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ABraytCSPfuture

Air-Brayton Cycle **C**oncentrated **S**olar **P**ower **future** plants via redox oxides-based structured thermo-chemical heat exchangers / thermal boosters

Deliverable D2.4.

Optimized redox oxide powder formulations for model ceramic pieces manufacture

Dissemination Level: Sensitive

WP2 Redox oxide materials powder synthesis and application-specific evaluation

Date: 30.04.2024

https://www.abraytcspfuture.eu/

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Disclaimer

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About the Project

ABraytCSPfuture sets forth an innovative, carbon-neutral way for implementing the highly efficient air-Brayton gas turbine power generation cycles into future air-operated Concentrated Solar Power (CSP) plants. Air-Brayton cycles are used in traditional power plants where, however, involve fossil fuels combustion via pressurized air. *ABraytCSP-future*'s carbon-neutral approach aims at achieving higher solar-to-electricity efficiencies, vital for competitiveness of CSP and non-reachable by either PVs or molten salts and thermal oils, increasing in parallel significantly the plants' storage capability. The project will develop and demonstrate a first-of-its-kind compact, dual-bed thermochemical reactor/heat exchanger unit that will transfer heat from a non-pressurised air stream to a pressurised one, while also operating as a thermal booster, raising the temperature of the pressurized stream to the level required for Brayton cycles. Furthermore, the volumetric solar energy storage density of air-operated CSP plants will be significantly increased by rendering their current sensible-only regenerative storage systems to hybrid sensible-thermochemical storage ones within the same storage volume. Both these functionalities will be materialized by thermochemical reactor/heat exchanger units comprised of non-moving, flow-through porous ceramic structures (honeycombs or foams) based on earth-abundant, cost-efficient, non-toxic oxide materials and exploiting reversible reduction/oxidation reactions of such oxides in direct contact with air, accompanied by significant endothermic/exothermic heat effects. The proposed technology is set forth by an interdisciplinary partnership spanning the entire CSP value chain, comprised of leading research centres, universities, innovative SMEs and large enterprises, including ancillary services providers and technology end-users.

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Centre for Research & Technology Hellas, **CERTH**	EL	
University of Twente, **UT**	NL	
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This deliverable is part of a project that has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement no 101084569.

Executive Summary

The present document constitutes Deliverable D2.4 "Optimized redox oxide powder formulations for model ceramic pieces" developed within WP2 of the HORIZON EUROPE 2020 ABraytCSPfuture project, according to the project's progress at the time of its submission (M18). The document provides the final shortlist with compositions selected for the manufacture of model structured pieces (i.e. foams and extruded honeycombs) in WP3. The choice is based on optimal combination of properties determined through experiments with powders. The expected outcome is the identification of at least one composition of earth-abundant materials with suitable properties.

The deliverable takes into account the results of Tasks 2.3 (*Evaluation of synthesized powders with respect to long-term cyclic pressurized operation*) and preliminary findings from 7.1 (*Life Cycle Analysis and recyclability potential*). It also relates to the experimental work reported in deliverables D2.2 and D2.3 and to an extent to the computational work reported in D2.1. The materials of choice, 7 in total including 5 redox ones and 2 suitable for sensible heat storage only, are listed and their main characteristics of interest are summarized. Additional physico-chemical characterization studies of the 2 sensible heat storage materials are provided as those were not included in D2.2 and D2.3 that focused on the core aspect of redox thermochemical operation and its hybridization with storable sensible heat in the same redox material. The goal of the deliverable is to document ''*identification of at least one composition* [in powder form] *of earth abundant materials with suitable properties*''. **Based on studies carried out so far, $CaMnO_3$ is a composition meeting all criteria as set by WP2 objectives and project's milestone MS1 (see deliverables D2.2 and D2.3).** Relevant work will continue in order to further shortlist the other 6 compositions, systematically considering from now on also findings of WP3.

With respect to the technical aspects, the work already performed in the project has proceeded according to schedule and the currently available results prove that the milestone targets set up to M18 of the project have been met within the initially foreseen timeframe. Therefore, at least until the submission of the current deliverable, no revisions are needed with respect to the management of the technical part of the project.

