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The Prototype of Reactor for Carbon Capture in Molten Salts

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Abstract: Carbon Capture in Molten Salts (CCMS) a new method of capturing CO_2 was developed on a sorption and desorption principle similar to that used in the calcium loop, but proceeding in the molten salt environment (alkali metal chlorides and fluorides): $MeO_{\text{(s, diss. in molten salts)}} + CO_{2\,(g)} \leftrightarrow MeCO_{3\,\text{(diss. in molten salt)}}$
The idea of the CCMS reactor presented in the only patent assumes its operation in a two-chamber system, allowing to separate the stages of CO_2 sorption and desorption. The paper presents the development of a reactor prototype consisting of three basic elements, i.e. a sorption, desorption an intermediate chamber. The transport/pumping of salt between the reactor elements will take place on the principle of a gas lift, i.e. the transport will be forced by the pressure of inert gas. It was necessary to determine what the gas pressure in the gas lift should be to effectively pump molten salts The reactor chambers will be located inside the heating modules however, some elements for transporting molten salts will protrude above the heating zones and they must be thermally insulated. And here another problem arose , whether the insulation of the pipelines for the transport of molten salts is sufficient to protect them from freezing during contact with colder elements, and if not, then how to prevent it. The scope of the research included performing numerical simulations in order to:
• determination of the gas pressure needed to pump the molten salt between the reactor chambers;
• determination of the temperature distribution as the molten salts flow through the conveying system to anticipate the possibility of loss of pumpability due to salt freezing.
The above-mentioned problems of the CCMS reactor prototype operation were solved by means of thermal-flow analysis, performed using computational fluid mechanics methods (Ansys Fluent and SolidWorks programs).

Keywords: Carbon capture, Molten salts, CCMS reactor

Introduction

Calcium loop (CaL) is a carbonate looping method (MacDowell et al., 2010) in which a metal (Me) undergoes a reversible reaction between its carbonate ($MeCO_3$) and its oxide form (MeO) to separate carbon dioxide from other exhaust components:

$$MeO_{(s)} + CO_{2(g)} \leftrightarrow MeCO_{3(s)} \tag{1}$$

The processes of oxide carbonization/CO_2 sorption and carbonate calcination/CO_2 desorption take place in a fluidized bed in separate reactors. One of the major challenges of this technology is the relatively fast sorbent reactivity decay resulting in a residual activity of 8-10% after about 20, due to sintering during calcination (Blamey et al., 2009). For this reason, it is necessary to periodically remove part of the sorbent from the system and replace it with fresh.

In the 21st century, a new method of capturing carbon dioxide was developed on a sorption and desorption principle similar to that used in the calcium loop, but proceeding in the molten salt environment (CCMS - Carbon Capture in Molten Salts) (Olsen et al., 2013; Tumkote et al., 2013, 2014). In this method, the unreacted sorbent as CaO and as $CaCO_3$ after CO_2 sorption are found in solutions of molten salts (alkali metal halides - Ca, Na, Li, mainly chlorides and fluorides):

$$MeO_{\text{(s, diss in MS)}} + CO_{2\,(g)} \leftrightarrow MeCO_{3\,\text{(diss in MS)}} \quad (2)$$

In this concept, molten salts are used as solvents of the active sorbent in CaL, with the main idea of hindering CaO particles degradation. Exhaust gases containing CO_2 go to the absorber, where CaO is in the form of molten salts. $CaCO_3$ is formed through reaction (2) and dissolves continuously in the melt, leaving highly reactive surfaces of CaO readily available. Molten salts containing $CaCO_3$ are directed to the desorber chamber operating at a higher temperature. The calcination reaction takes place, and the pure CO_2 is removed from the desorber (Figure 1).

