ME4TES – PPP

Multi-scale modelling and Experimental validation of Thermochemical Energy Storage materials

(Particle – Pellet – Packed bed)

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1 Introduction

Thermochemical energy storage materials (TCMs) are the heart of the so-called 'Heat Battery', which is/has being developed in several TKI Urban Energy projects (Tweede warmterevolutie (MJP CCO), Energy-Pads) and European H2020 / EEB projects (MERITS & CREATE). ME4TES has performed multi-scale modelling and experimental validations in order to further develop fundamental understanding of TCMs in the area of heat and mass transfer on several length-scales, which was the main objective of this project. However, the long-term aim would be to accelerate the development of an efficient and compact heat battery and to support other running projects as mentioned above.

ME4TES has exploited hydrated salts as TCMs that have shown energy storage capabilities significantly higher than water (with relevant temperature difference). The developed models have predictive value, providing design criteria for optimal functionality TCMs in the heat battery. The University of Twente has performed the multi-scale modelling (particle – pellet – packed bed, PPP) activities within WP1 with FPSIM giving input, while TNO has performed the synthesis and characterization of TCMs with help from De Beijer RTB and PCM Technology within WP2. The following sections will explain the main activities and results from WP1 and WP2.

2 WP 1

The main objective of this WP was to investigate how heat and mass transfer influence the (de)hydration of salt hydrate in a closed TCHS-system. In this study, K_2CO_3 was chosen as the TCM; as it has the highest potential in the build environment based on the working conditions, cost, safety and energy density. This objective has been achieved by applying and developing a coupled computational fluid dynamics discrete element method (CFD-DEM) as a numerical modelling tool. The details about the numerical methods are given in ref [1].

In WP1 comparisons have been carried out for the numerical results of the hydration and dehydration process in a single K_2CO_3 particle with the measurements obtained from experiments performed in WP2, showing a very good agreement. The impact of the particle size on the hydration process is also studied. Furthermore, to understand how heat transfer will be affected by applied pressure, in different packings with different particle sizes, the effective thermal conductivity (ETC) of the packed beds of salt hydrates is calculated by using the developed numerical model. Validations of the numerical ETC results are done by comparisons with the obtained experimental measurements performed in a vacuum oven [2].

Moreover, simulations for the hydration of a packed bed were performed, though the general trend in behavior of particles is comparable, the results predicted by the model has a considerable deviation from the experimental measurements; the main reason for this deviation is that there are some physical phenomena which are still unclear or not yet understood such as particles' volume change. In order to propose a design criterion for optimal TCMs and for the development of an improved TCHS-system, further research is required which involves the better understanding of the inherent mechanism of particles' volume change.

3 WP 2

WP 2 has provided the experimental data, i.e. the kinetics and material characteristics of grains/tablets of a TCM, required to model a reactor. The kinetics has been studied for pure grains, tablets produced with the project partner “PCM Technology” and coated tablets. The tests on tablets, however, were not successful, since after 10 hydration/dehydration cycles the material could not be recognized anymore as tablet. So only the data on the pure grain was used for the modeling purpose in WP1.

Mercury intrusion porosimetry (MIP) measurements were performed on a variety of samples to determine the pore volume, porosity, and the pore size distribution. These measurements have shown that the pore volume/porosity is increasing by increasing number of cycling, meaning that the overall grain expands during hydration/dehydration cycles.

In addition, calorimetric measurements have been performed on a simple heat transfer unit, investigating full-reactor scale system characteristics with respect to material size and shape. In order to directly measure the generation of heat and study the effect of dense particle packings, a simple mock-up heat transfer setup has been used, consisting of 2 metal plates inside a packed bed of the active material. With this setup, effects of heat exchanger fins on effective thermal conductivity (ETC) of a packed bed of material was investigated. The setup is flexible, meaning that multiple sizes and shapes of the active material, as well as multiple reactor materials (fin shapes, materials, thicknesses, etc.) could be in principle investigated. This set-up represents the smallest repeating unit (2 fins of a heat exchanger with material in between) of a TCM reactor module and it should therefore be representative for larger systems.

4 Results & Conclusion

In this project we made a first step in characterization of a TCM as single grain and also a reactor bed. The exact tests are not that straight forward, and the test equipment cannot simply be bought. In addition, the material is hard to handle in pure form, which was needed for the modelling purpose. In future studies the material should first be stabilized before analysing. Development of the mathematical and numerical simulation model and the validation of the obtained numerical results against the experimental measurements done at particle and bed scales are the key contributions of this research work.

