INNOSTORAGE – USE OF INNOVATIVE THERMAL ENERGY STORAGE FOR MARKED ENERGY SAVINGS AND SIGNIFICANT LOWERING CO_2 EMISSIONS

Beneficiaries:

UNIVERSITAT DE BARCELONA

Universitat de Lleida

UNIVERSITÉ DE LYON

Ben-Gurion University of the Negev

Partners:

THE UNIVERSITY OF AUCKLAND NEW ZEALAND Te Whare Wananga o Tamaki Makaurau

University of South Australia

AUBURN UNIVERSITY

D7.2 - Report on Staff Exchanges

	Name and Institution	Date
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Contents

1 Objectives

The present secondment is included in

Workpackage 1: Material development and characterisation. The main objectives of this workpackage are:

- Develop new materials to be used in thermal energy storage
- Look for possible existing materials to be used in thermal energy storage, especially low cost materials, including wastes and by-products
- Characterise the newly developed materials or the newly considered materials
- Compare and contrast characterisation procedures for testing of thermal energy storage materials

Workpackage 3: Industrial applications. The main objectives are:

- Use of TES for refrigeration applications
- Use of TES for solar cooling, CSP and other high temperature applications
- Waste heat recovery and reuse through TES

Specifically, this secondment is involved in the following tasks:

- Task 1.1: Staff exchanges
- Task 1.2: New materials
  - Develop new materials to be used in TES
  - Look for possible existing materials to be used in thermal energy storage, especially low cost materials, including wastes and by-products
  - Develop a data base for materials to be used in TES
- Task 3.1: Staff exchanges
- Task 3.2: Advanced TES for refrigeration applications
  - System design
  - System testing at pilot plant scale

Thus, the objectives of the secondment were:

- To set up the experimental procedure to characterize the corrosion resistance of materials for containers of molten salts, especially carbonate based mixtures.
- To develop a data base for the selection of materials for high temperature latent heat thermal storage and for the design of advanced TES for refrigeration applications.
- To stablish the best compositions of carbonate mixtures to work at high temperatures as thermal energy storage systems.

2 Introduction

Lots of efforts have been devoted to the characterization of thermal properties of the different types of systems to be used as thermal energy storage (TES) media, but scarce literature exists concerning the materials to manufacture the tanks that will be used to contain these systems. One of the main concerns when selecting the most suitable material for these tanks is its resistance to corrosion due to molten salts that constitute the TES system. Another important issue is the cost of these materials.

The aim of this work is to study the material used to contain the latent heat storage (LHS) media. When the plant is going to operate for a long time, it is necessary to foresee the possible changes that may occur over time. The containment material suffers the same thermal cycles as LHS, thus introducing changes in dimensions due to the temperature difference (which is related to its thermal expansion coefficient), or inducing creep (an increase in temperature lowers most of the mechanical properties, so that materials suffer a slow and continuous deformation that ends in failure even at stresses below the yield strength).

On the other hand, if the material used as LHS is highly corrosive, any other one in contact with it will present, sooner or later, corrosion problems. Plant lifecycle not only depends on the stability of the LHS material but also on the lifetime of the rest of materials involved in its construction. So, one of the main interest of this work is to predict the lifetime of the containment materials by studying their interaction with LHS media during their use.

Among all the LHS media, carbonate mixtures have been chosen for this work as they present a good performance at high temperatures. Although there is some data about these systems already used as energy storage media in CSP plants [1], scarce information about their behavior when used as TES can be found in bibliography [2], and much less about their interaction with potential materials for containers tanks.

In this work, the chemicals used for TES media are of commercial purity. Therefore, apart from a lower cost than analytical grade chemicals (or pure), they are more affordable and more easily attainable for their implementation in CSP. Nevertheless, they can present small amounts of impurities that could affect not only the thermal properties of the carbonate mixture (melting point, latent heat) but also the interaction with the containment material. Other studies about corrosion in steel concluded that the impurities typically contained in commercial grades of alkali nitrates have relatively small effects on corrosion of stainless and carbon steels in molten salts prepared from these constituents [3], but no references have been found concerning molten carbonates.