Changes with respect to the DoA

An Amendment of the Grant Agreement was initiated on 24.10.2023, requesting the termination of participant OPRA due to its insolvency and inclusion of a new entity, Destinus-Energy the successor of OPRA, as a replacement. As OPRA had no involvement in WP2, the particular change had no effect whatsoever on the timely preparation of the present deliverable and the workplan of WP2.

1. Introduction

Deliverable 2.4 has been produced within the work package *Redox oxide materials powder synthesis and application-specific evaluation* (WP2) and specifically within Task 2.5. "*Evaluation of test campaigns and selection of material compositions*", in which the project partners LET, DLR, CERTH, IWKS and KB are involved. The report provides the final shortlisted material compositions in the framework of Task 2.5 and this is done mainly considering the outcomes of deliverables D2.2 and D2.3. In addition to the redox compositions already characterized, evaluated and selected in the aforementioned deliverables (5 in total), 2 ceramic material compositions from partner KB are also listed and characterized here as additional options. Such materials, constituting residual byproducts from the steel industry, are known to be redox-inactive but their very low cost, high abundance and the fact that they are already used as sensible heat storage medium in KB's heat storage/recovery systems make them excellent candidates for consideration in ABraytCSPfuture project as supplemental/additional contributors to the redox materials for high-temperature, hybrid sensible/thermochemical heat storage concept. A first matrix of small-scale structures currently prepared or to be prepared in the near future in the framework of WP3 activities is also provided here.

Naturally, further shortlisting of material compositions will continue to take place in the framework of both WP2 and WP3 with the aim to identify the optimum one(s) for consideration in the project's lifecycle. In the meantime and as indicated in the present deliverable, there are suitable materials/safe options to interact with other project's either running WPs (WP3, WP4, WP7) or planned to start later (WP5, WP6).

2. Final shortlisted materials

2.1 Physicochemical characterization of KB's materials

The present section relates to selected physico-chemical characteristics of interest with respect to KB's two common materials, which constitute industrial by-products. Their use in ABraytCSPfuture project, in the frame of its hybrid sensible storage/TCS concept is important because it enhances the sustainability and circularity of the technology under development.

With this in mind, these two materials, namely A4 and BM/B as referred to my KB, were studied to further validate their suitability for use in the project. Since both compositions are by-products and may contain a number of different unknown components, their characterization began with SEM/EDS analysis to identify the elements that make up each sample. The SEM images and EDS qualitative results for the two samples are shown in Figure 1 and Figure 2 respectively, while Figure 3 shows a comparative bar chart showing the semi-quantitative results.

