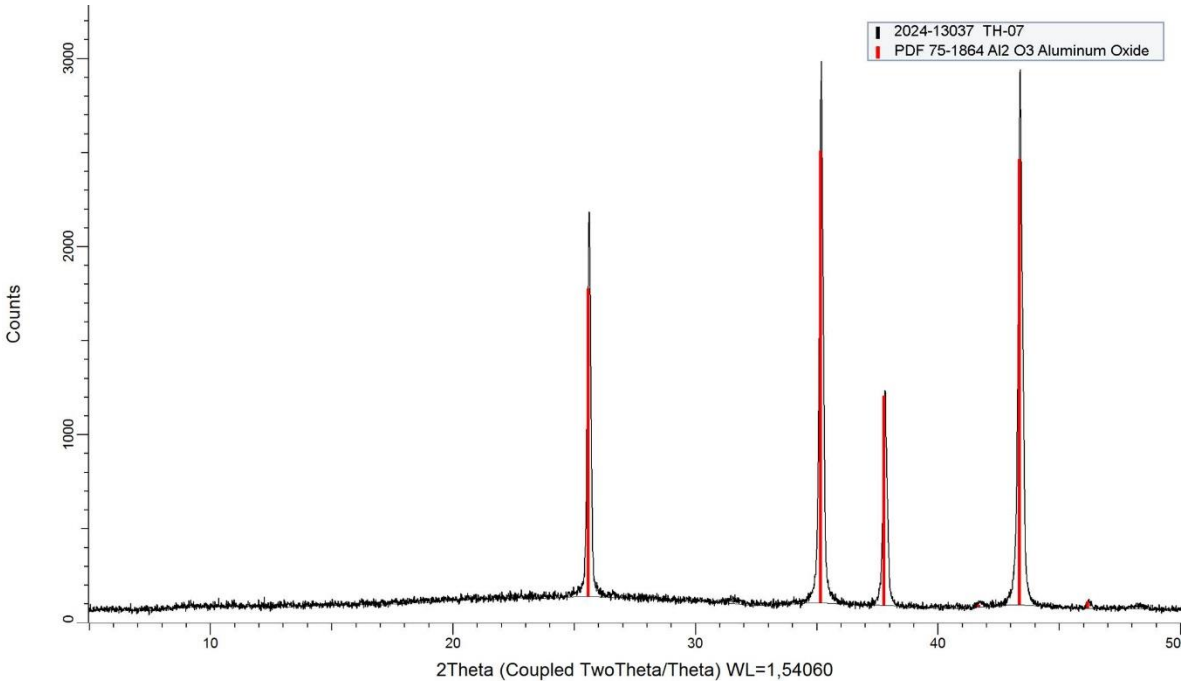


Figure 21 XRD for HT07

In Figure 22 and Figure 23 surface microstructure and SEM-EDAX for HT06/ HT07 are shown.