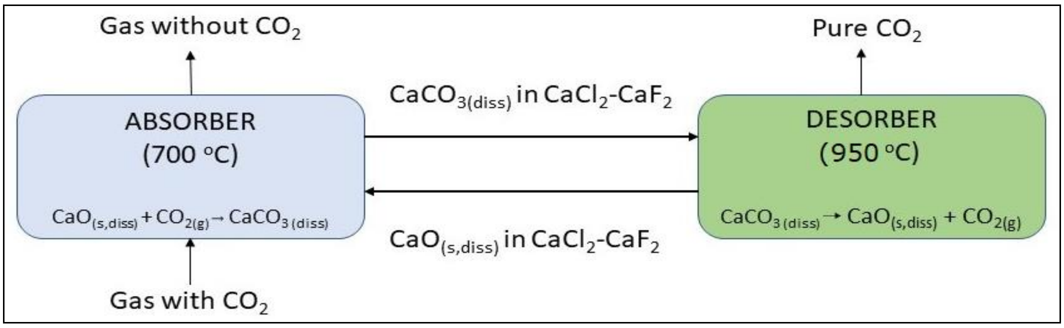

Figure 1. Scheme of CCMS process

So far, the CCMS method is at the stage of advanced research on a laboratory scale (Olsen et al., 2013; Nygård et al., 2017; Nygård et al., 2019). The salt solutions in which the capture was carried out were based on the CaF_2-$CaCl_2$ solutions with the addition of CaO. The studies of sorption and desorption cycles were carried out only in a single-chamber reactor. The process is carried out cyclically, i.e. after the sorption process is completed (no CO_2 capture), the flow of the exhaust gas mixture is closed and the reactor is heated to a higher temperature at which the thermodynamically justified reaction (2) proceeds to the left towards the decomposition of calcium carbonate and desorption of pure CO_2. After the completion of CO_2 desorption is confirmed, the reactor is cooled again to the temperature at which the reaction (2) proceeds from left to right and the process of CO_2 sorption from the flue gases is carried out.

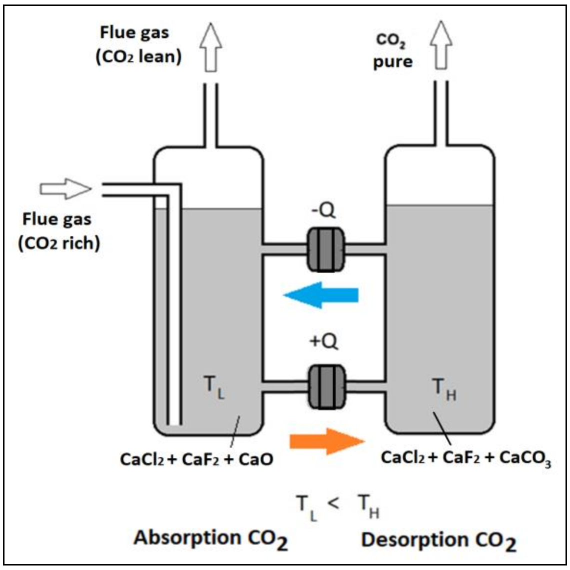

Figure 2. Two chamber reactor CCMS –simplified and adapted (Olsen, 2013)

The idea of the CCMS reactor presented in the only patent (Olsen, 2013) assumes its operation in a two-chamber system, allowing to separate the stages of CO_2 sorption and desorption. However, the reactor presented in the patent solution provides that the exchange of molten salts will take place by convection, through a system of two channels connecting both chambers. One of them will cool the melted salts flowing to the desorption chamber to the temperature of about 700^0C, while the other one will heat the melted salts flowing to the desorption chamber to the temperature of about 950^0C (Figure 2). That solution is to enable the reactor to operate continuously. However, there is a concern that this will make it difficult to complete the sorption and desorption of CO_2 and make it difficult to fully use the sorption capacity of the sorbent. This paper presents the completely new development of the reactor prototype (Pietrzyk, 2023) consisting of three basic elements, i.e. a sorption and desorption chamber and an intermediate one (auxiliary tank) (Figure 3).