The corrosion of different stainless steels (ferritic and austenitic) has already been studied in ternary molten Li_2CO_3-Na_2CO_3-K_2CO_3 (43.5:31.5:25.0 mol%) mixture at different temperatures (475-550°C), using galvanostatic polarization and cyclic voltammetry [4], indicating that the corrosion resistance of the austenitic stainless steel is higher than that of the ferritic steel. The scales formed on austenitic steels were found to be multilayered, whereas those formed on ferritic steels consisted of a single uniform layer. Nevertheless, their interaction with other carbonate mixtures has not been found, as well as their behavior under thermal cycling conditions.

3 Description of work

Collaboration between both Universities was set up, concerning corrosion tests on materials that can be used for PCM containers. The research group at Universitat de Barcelona has a large experience in the characterization of materials, as well as their behaviour under corrosion atmospheres. Thus, an experimental procedure was set up at UniSA to proceed with corrosion tests. On the other hand, the research group at UB has also a great knowledge about selection of materials, and thus can bring all their experience to solve the problems of selection of materials in the everyday life of the host group.

Secondly, the experience of Unisa in the thermal transfer issues can help UB team to better understand the role of materials in thermal energy storage systems.

4 Materials and Methodology

Different stainless steels (316 and 304 SS) were used as samples to be immersed in different mixtures of carbonate salts. Three different mixtures of Li_2CO_3-Na_2CO_3-K_2CO_3 were used, selected from the phase diagram in which the eutectic compositions can be found, which is shown in next figure.