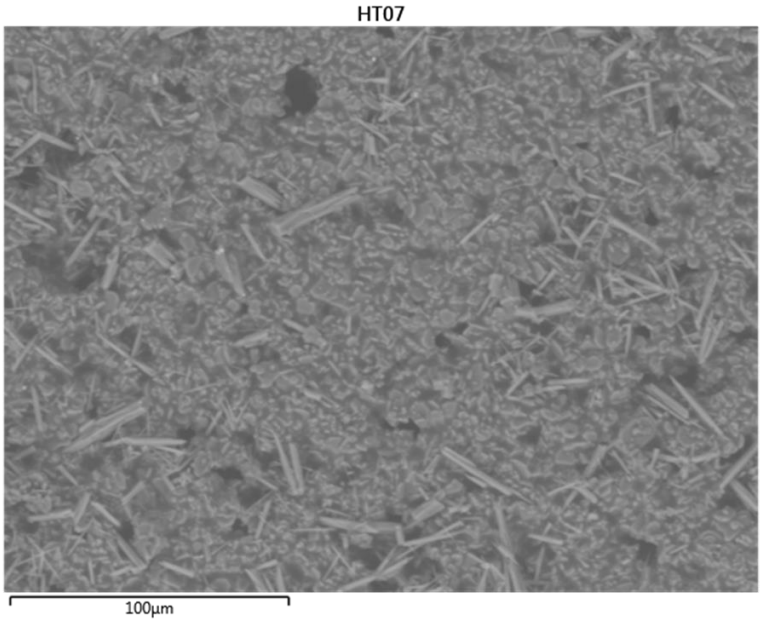


Figure 22 Microstructure HT07

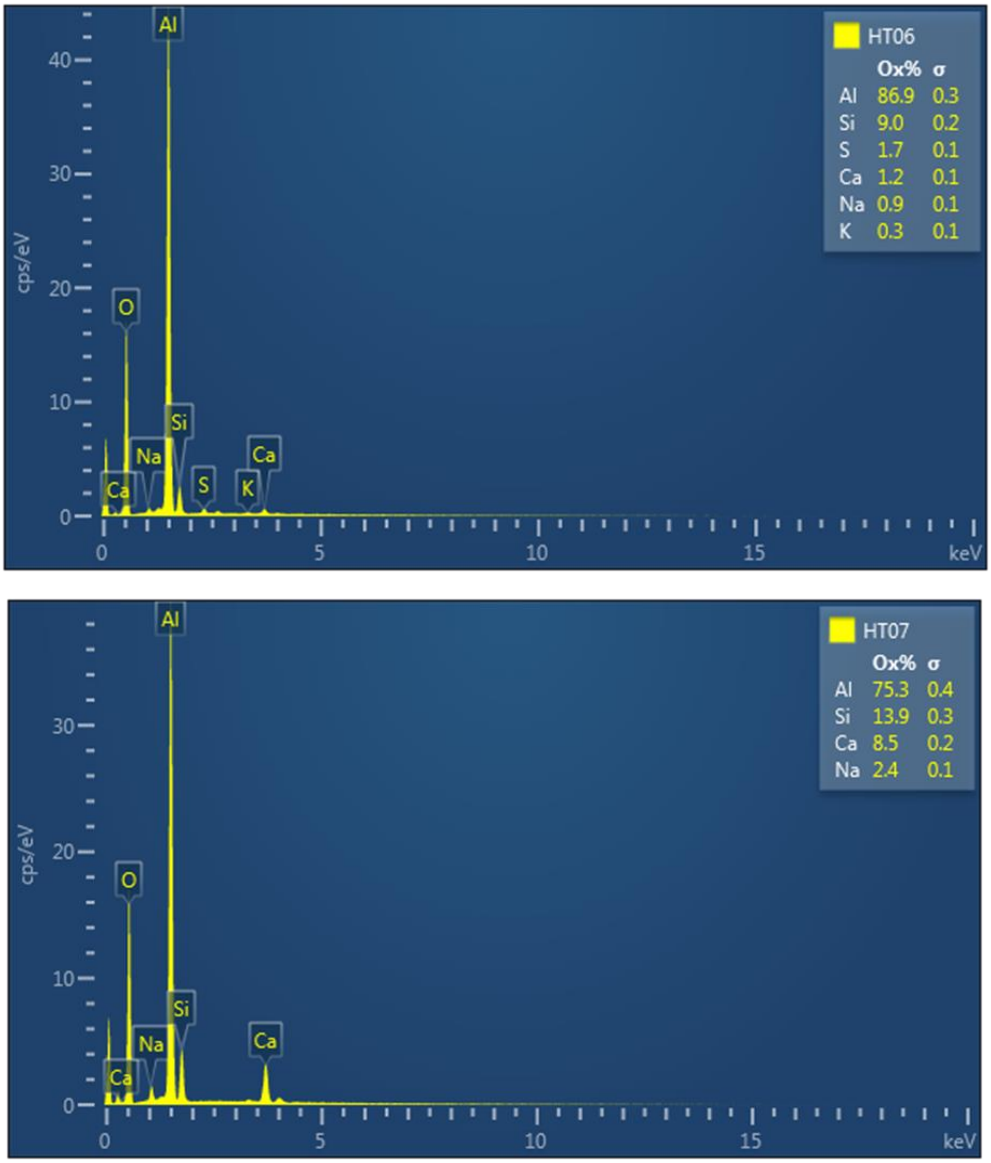


Figure 23 SEMDAX HT06-07

The ceramic compositions HT03 to HT08 were prepared by mixing raw materials, milling raw materials in wet state using ceramic balls 20 mm in diameter, to reduce particle size below 60 microns. The slurry was spray dried, milled and screened through 62 microns mesh to avoid agglomerates. Figure 24 shows some particle size distributions.

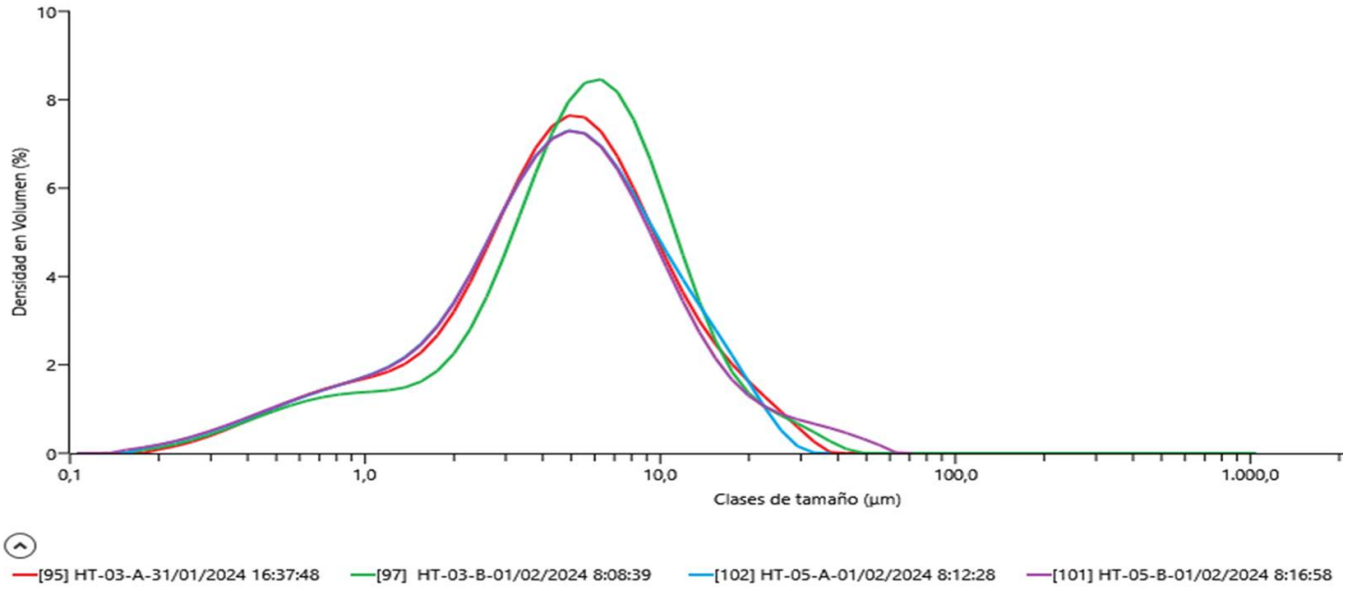


Figure 24 particle size

2.3 Material performance under TESS conditions.

2.3.1 Preliminary PCM-refractory compatibility

Developed ceramic materials, both those starting from conventional processing, as well as materials for 3D printing, were tested for compatibility with the Al alloys.

TCID tested pressed discs of ceramic materials sintered, and a hole inside. Al alloy was placed inside and heating cycles up to 850 ºC were carried out to test the performance as shown. After each cycle, the sample was evaluated to detect the stacking of molten aluminium to the surface. As can be seen, in Figure 25 material performs well except HT01 in which the alloy got stuck to the surface.