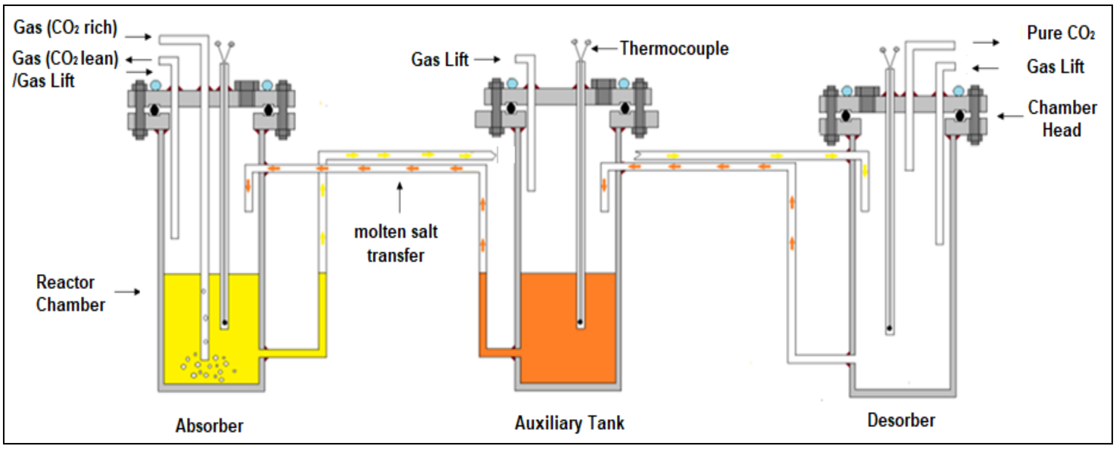

Figure 3. The new design of the CCMS reactor (Pietrzyk, 2023)

This solution will shorten the duration of a single cycle. Waiting for the end of sorption processes (depletion of the ability of CaO to capture CO_2) or the desorption process (no release of CO_2 from the decomposition of $CaCO_3$) will be eliminated. The reactor will be operated cyclically and each cycle will consist of three stages and a $CaCl_2$-CaF_2 solution will be used. In each stage of the cycle, only two of the three reactor elements contain molten salts and one always remains empty, ready to be filled with them in the next stage. Figure 4 shows the reactor chamber design stages.

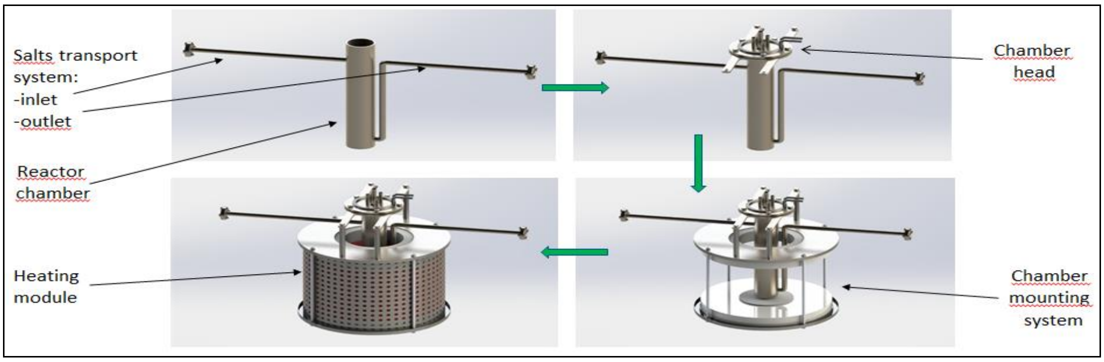

Figure 4. Reactor chamber design stages (made in SolidWorks)

Methods

During the design of the reactor prototype, many design problems were encountered that needed to be resolved by numerical simulations, of which only two are presented in this article. The scope of the research included performing numerical simulations in order to:

a). determination of the gas pressure needed to pump the $CaCl_2$-CaF_2 molten salt between the reactor chambers;

b). determination of the temperature distribution as the molten salts flow through the conveying system to anticipate the possibility of loss of pumpability due to salt freezing and pipelines clogging.

The above problems were solved using simulation methods available in the following programs: AnsysFluent® and SolidWorks®. Ansys Fluent as a computational fluid dynamics (CFD) software was used to model molten salts flow, heat and mass transfer in chambers of reactor. This software was also used to solve problem (a). In turn, SolidWorks is software (CAD) used for parametric three-dimensional modeling. It allowed us to design individual reactor details and assemble them into a whole. This software was also used to solve problem (b).