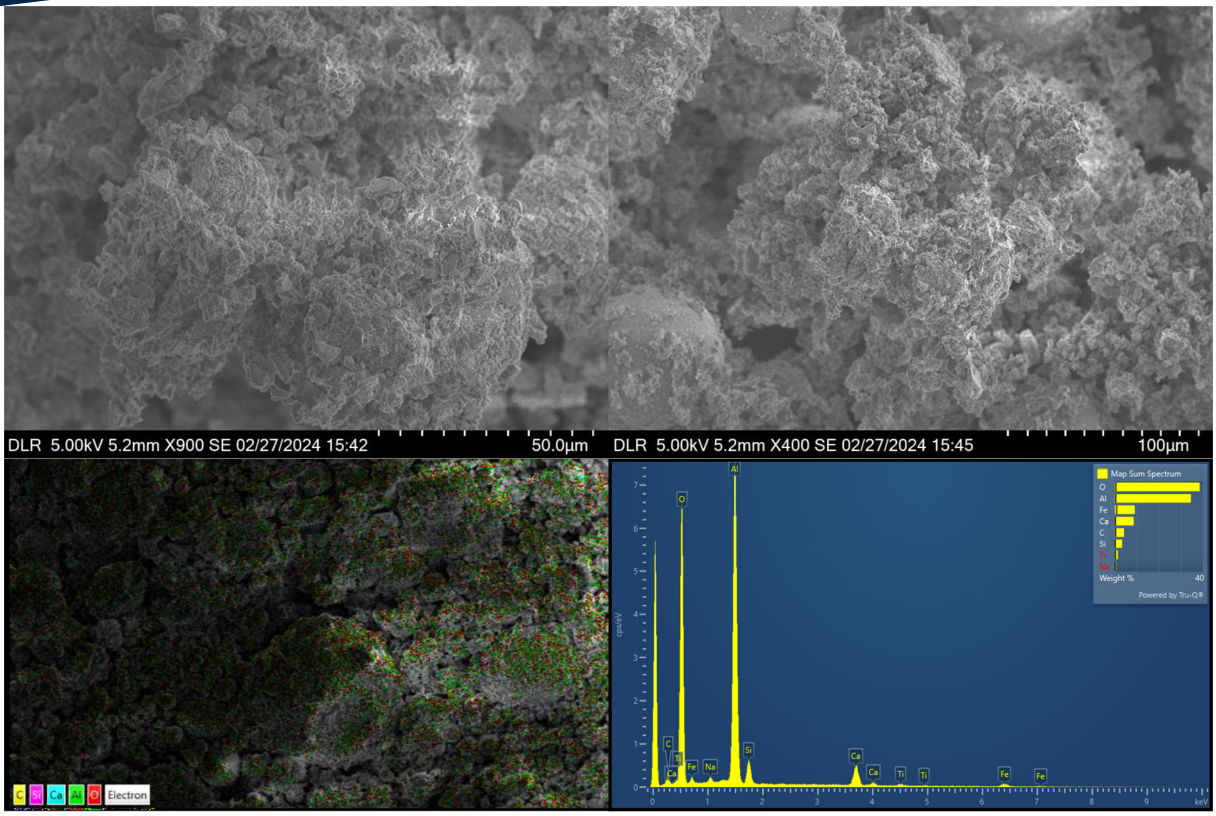

Figure 1: SEM images (top row) at different magnifications and EDS results (bottom row) on the A4 KB sample.