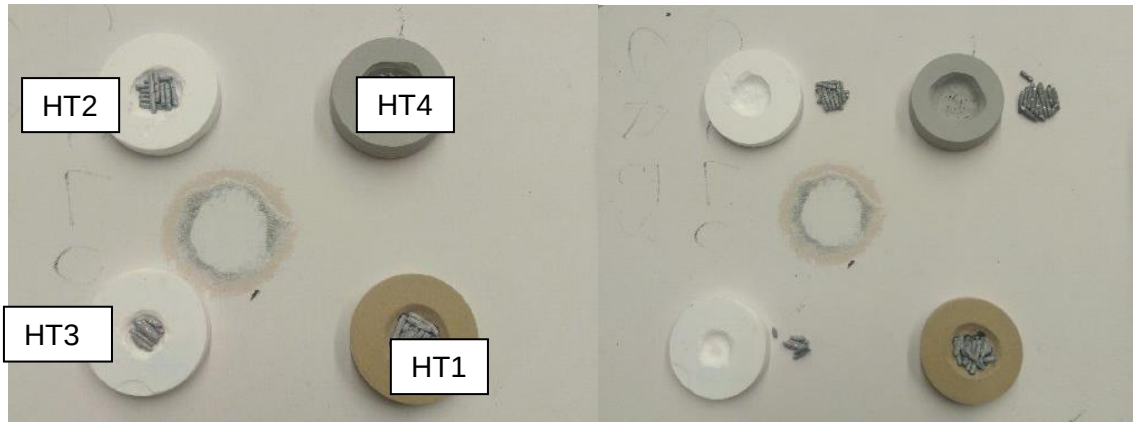
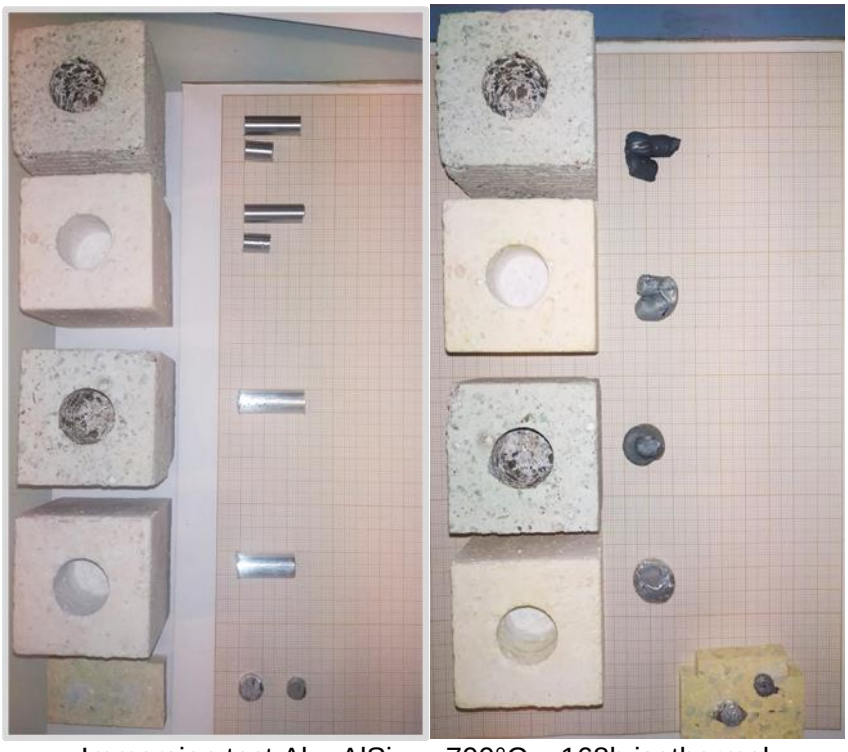


Figure 25 TESS performance: Al alloy-3D refractories preliminary compatibility.

For conventional casted samples, CALD and CEA evaluated thermal stability. On one hand, thermal stability at 800 ºC was studied and compatibility with Al alloys was performed as shown in Figure 26. For doing these tests, a hole was drilled on surface. PCM was inserted and fired at 800 C from 24 h to 168 h. Table 7 shows data for 168 h on the mass lost on the refractories after being in contact with the molten metals.

Initial Mass (g)		Final Mass (g)
$AlSi_{12}$ Alkon Cast	4.77	4.78
$AlSi_{12}$ Alkon Chem	4.82	4.82
Al Alkon Cast	6.00	6.00
Al Alkon Chem	5.17	5.17

Table 7 Refractory stability (standard processing)



Immersion test Al – $AlSi_{12}$ – 700°C – 168h isothermal

Figure 26 Al alloy compatibility

CEA has in addition characterized properties of selected Alkon Cast M90 related to the TESS performance together with CALD.

2.3.2 2.3.2. Density, dilatometry, creep test, mechanical test and microstructural analysis

- *Density*: Density measurements have been performed in the laboratory using a helium gas pycnometer (Accupyc 1340 Micromeritics). The measurements have been performed on ceramics, directly received from CALD. The analysis was performed at room temperature revealing the value of 3.57 g/cm^3. In addition to the density analysis prefired on raw ceramic, it is highlighted on the technical data of the refractory that the bulk density after firing at 800°C is 3.03 g/cm^3.
- *Dilatometry:* Figure 27 shows the displacement in percentage for the refractory brick ALKON CAST MT 90, which has been prefired at 600°C for 5 hours. The coefficient of thermal expansion is expressed in the order of 8.10^{-6}/°C, therefore the calculation for the first cycle is CTE (50-850°C) 8.20 10^{-6}/°C, CTE (150-850°C) 6.78 10^{-6}/°C and CTE (150-1000°C) 6.06 10^{-6}/°C.. Furthermore, for a second cycle it was noted the values CTE (50-850°C) 8.20 10- 6/°C, CTE (150-850°C) 7.44 10-6/°C and CTE (150-1000°C) 7.59 10-6/°C. However, based on data received from WP4, UGENT, the values noted for the CTE is 9.2 10- 6/°C. Based on the technical data of the ceramic ALKON CAST MT 90, the reversible thermal expansion after firing (20-1000°C) is 0.88%.

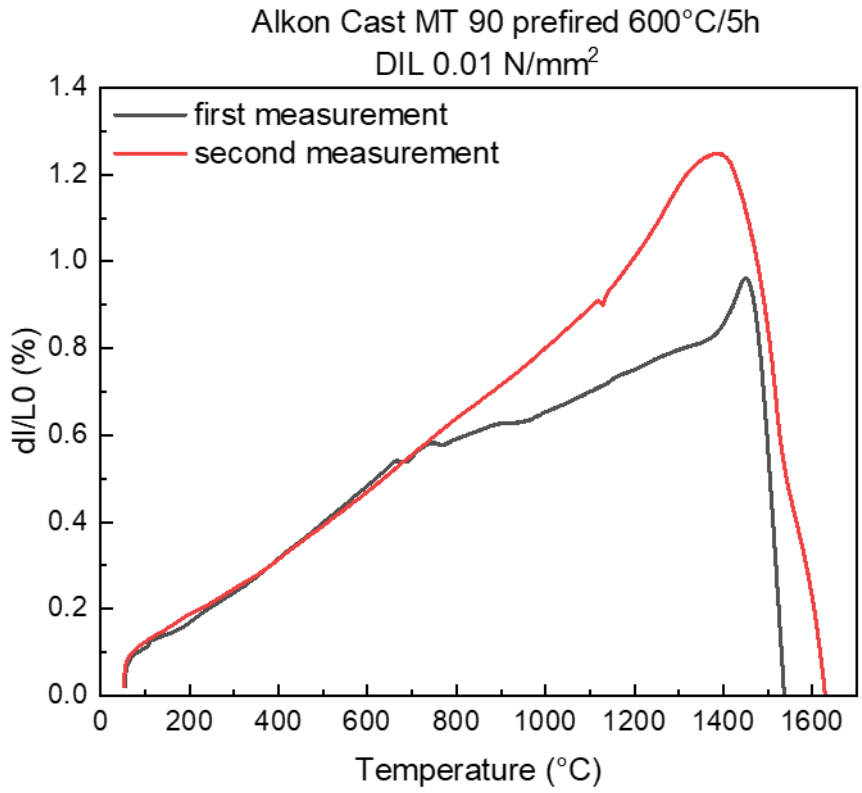


Figure 27Dilatometry data obtained on Alkon CAST MT 90, ceramic prefired at 600°C for 5 hours.