Results and Discussion

The transport of molten salts between the reactor elements will take place on the principle of a gas lift, i.e. the transport will be forced by the pressure of inert gas (N_2 or Ar) ((Mullen et al., 2017). The gas will be pumped under increased pressure into the chamber, above the level of molten salts, which will cause their pumping to the next element of the reactor . The effectiveness of the "gas lift" method was verified by testing on water, which has a density of approximately 1 g/cm^3, while the density of liquid $CaCl_2$ is 2.01 g/cm^3 at a temperature of 775^{o}C, which is more than twice as high (Janz, 1988) Therefore, computer simulations were carried out for the medium in the form of molten salts at the operating temperatures of the reactor chambers. It was necessary to determine what the gas pressure in the gas lift should be to effectively pump molten salts. An example of the simulation results of the operation of a gas lift is shown in Figure 5.

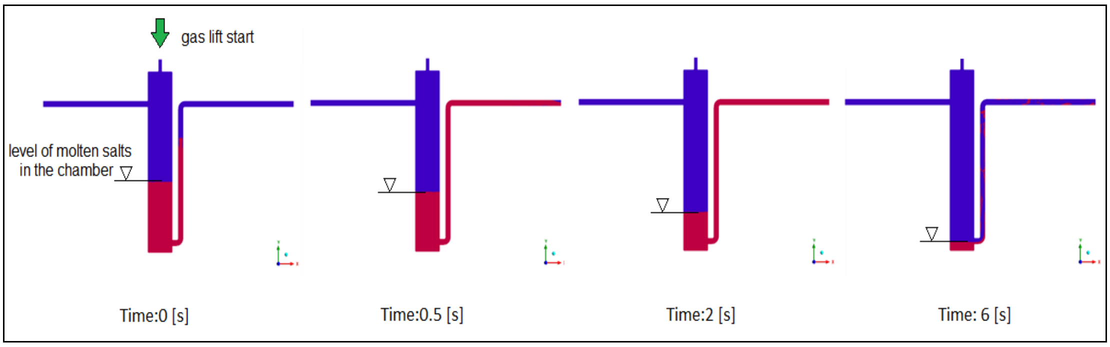

Figure 5. Simulation of the transport of molten salts using a gas lift (made in Ansys Fluent)

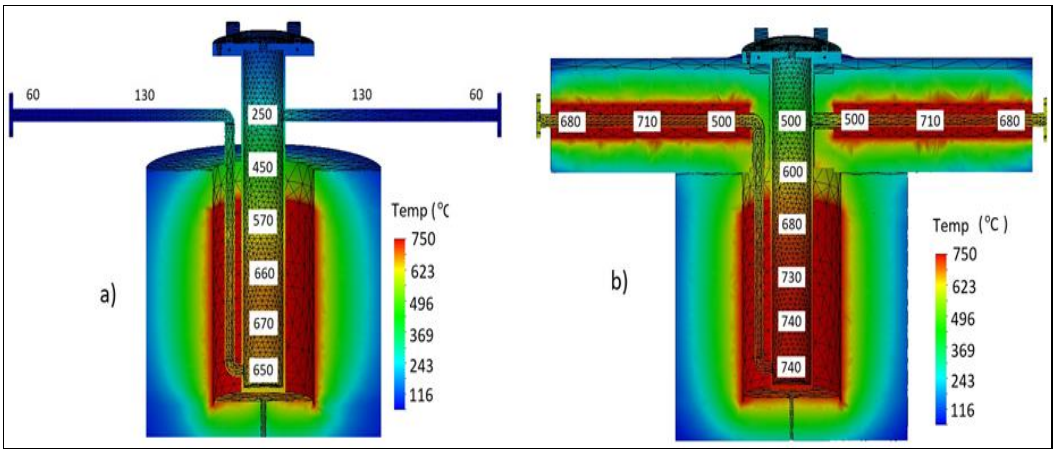

Figure 6. Simulation of the temperature distribution of a low-temperature chamber (made in SolidWorks)