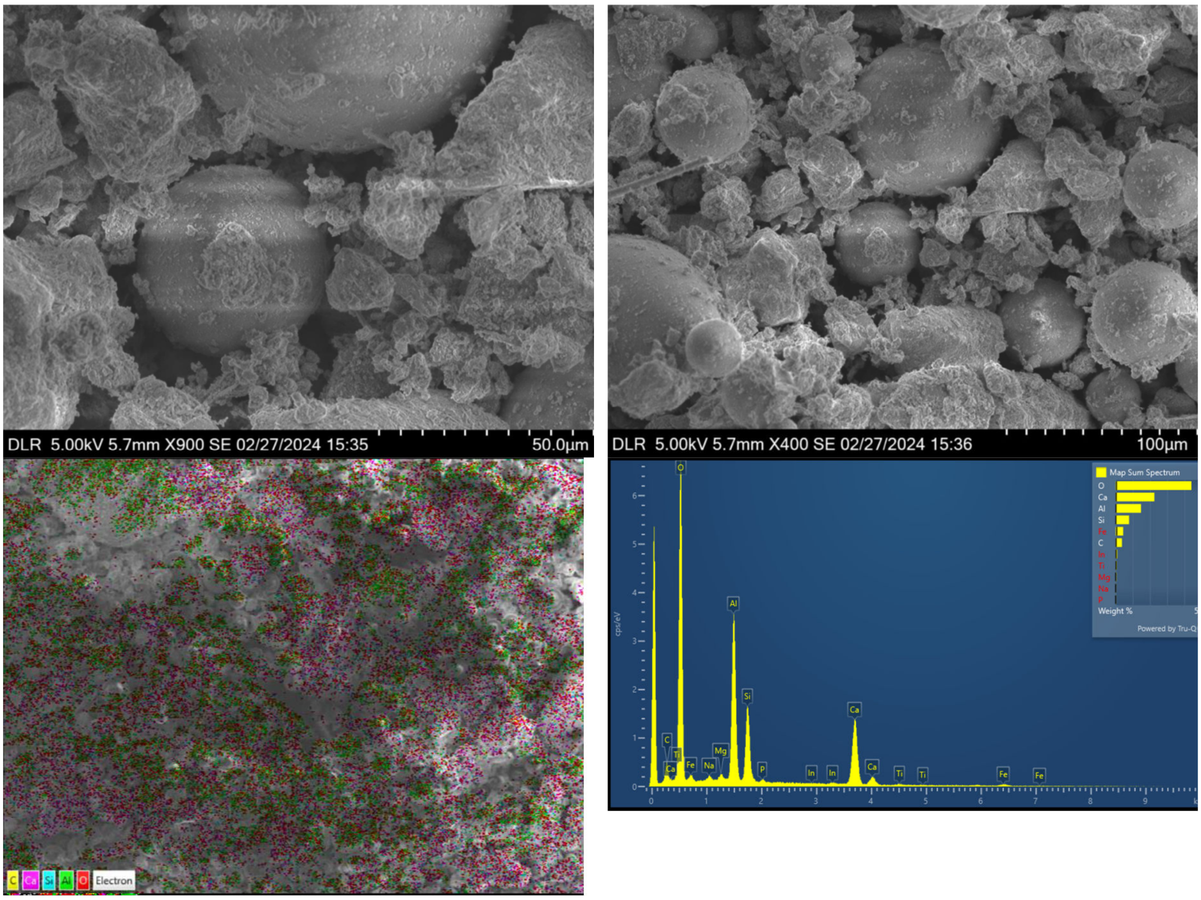

Figure 2: SEM images (top row) at different magnifications and EDS results (bottom row) on the BM/B KB sample.

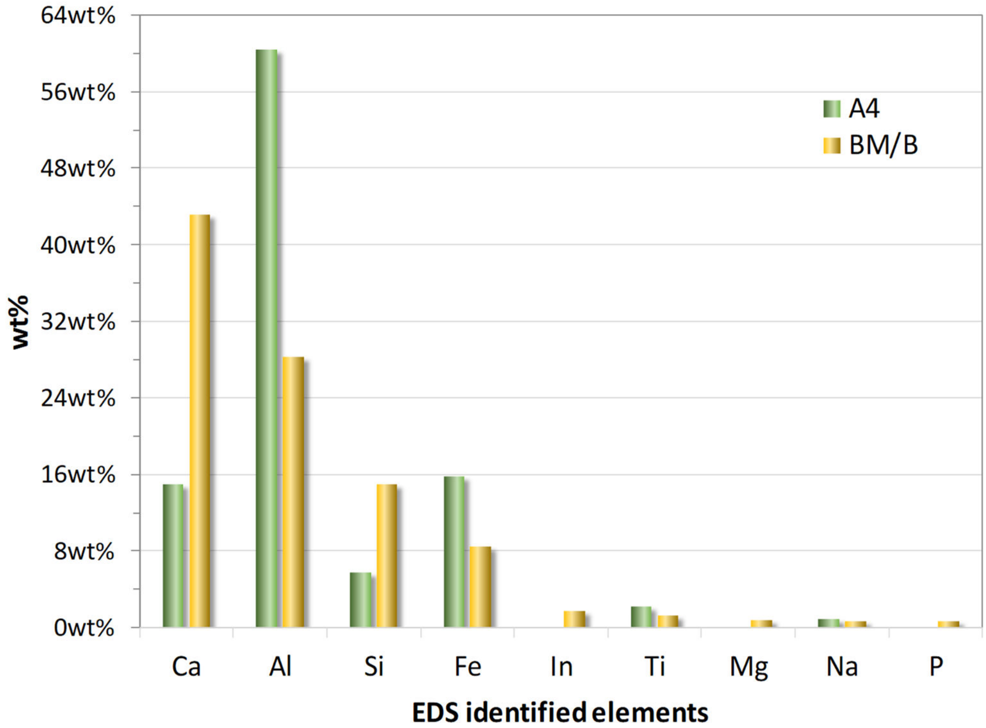

Figure 3: Comparison of EDS semi-quantitative results on samples A4 and BM/B.

SEM/EDS analysis revealed that both samples contain significant (>8 wt% per element case) amounts of Ca, Al, Si and Fe. In lower amounts per element case (<2.3wt%), A4 contains Ti and Na (3.2wt% in total), whereas BM/B contains In, Ti, Mg, Na and P in concentrations <1.8wt% per case (5.2wt% in total). BM/B seems more granulated and with more distinct larger particles while A4 seems quite agglomerated with its grains being substantially smaller.

The elements identified by EDS were considered for phase identification of the samples by XRD. A comparative pattern is shown in Figure 4. Both samples contain significant amounts of calcium hydroxide ($Ca(OH)_2$ / portlandite), as confirmed by the weight losses recorded by thermogravimetric analysis (Figure 5). The TGA profiles obtained from the two samples up to approximately 1000°C are rather similar, with both of them exhibiting two distinct bed weight loss regions: the first (~1.2wt%) at ~450°C that could be attributed to dehydration of $Ca(OH)_2$ and a second one at ~750°C, that could probably be attributed to the initiation of mixed oxides formation (e.g. most probably among the Ca, Al and Fe) accompanied by limited O_2 removal. The continuous weight loss at low temperatures (< 400°C) can be mostly attributed to absorbed humidity, thereby indicating that the materials are quite hydroscopic.