- *Creep Test:* Creep test have been performed by CALD, on a 48.8 mm sample, at the temperature 850°C, for 50h. The ceramic has been prefired before at 600°C. In Figure 28 is observed the creep graphic, where it was noted that the aspect of the curve is a bit unusual. One of the reasons might

be due to a transient plastic phase with evolution of the plasticity with time, mainly due to crystallography evolution.

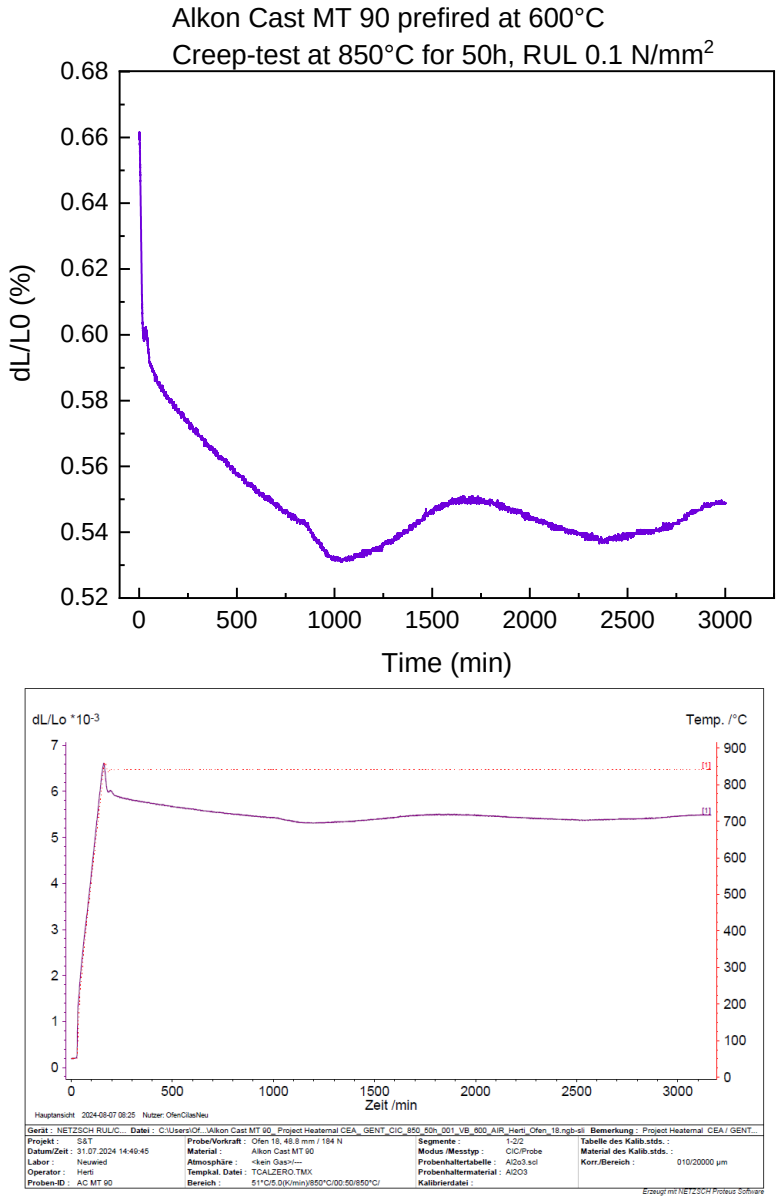
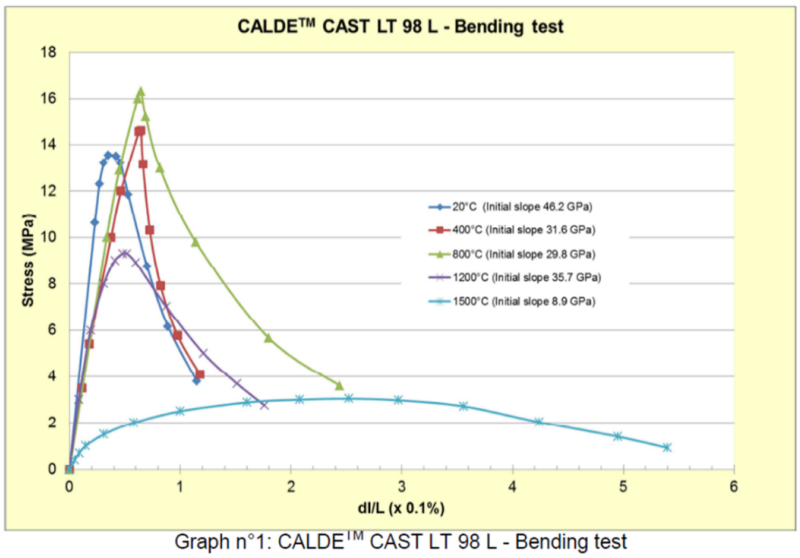


Figure 28 Creep test at high temperature, performed on ALKON CAST MT 90.

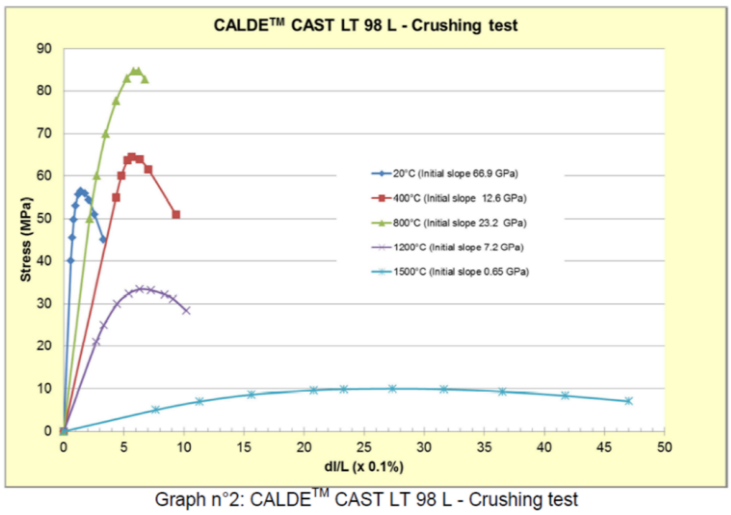
- *Mechanical tests:* Mechanical test are still underway. Calderys provided some mechanical data test that have been made on refractories similar (CALDE CAST LT 98 L) to the refractory used for HEATERNAL prototype. Figures below show the data from CALD for bending and crushing test performed on ceramic CALDETM CAST LT 98L. For the bending test, it can be noted that at 20°C the maximum stress was noted the value ~ 13.5 MPa, for 400°C the value ~14.5 MPa, for 800°C ~16 MPa and for 1200°C ~ 9 MPa. Furthermore, crushing test have been performed as well, at high temperature. The crushing test, the maximum value for 20°C was noted of ~58 MPA, for 400°C

the value of ~ 65 MPa, for 800°C around 85 MPa and for 1200°C was recorded the value of ~35 MPa. In the end, Table 8 Summary data used by UGENT from Calderys data base,shows the data as well as the Young Modulus calculated by UGENT, based on the data received from Calderys.