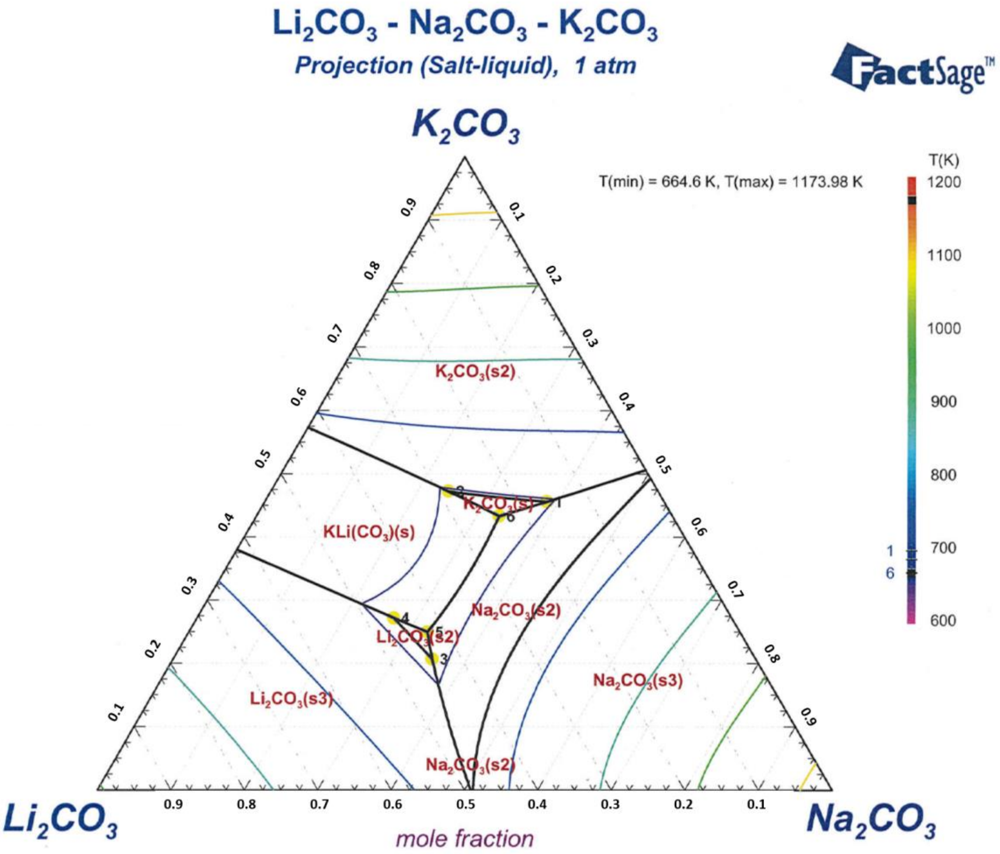

Figure 1.- Phase diagram salt-liquid projection, obtained with **FactSage**© - Phase Diagram module, for the Li_2CO_3-Na_2CO_3-K_2CO_3 system at atmospheric pressure.

Three compositions of this system have been used in the present work, one of them presenting the lowest melting temperature among all the possible mixtures, which corresponds to point 6 in Figure 1, another with the highest melting point and the lowest amount of lithium carbonate (point 1 in Figure 1), and the third being an intermediate of both (point 4 in Figure 1). The compositions of the three mixtures are shown in next table.

Table 1. Composition of molten salts.

Mixture name	Intersection point in phase diagram	Molar fraction			wt%			T_m (°C)
		Li_2CO_3	Na_2CO_3	K_2CO_3	Li_2CO_3	Na_2CO_3	K_2CO_3	
PCM1	1	0.15966	0.38437	0.45597	10.2	35.3	54.5	421.9
PCM2	6	0.23597	0.33074	0.43328	15.5	31.2	53.3	391.5
PCM3	4	0.46039	0.26790	0,27171	34.0	28.4	37.6	410.0

Metallic samples were cut, polished and cleaned before being immersed in different alumina crucibles containing each of the three carbonate mixtures. One sample of each steel was kept as reference for comparison with its correspondent corroded samples. The temperature of the furnace was increased up to 580°C and maintained for different exposure times: 24h (1 day), 48h (2 days), 168h (7 days), 360h (15 days), 600h (25 days) and 1200h (50 days). An extra alumina crucible contained a thermocouple to ensure that all the mixtures achieve the target temperature.

After each experiment, all the samples must be carefully cleaned, dried and weighed in order to obtain the weight gain/loss. Afterwards, each sample is immersed in a Clark solution to remove the oxide layer that could have been formed. With the obtained results, the thickness of oxide scales can be determined and thus the corrosion rate calculated.

When all the experiments are finished, all the obtained metallic samples, as well as a sample of each carbonate mixture, are going to be sent to UB to be characterized by means of Scanning electron microscopy and X-Ray diffraction.

Once this set of experiments is finished, a new series of experiments has been scheduled in which the metallic samples will be also immersed in the different carbonate salt mixtures, and the system will be submitted to thermal cycling between 290°C and 550°C. The profile of the cycle includes 6 hours for heating and maintaining the temperature at 550°C, and another 6 hours for cooling and maintaining the temperature at 290°C, so that each cycle lasts 12 hours. This setup was though as being quite representative of the behavior in a real TES plant. Samples will be taken after 10, 20, 40, and 100 cycles to study the evolution of corrosion scales with the number of heating/cooling cycles.

After these cycles, samples will be treated as previously, and fully characterized.

On the other hand, a database containing the data found in the bibliography concerning nearly 300 inorganic salt mixtures for LHT systems [5] [6] [7] was built. The Granta software Selector [8] was used to represent the thermal properties of these mixtures as well as those obtained at the UniSA lab, to compare them. The idea is to complete the database initiated at UB with low temperature PCMs and materials for sensible heat transfer, with those used at high temperatures for LHT.

Two examples of plots obtained with this data base are shown in next Figures.