As already indicated by EDS analysis, the pattern of A4 sample appears to be purer, with alumina and hematite being identified by XRD, while in the BM/B samples numerous secondary, mostly mixed, phases are evident.

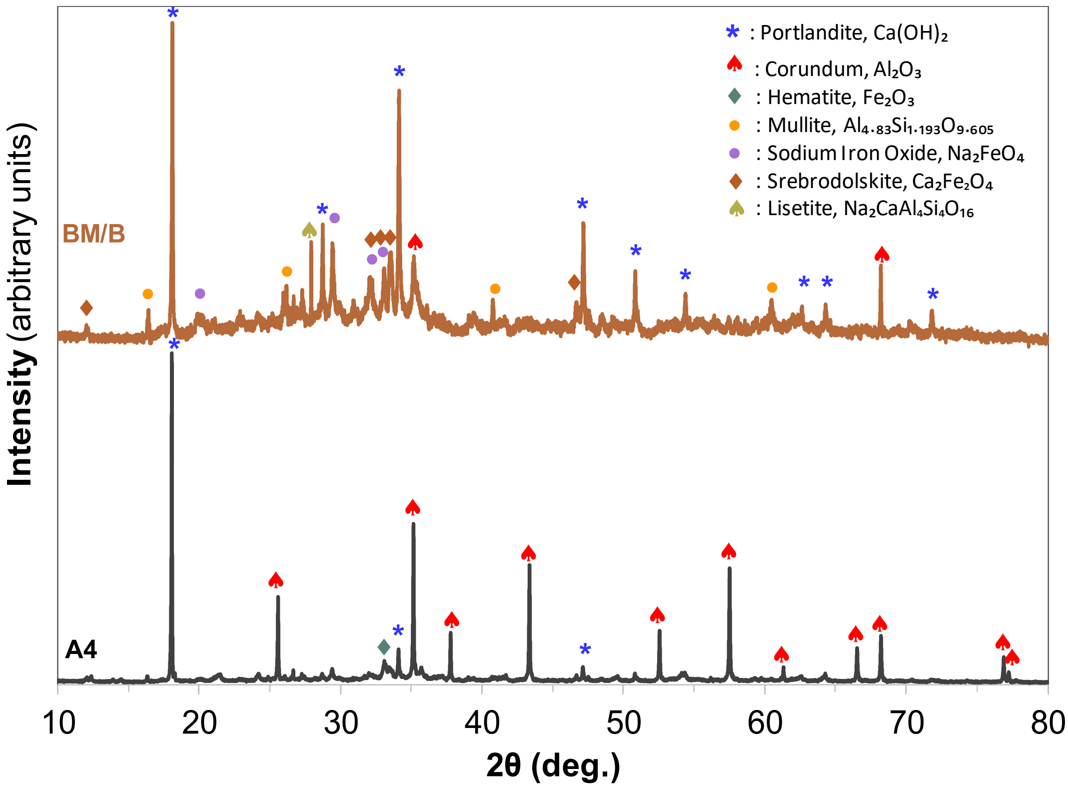

Figure 4: Comparison of phases identified by XRD analysis.