Graph n°1: CALDE™ CAST LT 98 L - Bending test

Figure 29 *Bending tests made on refractories similar in properties to the refractories Alkon CAST 90 MT, at high temperatures.*



Graph n°2: CALDE™ CAST LT 98 L - Crushing test

Figure 30 *Crushing tests made on refractories similar in properties to the refractories Alkon CAST 90 MT, at high temperatures*

Table 8 Summary data used by UGENT from Calderys data base, for the studied refractory ALKON CAST MT 90, with data summary of mechanical tests (maximum stress) made on CALDETM CAST LT 98L (data received from Calderys).

Analyse	Temperature	Results	Units
Density		3.03	g/cm^3
Thermal expansion		9.2	10^{-6}/°C
Poisson Ratio		0.2	
Young Modulus (as a function of temp)	20°C 400°C 800°C 1200°C 1500°C	42 32.1 27.8 32.9 12.8	GPa vs °C

Data Received from Calderys based on Mechanical Test
Ceramic CALDE™ CAST LT 98L

Analyse	Temperature	Results	Units
Bending Test (maximum stress)	20°C 400°C 800°C 1200°C	~ 13.5 ~ 14.5 ~ 16 ~ 9	MPa
Crushing Test (maximum stress)	20°C 400°C 800°C 1200°C	~ 58 ~ 65 ~ 85 ~ 35	MPa

Table 8 Summary data used by UGENT from Calderys data base,

- *Microstructure Analysis*: SEM imagery (LÉO 1530 VP Gemini, Elektronenmikroskopie GmbH) made possible to observe the microstructure of alloys (Figure 31), on thick polished sections. The acquisition of spectra (EDX) was made by using an acceleration voltage from 5kV until 16kV. The standard corrections were calculated using the Esprit 1.9.4 software internal standard.

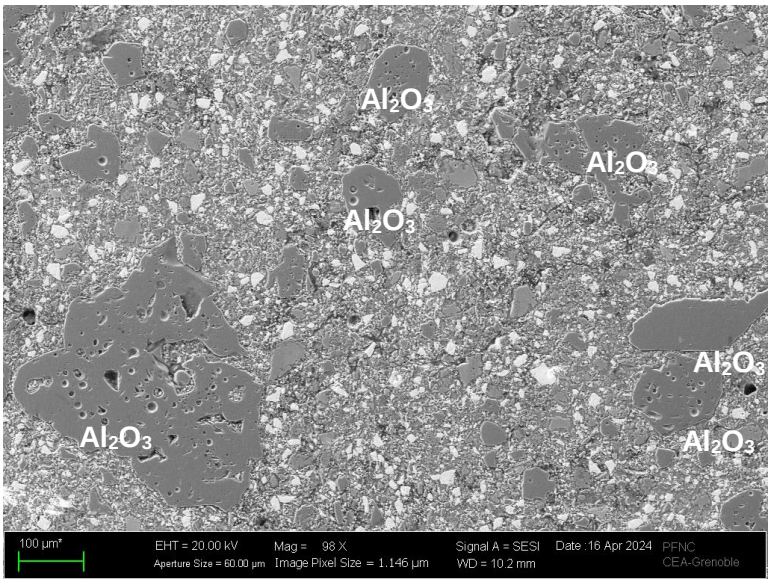


Figure 31 BSE SEM images showing alumina (Al2O3) inclusions on ALKON CATS MT 90 ceramic

Due to SEM–EDX, the values obtained from the bulk section were expressed weight percentages, choosing the average value of the spectra (Table 9).

Chemical analysis	Average values (wt%)
Al	30.91
Ba	14.17
Ca	8.97
Si	0.97
O	44.98

Table 9 Average chemical composition (wt.%) of ceramic by SEM–EDX.

The quantification of the chemical composition was obtained from an average of two areas of 0.11 mm^2 .

- *Porosity (CICe)*: Measuring porosity is critical for understanding the material's thermal properties, as it directly influences thermal conductivity and diffusivity. High porosity can result in lower thermal conductivity due to the presence of air-filled voids, which act as thermal insulators. Therefore, accurately determining the porosity is essential for a comprehensive understanding of material performance in thermal applications. Mercury Intrusion Porosimetry (MIP) measurements were carried out at CICe using an Auto Pore IV 9500 porosimeter (Micromeritics Instrument Corporation, Norcross, USA), where the penetrometer was evacuated to a pressure less than 7 Pa, followed by filling with mercury to 190 MPa.

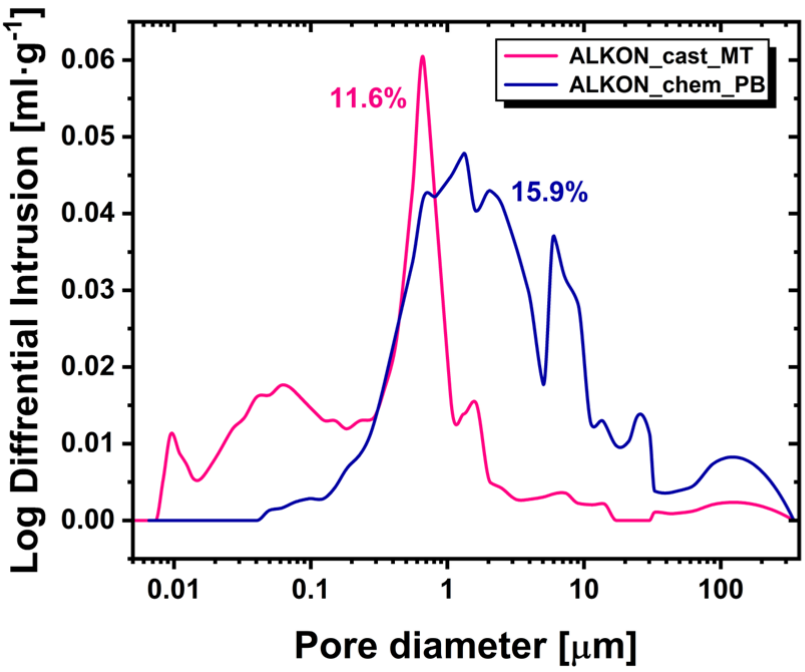


Figure 32: Pore size distribution and total open porosity for the standard refractories.

2.4 Thermal properties

The primary thermal properties of the developed refractories have been thoroughly analysed at CICe. For the formulations designed for 3D printing, thermal conductivity was measured using the hot disk method. In contrast, refractories produced through conventional manufacturing processes underwent comprehensive thermal characterization, including laser flash analysis and differential scanning calorimetry (DSC), to determine thermal diffusivity, thermal conductivity, and specific heat.