The time needed to pump the molten salts from the chamber is 6 seconds and the gas overpressure at the inlet of the gas lift is 10 kPa. The reactor chambers will be located inside the heating modules, allowing to maintain the temperature of the working medium at an appropriate level, however, some elements for transporting molten salts will protrude above the heating zones and they must be thermally insulated. And here another problem arose that had to be solved during the design of the reactor prototype, namely whether the insulation of the pipelines for the transport of molten salts is sufficient to prevent the salt from freezing, with an excessive drop in their temperature during contact with colder elements, and if not, then how to prevent it.

The simulation results of the temperature distribution in the low-temperature reactor chamber showed the existence of underheated places on the pipelines transporting salts, which could lead to their solidification and clogging. Similar, underheated zones also confirmed the simulation results of temperature distribution in the high-temperature chamber. Fig. 6 shows a comparison of numerical simulations of the temperature distribution in a situation where the horizontal molten salt transport pipelines: (a) were not and (b) were insulated and heated by additional heating elements. The results of the thermal simulations showed the necessity of installing additional thermal insulations and heating modules on the horizontal pipelines transporting molten salts, between the chambers (Figure 7).

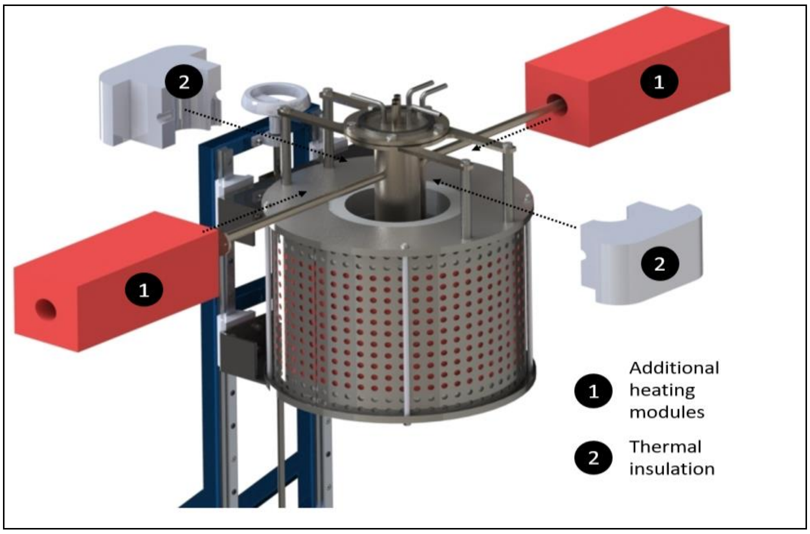

Figure 7. 3-D model of low-temperature chamber with additional thermal insulations and heating modules (made in SolidWorks)

The results of computer simulations were used to design and build a prototype of the CCMS reactor (Figure 8). The constructed prototype is equipped with six independent programmatically controlled heating systems (three for the reactor chambers/tanks and three for the pipelines transporting molten salts between them). The pipeline transporting system has been equipped with high-temperature valves, allowing for the isolation of individual sections and the use of a gas lift to transport molten salts between tanks after the completion of the absorption/desorption processes.

Figure 8. CCMS reactor prototype designed and built at AGH-UST

Conclusions

Based on the obtained results of computer simulations, the following conclusions were reached:

- The designed and constructed prototype of reactor enables cyclic operation of CO_2 capture from the flue gases and release a pure CO_2
- The use of an auxiliary tank allows for the separation of sorption/desorption cycles and maximizes the use of CaO sorption capacity (recently, the first successful tests were carried out on a prototype of a three-chamber reactor, confirming the above-suggested thesis).
- The operating conditions of the gas lift, calculated on the basis of computer simulations, have been checked and confirmed in the operating conditions of the reactor prototype and ensure effective transport of molten salts.

- The use of additional thermal insulation and heating modules allows for the preheating of the transporting system for molten salts, preventing their solidification and clogging of the pipeline.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

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