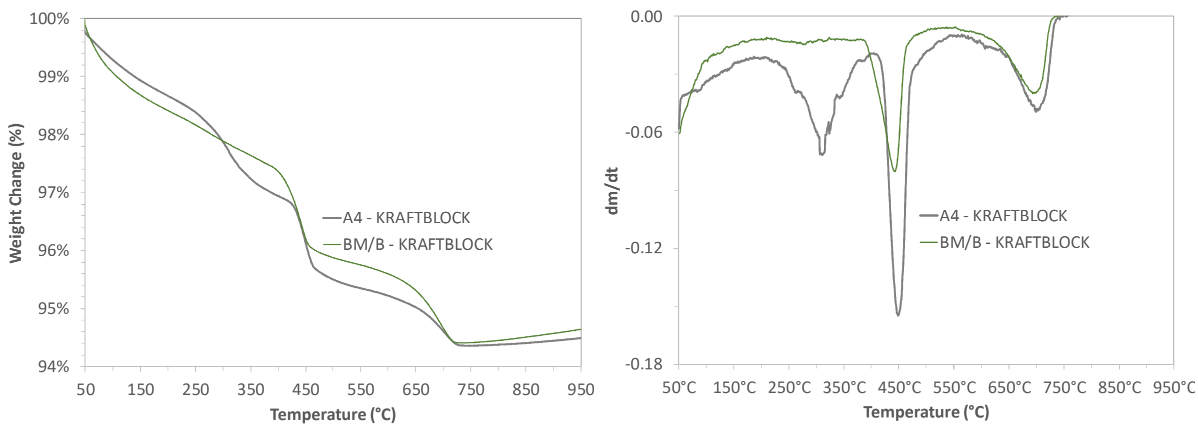

Figure 5: Comparison of weight loss recorded via thermogravimetric analysis. Left: wt% weight loss and right weight loss rate as a function of temperature.

2.2 Overview of materials of choice

The Table 1 below provides an informative overview of the 7 powder compositions shortlisted so far and their main attributes of interest that have been either determined within WP2 via relevant already completed work or planned to be identified after submission of this deliverable. All 7 of them have been fed to WP3 for consideration; i.e. tests on their shaping into structures suitability, redox/ thermochemical/ thermomechanical/ physicochemical evaluation and characterization etc. Calcium manganite ($CaMnO_3$) and certain Sr-doped compositions derived from it are the primary materials of choice at the time of preparation of this deliverable (M18).

Composition	Non-stoichiometry parameter (δ)	Cyclability (5 cycles) / long-term cycling (> 500 cycles)	Measured energy density (J/g)	Heat Capacity (J/g/K)	Comments on potential important aspects for consideration in the project
$CaMnO_3$ (redox)	**up to 0.19**	**Excellent / Excellent**	**up to 137**	**1.21**	**1. Prone to substantial sintering upon calcination > 1100°C 2. Orthorhombic to cubic phase transformation may induce lattice distortions → low thermomechanical stability of WP3 structures**
$Ca_{0.95}Sr_{0.05}MnO_3$ (redox)	up to 0.20	Excellent / not measured yet	up to 108	**1.27**	1. Prone to substantial sintering upon calcination > 1100°C 2. Orthorhombic to cubic phase transformation is substantially mitigated due to Sr-doping → improved thermomechanical stability of WP3 structures
$Ca_{0.90}Sr_{0.10}MnO_3$ (redox)	up to 0.19	Excellent / not measured yet	up to 99	Not measured yet	1. Prone to substantial sintering upon calcination > 1100°C 2. Orthorhombic to cubic phase transformation is essentially non-existent due to Sr-doping → improved thermomechanical stability of WP3 structures

$Ca_{0.75}Sr_{0.25}MnO_3$ (redox)	up to 0.22	Excellent / Not measured	up to 99	Not measured yet	1. Prone to substantial sintering upon calcination > 1100°C 2. No orthorhombic to cubic phase transformation due to high Sr-doping → substantially improved thermomechanical stability of WP3 structures
$SrFeO_3$ (redox)	up to 0.24	Excellent / not measured	up to 35	Not measured yet	1. Profound sintering upon calcination > 1100°C 2. No orthorhombic to cubic phase transformation
KB – A4 (non-redox)	Not applicable	Not applicable – material is very stable up to 1250°C	Not measured yet – sensible only	Not measured yet	1. Not prone to any sintering up to 1250°C as opposed to all perovskites/ 5 redox compositions above. 2. Challenges in materials pre-processing (difficult to mill/sieve) → potential difficulties in extrusion of "delicate" structures
KB – BM/B (non-redox)	Not applicable	Not applicable – material is very stable up to at least 1250°C	Not measured yet – sensible only	Not measured yet	

Table 1: Overview of 7 compositions shortlisted so far and their main attributes. These materials are qualified for further experimental consideration in WP2 and WP3.