2.4.1 Hot disk method (3D printing refractories)

The Hot Disk method, based on the Transient Plane Source (TPS) technique, measures the thermal conductivity of materials by using a thin, double-spiral sensor made of nickel. This sensor is placed between two samples or embedded in the material being tested. When a current is applied, the sensor acts as a heat source and a temperature sensor. As heat flows into the material, the sensor records the temperature rise over time. The rate of temperature increase is related to the material's thermal conductivity and diffusivity. By analysing this transient temperature response, both thermal conductivity and diffusivity can be accurately determined.

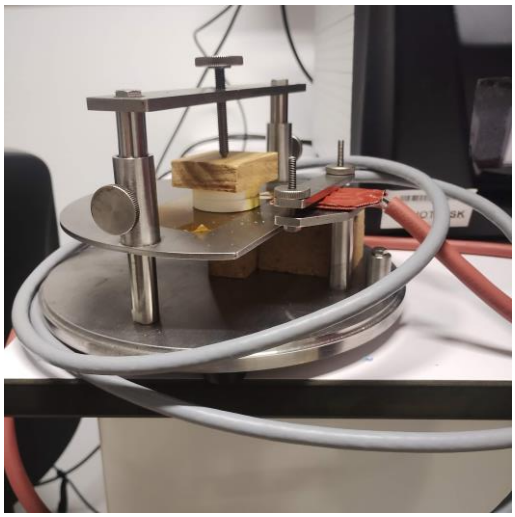


Figure 33:experimental setup- Hot disk

The samples are cylindrical (ca. 36 mm diameter and 6 mm thickness) and considered to be identical. Parameters of the experiments and sensor size were chosen following the guidelines from the norm Hot Disk ISO 22007-2:2015 [Iso 22007-2: Plastics -determination of thermal conductivity and thermal diffusivity - transient plane heat source (hot disc) method (2015)]. A Hot Disk TPS 2500S instrument was thus equipped with a Kapton sensor of 2.001 mm in radius (sensor type 7577 F1) carefully positioned to ensure a flat and smooth contact surface and minimal air gaps.

Despite these precautions, the contact between the sensor and the samples proved to be particularly poor. To overcome this problem, thermal grease was added to mitigate the strong impact of the contact resistance on the experiments and estimated parameters. In addition, a thermocouple (type K) was positioned on the rear face of one of the tested samples to ensure that i) the semi-infinite medium assumption required by the model used for parameter estimation was respected and ii) that the data processed corresponded to the sample being characterized and not to the layer of thermal paste.

Measurements were performed at room temperature (23 °C). The power applied to the sensor was set to between 40-200 mW and applied over 10s. Thermal conductivities were estimated over the time range 2.5-6 s.

The obtained results are summarized in the following tables.

Table 10. Thermal conductivity of HT02

HT-02	*Th.Conductivity*
HT-02_Row1.0.0	7.029 W/mK
HT-02_Row1.1.0	7.369 W/mK
HT-02_Row1.2.0	7.703 W/mK

HT-02_Row1.3.0	8.010 W/mK
HT-02_Row1.4.0	7.069 W/mK
Average	**7.436 W/mK**
Standard Deviation	**0.420 W/mK**

Table 11: Thermal conductivity HT-03

HT-03	*Th.Conductivity*
HT3ab_Row1.9.0	7.660 W/mK
HT3ab_Row1.10.0	7.811 W/mK
HT3ab_Row1.11.0	7.345 W/mK
HT3ab_Row1.12.0	7.035 W/mK
Average	**7.463 W/mK**
Standard Deviation	**0.299 W/mK**

Table 12:_Thermal Conductivity HT-04

HT-04	*Th.Conductivity*
TestKyran_Row1.8.0	1.358 W/mK
TestKyran_Row1.9.0	1.513 W/mK
TestKyran_Row1.10.0	1.089 W/mK
TestKyran_Row1.11.0	1.358 W/mK
TestKyran_Row1.12.0	1.527 W/mK
TestKyran_Row1.13.0	1.590 W/mK
Average	**1.406 W/mK**
Standard Deviation	**0.182 W/mK**

Table 13:Summary of thermal conductivities

Sample	Thermal conductivty(W/mK)	Standard deviation(W/mK)
HT-02	7.436	0.42
HT-03	7.463	0.299
HT-04	1.406	0.182

The results presented in Table 13 to 13 will be used to inform the design of the HEATERNAL system. They are as expected for ceramic refractories as presented above.

2.4.2 Specific heat – Refractory ALKON CHEM PB 85

The specific heat capacity (Cp) was predicted using the FACTSage software, incorporating the following databases: FTmisc, FToxide, FTsalt, FTsulf, and ELEM. Additionally, Cp was experimentally measured using Differential Scanning Calorimetry (DSC) for ALKON CHEM PB 85 see (Figure 36). The combination of software predictions with experimental data provides a robust estimate of the thermal properties of the materials. The compositions of ALKON Cast MT90 and ALKON CHEM PB 85 for FACTsage predictions were determined based on the average values provided in their respective data sheets see

PRODUCT PROPERTIES	STANDARD	AVERAGE VALUES	UNITS
CHEMICAL ANALYSIS			
Al2O3	EN ISO 1927-3	90.0	%
BaO	EN ISO 1927-3	6.5	%
CaO	EN ISO 1927-3	2.9	%
SiO2	EN ISO 1927-3	0.2	%
Fe2O3	EN ISO 1927-3	0.1	%

Figure 34 Alkon cast chemical analysis

PRODUCT PROPERTIES	STANDARD	AVERAGE VALUES	UNITS
CHEMICAL ANALYSIS			
Al2O3	EN ISO 1927-3	85.0	%
P2O5	EN ISO 1927-3	5.4	%
MgO	EN ISO 1927-3	2.9	%
SiO2	EN ISO 1927-3	2.4	%
Fe2O3	EN ISO 1927-3	0.8	%

Figure 35: ALKON CHEM PB85 average composition (data sheet).

The results for ALKON CHEM PB 85 demonstrate the versatility and accuracy of FACTSage in predicting Cp values for ceramic refractories. The FACTsage predictions align with typical Cp values expected for alumina-based ceramics and have been confirmed through experimental measurements (see Figure 36)