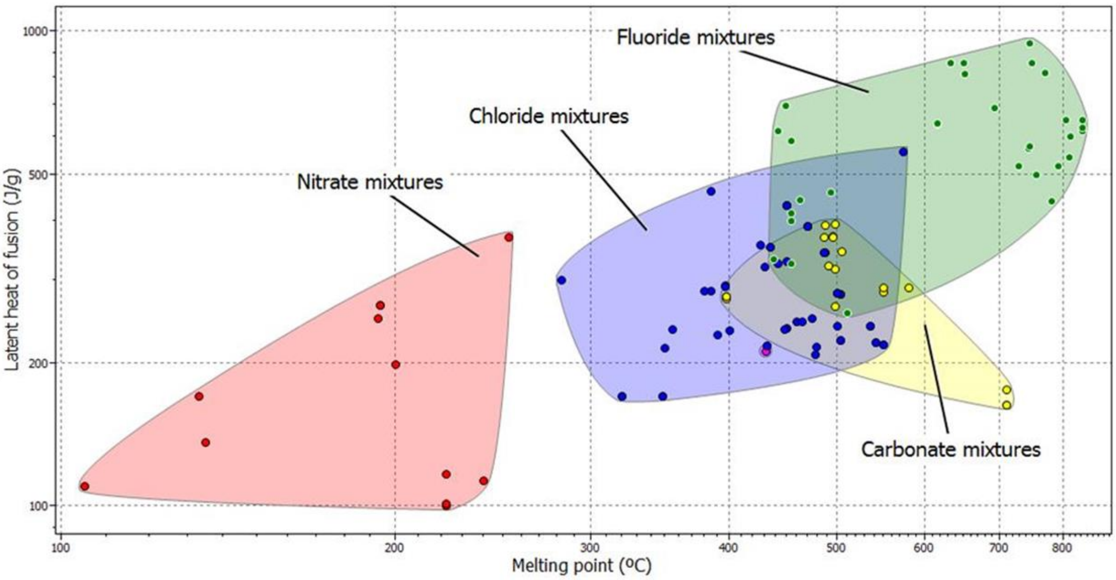

Figure 2.- Thermal properties of different salts.

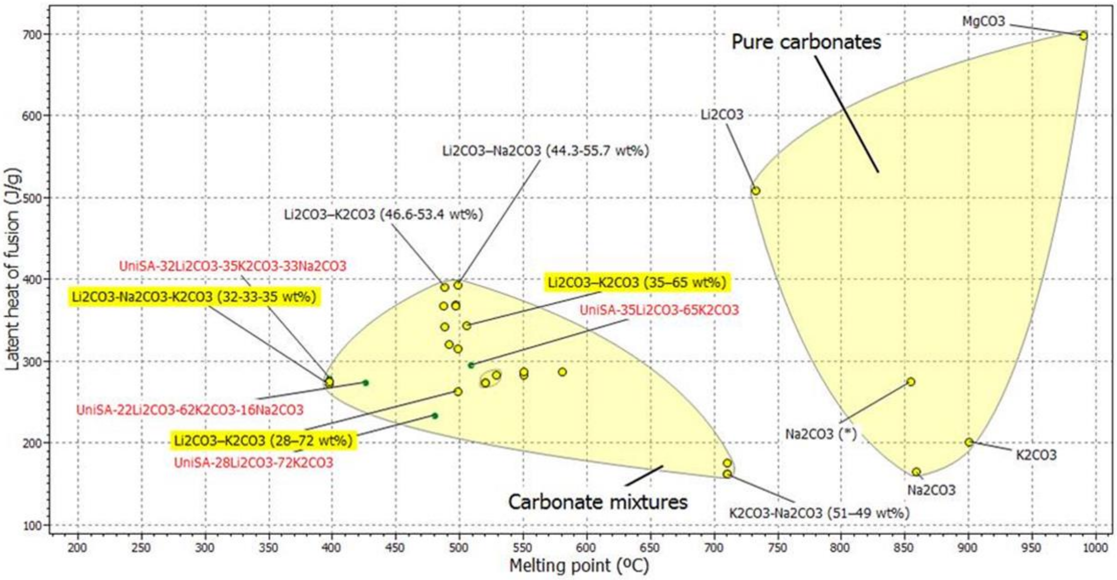

Figure 3.- Thermal properties of different carbonate mixtures, including those used for corrosion experiments during this secondment (UniSA labeled).