Based on the Table above, the following conclusions can be drawn:

- $CaMnO_3$ is an excellent composition as it combines the highest thermochemical energy density among the 5 redox ones with high heat capacity and its cyclability in the course of > 500 cycles has already been assessed as excellent (see D2.3). An expected challenge relates to its phase transformation from orthorhombic to cubic (see D2.2) when the operating temperature range of 300-1100°C is considered. This may be proven detrimental to the thermomechanical stability of structured bodies because phase transformations are known to induce lattice stresses that translate to swelling/shrinkage of structures at macroscopic scale (currently under evaluation in WP3).
- Sr-doping mitigates or eliminates this phase transformation and thus improved thermomechanical stability is expected. Sr-doping seems to measurably improve heat capacity and thus sensible heat storage potential. On the other hand, the thermochemical heat storage potential is lower – albeit not detrimentally – cf. $CaMnO_3$.
- All perovskites are prone to substantial sintering upon calcination. This is expected to facilitate robustness of structured sintered bodies (WP3) but may pose a challenge to performance due to deactivation of the material. This was not the case for $CaMnO_3$ (see D2.3) and Sr-doped derivatives are also expected to exhibit a similar behavior.
- $SrFeO_3$ exhibits the highest δ value among the 5 qualified redox compositions but its energy density is very low. It currently seems the least promising for TCS but it is worth being studied because useful results in terms of other more suitable applications (e.g. N_2/O_2 separation) may be produced. Moreover, and prior to any potential elimination, its Cp value must be measured to assess its sensible heat storage potential.
- KB's materials are to be tested as sensible heat storage media only. They constitute thermally stable compositions and their further consideration in the project will be largely defined by their ''shapeability'' into structures and the value of their heat capacity (to be measured).

Until submission if this deliverable (M18), quantities of 0.2 – 2 kg from $CaMnO_3$, $Ca_{0.95}Sr_{0.05}MnO_3$ and $Ca_{0.90}Sr_{0.10}MnO_3$ had been synthesized successfully and used for the preparation of several shaped structures needed for properties measurements by CERTH, DLR and with the aid of LET's consultation as reported in brief in the WP3 section of 1st periodic report (due M18). Further details will be provided in future deliverables D3.1, D3.2 and D3.3, all due in M27.

3. Overview of structures already and/or to be prepared in WP2 and WP3

The Table 2 below is a summary of existing capabilities of CERTH, DLR and LET to produce structured bodies, primarily for use in WP3 studies but also to determine key thermophysical properties of the shortlisted compositions. Some of these, as indicated in the Table, have already been used successfully by M18 (see WP3 section of the technical report of the 1st reporting period/RP1). Typical examples of such structures are shown in Figure 6.

Description of structure	Main geometry characteristics	Partner / status	Usage in the project
Small scale honeycombs – 90 cpsi	Monolithic cylindrical honeycomb with 90 cells per square inch (cpsi), ∅ 24 – 30mm and 25 mm in length	CERTH / already employed successfully (see WP3 section of RP1 technical report)	Extrusion feasibility assessment, use for thermal/thermochemical tests in WP3 & mechanical robustness assessment.
Small scale honeycombs – 44 cpsi	Monolithic cylindrical honeycomb with 44 cells per square inch (cpsi), ∅ 24 – 30mm and 25 mm in length		
Mini-scale foams	Monolithic cylindrical foams of 20, 30 pores per linear inch (ppi) ∅ ≤10 mm, L < 15 mm	DLR / already employed successfully (see WP2 section of RP1 technical report)	TGA test-scale level, use for thermal/thermochemical tests in WP2 (ongoing).
Small-scale-foams	Monolithic cylindrical foams, 10, 20, 30, 60 ppi ∅ ≤25 mm, L < 30 mm 36 ≤ ∅ ≤ 38 mm, L 42 mm		Tubular furnace and compressive strength test-scale level, use for mechanical robustness assessment in WP2.
Medium-scale foams	Ø ≤ 80 mm X L ≤ 100 mm with center hole		First feasibility assessment of scaled-up PU templating process, thermochemical storage test rig scale level, to be used by M20 in WP3
Medium-scale honeycombs	Ø ≤ 80 mm X L ≤ 100 mm (tentatively)	LET – to be prepared	First feasibility assessment of scaled-up extrusion, thermochemical storage test rig-scale level, to be used by M20 in WP3.

Table 2: Overview of structures already and/or to be prepared for WP3 with final shortlisted powders input (see Table 1) from WP2.