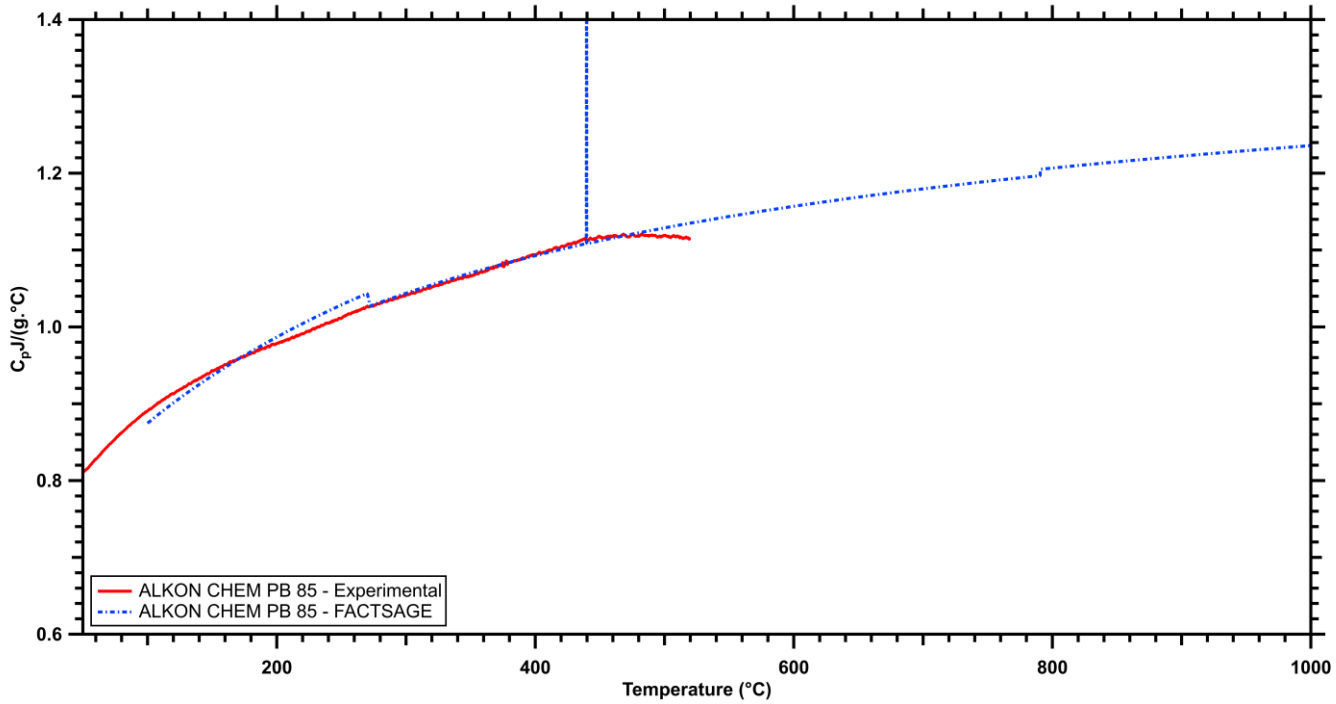


Figure 36:TDSC data (red) and FACTsage predicted values (blue) for the ALKON CHEM PB 85 ceramic.

2.4.3 ALKON CAST MT 90 thermal data

Alkon cast MT 90 was selected based on early compatibility tests where ALKON CAST MT90 shows superior resistance to corrosion. To analyse the thermal properties a combination of techniques has been included for comparison.

- Laser Flash Apparatus (LFA)

The thermal diffusivity of the studied materials was obtained by using the Laser Flash Apparatus (LFA) method], using a LFA-457 from NETZSCH. Square samples with a side length of 10 mm and a thickness of 2 mm were used. In order to minimize the experimental error, a graphite film prime was added over the samples and the reference surfaces.

The points in blue were extrapolated using a linear approximation Figure 37.

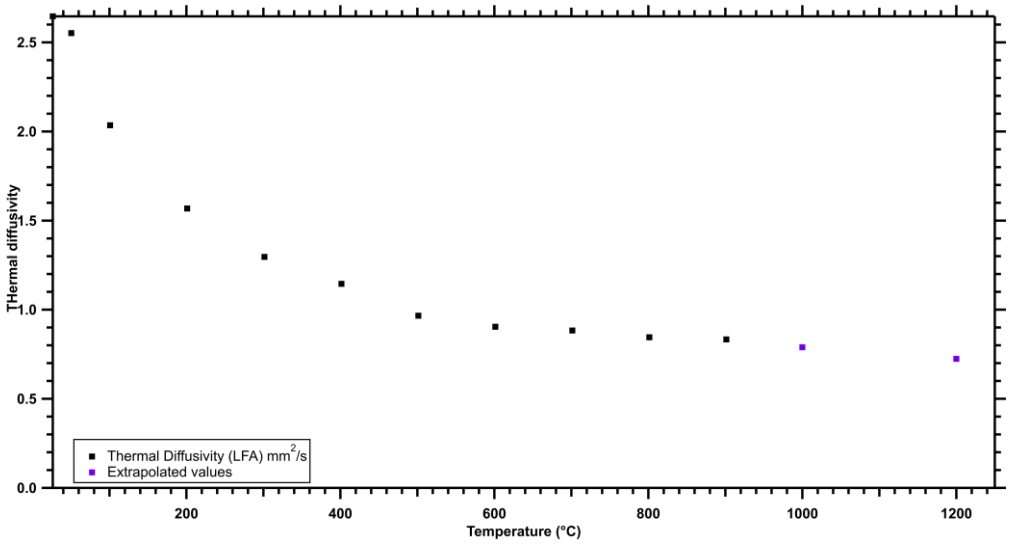


Figure 37:Thermal diffusivity results directly measured from LFA technique, the points in blue were extrapolated using a linear approximation based on values 700 °C - 900 °C.

The thermal conductivity (λ) values can be obtained in indirect way from the thermal diffusivity (α), density (ρ) and heat capacity (Cp), according to the following equation:

$$\lambda = \alpha \cdot \rho \cdot C_p. \quad (1)$$

LFA technique was also used for indirect Cp measurement of the samples in the 25 – 1000 °C temperature range. The LFA Cp experimental data were determined by a comparative heat capacity determination method, where the investigated Refractory sample and a reference material (in this case pyroceram ®) were measured subsequently under the same conditions. The heat capacity of the sample was calculated according to the following equation:

$$c_P^{Sample} = \frac{T^{Ref}}{T^{Sample}} \bullet \frac{(\rho \bullet l)^{Ref}}{(\rho \bullet l)^{Sample}} \bullet c_P^{Ref}, \quad (2)$$

Where (T) is the temperature and (l) is the thickness of the Refractory and (ρ) is the density of the reference sample.

The experimental error of this technique is typically below 5%.

However, due to the large, estimated grain size and inhomogeneity of ALKON CAST MT 90 the error is expected to be closer to 10-15%. For this reason, different methods to calculate the Cp were utilised and included for comparison (Figure 38.)