Finally, a seminar was held during this secondment, in which the research in thermal energy storage at the UB was presented. The usefulness of the Granta software was also explained, finding common issues to be discussed about the methodology for the selection of materials.

5 Results

At the time of writing this report, not all the samples have been obtained. Therefore, full results will be obtained in the next few months.

The first samples of 316 SS, obtained after 24, 72 and 148 h at 580°C are shown in next figure.

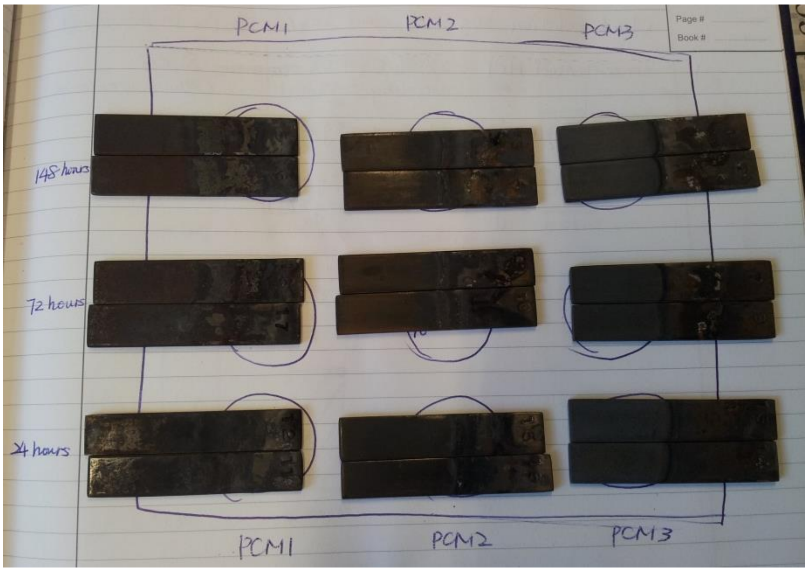

Figure 2.- Samples of 316 SS after being immersed in the carbonate salt mixtures at 580ºC for different times.

The naked eye observation of the samples shows that there is one of the carbonate salt mixtures (PCM3) that yields to uniform oxide layer on the entire surface that was immersed into the molten salts (that is, same thickness and composition) after a few hours of treatment. The other two mixtures (PCM1 and PCM2) yield to layers with different compositions (different colors on the surface) and with different thicknesses (surface irregularities). However, these preliminary results must be corroborated by microscopic characterization.

6 Outcomes or future work

The full results will be presented in the form of two articles that will be submitted to international journals. The first, related to the corrosion tests on different stainless steels in contact with different molten salts based on carbonates. The second will be related to the behaviour of stainless steel immersed in molten salts under cycling for long periods through their melting points. The results of this later will need at least six months to be completed, as the objective is to leave the samples under at least 100 cycles. Afterwards, the samples will be fully characterized in terms of weight loss, corrosion rate, thickness and composition of oxide scales, by means of scanning electron microscopy and X-Ray diffraction. The resulting salt mixtures will be also chemical and thermal characterized in order to find if there is any change in their composition and/or thermal properties.

It is proposed that the continuation of this work is done through studies of corrosion of other materials that can be used to contain other molten salt mixtures. The obtained results (thermal properties of salt mixtures, corrosion rates of each material for containers, and number of cycles) will be entered in the database to complete it.

7 References

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[7] S. Kuravi, J. Trahan, D. Y. Goswami, M. M. Rahman and E. K. Stefanakos, "Thermal energy storage technologies and systems for concentrating solar power," *Progress in Energy and Combustion Science,* vol. 39, pp. 285-319, 2013.

[8] Granta Design Ltd., «CES Selector Software,» Cambridge, UK, 2012.

8 Assessment

This has been a great time for me to dedicate to research and articles writing. The experience cannot be more profitable, as I had the possibility of knowing another way of working, finding a lot of things in common, trying to soak all possible skills, enjoy a pleasant stay, and experiencing research and knowledge sharing.