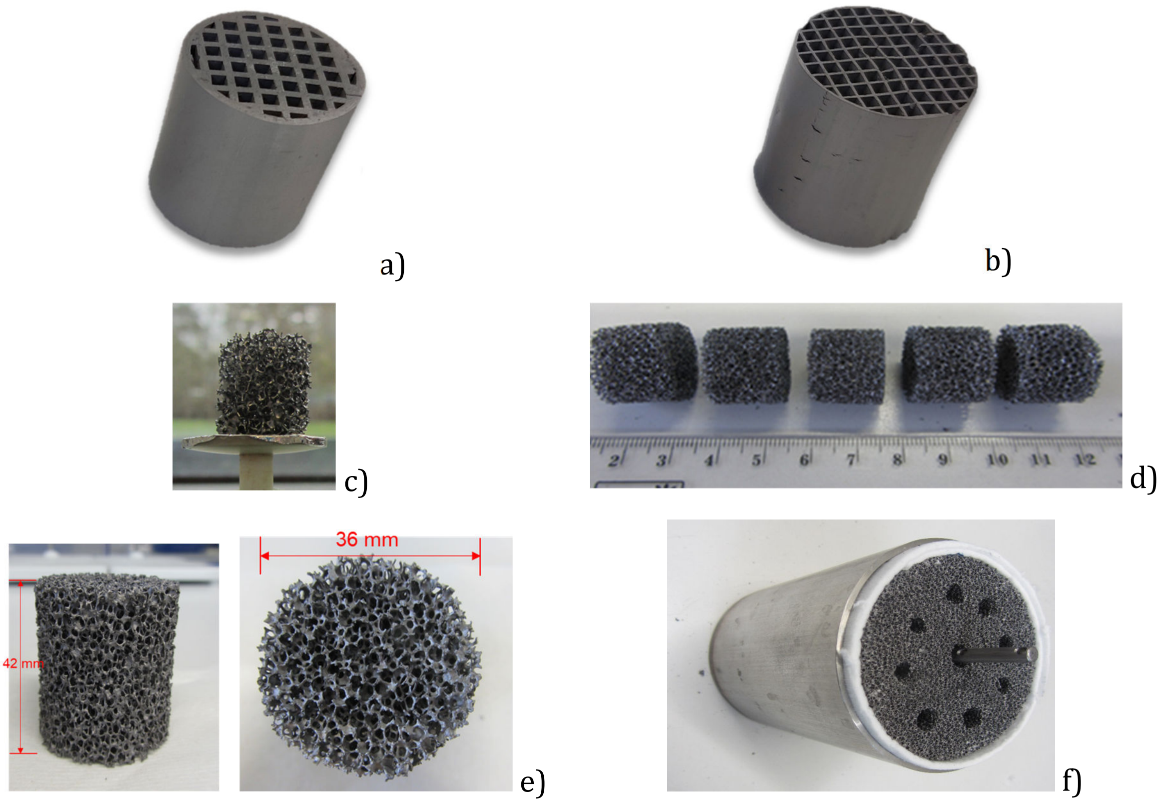

Figure 6: Typical examples of (a) and (b) $CaMnO_3$ honeycombs extruded by CERTH at 44 and 90 cpsi respectively; (c)-(f) $CaMnO_3$ 10-60 ppi foams prepared by DLR at various scales as per the needs of testing devices: c) for TGA, d) for tubular furnaces, e) for crushing strength tests, f) for future thermochemical tests in committed test rig (all dimensions as per Table 2).

4. Conclusions

Until submission of the present deliverable, 7 compositions have been shortlisted with 5 of them being redox-active and with validated TCS potential (see D2.2 and D2.3) and 2 of them being suitable for up to very high temperature (at least up to 1250°C) sensible heat storage only. The latter are considered as supplemental low-cost materials for the optimised hybrid sensible/TCS concept of the project.

All of them are based on abundant, cost-effective and non-toxic materials. Further shortlisting is underway and will be based on combined WP2 and WP3 experimental campaigns from now on. These will include application-specific evaluation of the materials in structured form and measurement of key properties like heat capacity, thermal conductivity, thermochemical energy storage/release potential, cyclability in the course of several tens to hundreds of cycles and thermomechanical stability of the structures in question.

A wide variety of structures and geometries per structure (honeycombs, foams, pellets, bars) are possible and will be considered for the most promising and readily available in the required quantities per case materials.