1. Factsage Results (black): These are calculated as described above.
2. Specific heat calc (green): The Cp was measured directly by using a sample of pyro ceramic with a known density and thickness using the following formula (2).
3. Specific heat calc from given thermal conductivity(red): This uses the values from the provided data sheet .with the measured diffusivity and density using equation (1)

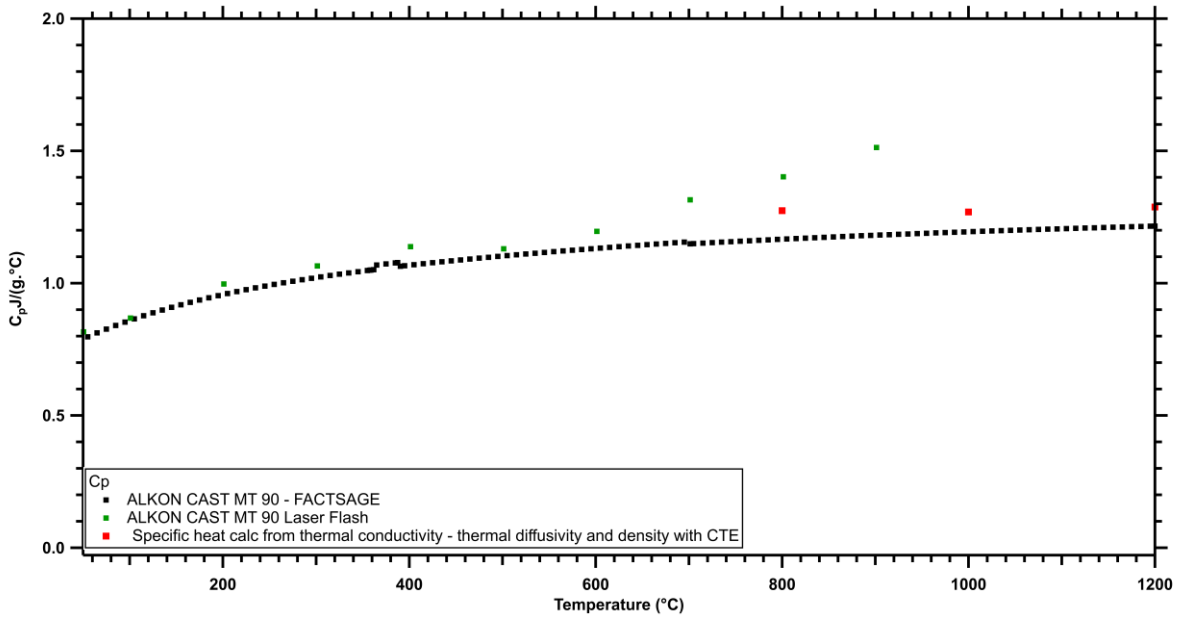


Figure 38:Specific heat values from FACTSAGE predictions (black) laser flash direct Cp measurement(green) and a calculation using the data sheets thermal conductivities(red).

The thermal conductivity values were calculated using the eq. (1) with FACTSAGE Cp values (purple), those calculated from the LFA indirect Cp measuring method (black) and finally the 3 points from the provided data sheet.

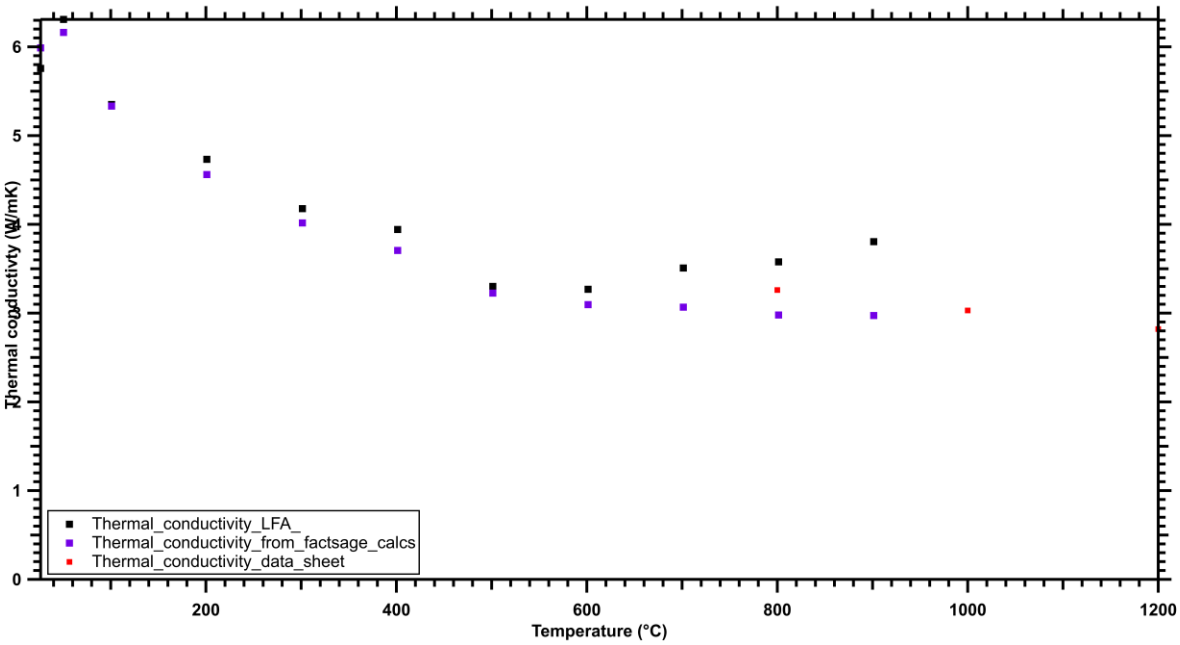


Figure 39: Thermal conductivity measurements using direct measurements from the LFA (black), provided measurements on the data sheet (red) and calculated from the FACTsage calculations (purple)

Example of the specific heat calculations used.

$$C_p = \frac{\lambda}{\alpha \cdot \rho}$$

SI units
λ is the thermal conductivity in W/m·K,
α is the thermal diffusivity in m²/s (measured using LFA),
ρ is the density in kg/m³ (adjusted for the CTE at 800 °C).

Data at 800°C:
Thermal conductivity (λ) = 3.26 W/m·K
Thermal diffusivity (α) = 0.845 mm²/s = 0.845×10 $^{-6}$ m²/s
Density (ρ) = 3028.94 kg/m³ include CTE on 3.03 g/cm³

Cp $_{(800C)}$= 3.26 / (0.845 x 10^{-6} x 3028.94) = 1274 J/kg = 1.274 J/g

3. Conclusions

Deliverable 3.3 provides summary of ceramic compositions compatible with the TESS concept of HEATERNAL. Alkon Cast MT90 and proper design has been chosen for the TESS prototype. For 3D systems, within ceramic like approach composition HT03 -HT05 has been developed, while for full ceramic type, compositions like HT05, HT07, HT04 are available. The achieved compositions allow to achieve OBJ#1 “Maximize thermal performance of TS unit” by providing on one hand ceramic compositions for 3D stable above 900 ºC and a ceramic refractory solution based on bricks. The gathered data will allow to advance in OBJ#3 “Assurance of economic viability and environmental/sustainable system”.

Based on the tests ceramic compositions were selected, Alkon Cast MT90 for the state of art processing, whereas for 3D printing HT08 was selected to be used for ceramic processing and HT05 for ceramic like.