The key findings from the two WPs are listed as follows:

On reaction kinetics:

- Hydration/dehydration cycles strongly affects the morphology of the TCM
- K_2CO_3 reacts faster in case of higher water vapor pressures due to a higher driving force for the reaction.
- During the hydration process of a single particle, the reaction rate is high at low temperatures when a constant water vapor pressure is applied
- the hydration and dehydration reaction rates are directly and indirectly proportional to the vapor pressure and temperature respectively.
- The particle’s size has an impact on the hydration reaction and the conversion time of the particle increases with increase in the size of particle.
- The reaction in the core of particle starts and ends with a time delay compared to its surface, also there is a small temperature gradient along the radius during hydration.
- The particles close to the wall easily give away the generated heat. Therefore, their temperature stays below the equilibrium temperature and hence, the hydration continues with higher rate. Where the particles that are far from the walls, have weaker heat transfer hence, their temperature is closer to the equilibrium temperature and the conversion is slower.
- The hydration in a packed bed starts in the regions close to the walls and moves towards the center of bed
- Expansion of the TCM during hydration/dehydration in pure form should not be neglected.

On effective thermal conductivity (ETC) measurements:

- Determining the ETC of a bed with enough accuracy (<5%) of TCM is hard.
- The ETC of a fresh bed is overestimating the heat conductivity of a TCM bed in a reactor.
- The total water vapor pressure inside the TCM bed strongly affect the heat conductivity of the TCM bed.
- Better heat transfer is observed in numerical experiments at higher vapor pressures because of natural convection.
- It is noticed that among the other heat transfer mechanisms in a packed bed conduction heat transfer is the dominant one.

Due to the major effects of particle expansion on both reaction kinetics as well as the effective thermal conductivity, a further research is required involving the discovery of the mechanism of volume change in salt hydrates during the hydration and dehydration reactions.

5 Challenges and Future work

Within this project an advanced numerical platform was developed capable of investigating the TCMs in the particle level. We focused on pure material for studying the reaction kinetics and exploring the effective thermal conductivity of the bed, this was Ok for modelling purpose in the grain scale however, moving to the bed modelling and experimental validation, it turned out that the material should first be stabilized before doing such analyses (e.g. coating the TCM). We also realized that in order to be able to predict the exact behavior of the material the effect of agglomeration and volume change of particles should be added as they have considerable effects during multicyclic performance. The performance of the material degrades due to agglomeration or clogging of grains over subsequent cycles and the volume change during de(hydration) will affect the reaction kinetics and therefore the power output of the reactor.

Thereby further investigations are required on:

1- Formulizing the agglomeration behavior of salt hydrates through both modelling and experiments
2- Understanding the aging effect of TCMs in the TCHS system, meaning that the mechanism of volume change in salt hydrates must be thoroughly studied.

Together with the industrial partners we defined the necessary steps to be taken after this project is finalized:

1- To focus on heat exchanger (HX) in a closed thermochemical storage system and investigate how materials interact with HX
2- Mechanical strength of TCM particles in a moving bed with focus on stability of material when moving from reactor to the storage

6 Knowledge dissemination

- Conference presentations:
  - Walayat, K., Mahmoudi, A., Duesmann, J., Cuypers, R. and Shahi, M., Study of heat transport in a packed bed of potassium carbonate, MSE-Congress 22-25 September 2020.

- Mahmoudi, A., Donkers, P., Shahi, M., Multi-scale modelling of charging/discharging of potassium carbonate particles in a thermochemical energy storage reactor, 8th International Conference on Discrete Element Methods, July 21-26, 2019, Enschede, The Netherlands.

- Master thesis
  - J.B.C. Duesmann, Hydration speed and bed effective thermal conductivity of sodium sulfide flakes for long-term heat storage applications, MSc Thesis, 2020, University of Twente.
  - T.C. Dirks, The effect of convection at low pressure on the heat transfer of K2CO3 particles in a numerical modeled packed bed, MSc Thesis, 2020, University of Twente.

- Project website:

  https://www.utwente.nl/en/et/tfe/me4tes/

- Journal publications:
  - Mahmoudi, A., Donkers, P. A.J., Walayat, K., Peters, B., and Shahi, M., A thorough investigation of thermochemical heat storage system from particle to bed scale, (2020) under review.
  - Walayat, K., Duesmann, J., Derks, T., Mahmoudi, A., Cuypers, R. and Shahi, M., Experimental and numerical investigations for effective thermal conductivity in packed beds of thermochemical energy storage materials, (2020) under review.

7 References

[1] T.C. Dirks, The effect of convection at low pressure on the heat transfer of K2CO3 particles in a numerical modeled packed bed, MSc Thesis, 2020, University of Twente.

[2] J.B.C. Duesmann, Hydration speed and bed effective thermal conductivity of sodium sulfide flakes for long-term heat storage applications, MSc Thesis, 2020, University of Twente.