THERMOCHRMICAL ENERGY STORAGE CACO3/CAO MATERIALS REVIEW AND PELLET REDUCTION SIMULATION

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ABSTRACT

Concentrated Solar Power technology (CSP) has been pursued during the past few decades as a qualified solution to the challenge imposed for the equalization of the balance between energy supply and demand. The effectiveness of CSP though is questioned due to the intermittent nature of solar energy. This can be addressed by the use of thermal energy storage systems. To this direction, Thermo-Chemical energy Storage (TCS) systems referring to calcium oxide (CaO) particles are here investigated, using the CaO/CaCO3 reaction. A Packed Bed Thermal Energy Storage System is filled with the material CaCO3 in pellet form which will be calcinated with a heated N_2 flow . This process is simulated using Comsol aiming to evaluate performance, operation and particle size of the porous media .

1 INTRODUCTION

Carbon neutrality that limits emissions of greenhouse gases to suppress global climate change requires the rapid growth of sustainable energy power, especially solar and wind. The intrinsic fluctuation and intermittence problem, however, poses a potential threat to efficiently utilize the solar energy.

It can be effectively solved by developing energy storage technologies. Among them, the high-temperature calcium-based thermochemical technology that converts solar energy into chemical energy by circulating the carbonation and calcination reactions of CaO and CaCO3, is considered as one of the most promising energy storage technologies, due to its advantages such as the high energy storage density, good chemical stability and low cost. CaCO3 is a promising material for thermochemical energy storage (TCES) systems. It can store and release heat

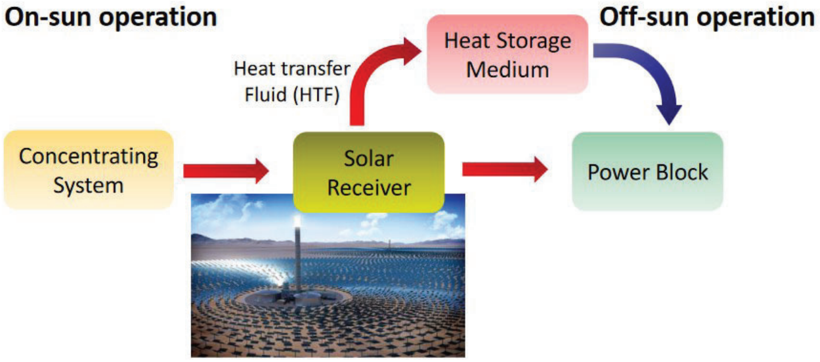


Figure 1: Schematic representation of a CSP unit combined with a TES system

https://doi.org/10.52202/077185-0187

upon reversible decarbonation to CaO, which emits heat through carbonation. Decarbonation temperature of CaCO3 directly affects the properties of CaO, which influences heat supply in result. The current research studies CaCO3/CaO system, specifically analyzing the conversion of CaO into CaCO3 (carbonation) for various CaO samples prepared at decarbonation temperatures between 600 and 975 °C.

CaO/CaCO3 Reaction Couple as TCS system

The CaO/CaCO3 couple is based on the reversible carbonation/calcination reactions and has been extensively studied by several scientific groups as a means for CO2 capture at high temperatures in the context of the CaO-looping technology (Dobner et al.,1977).

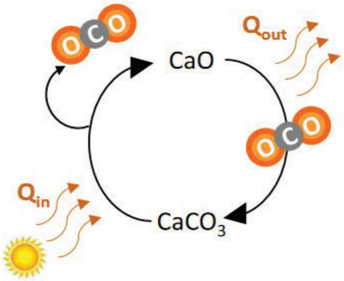


Figure 2: CaO/CaCO3 material couple studied as TCS system

However, theCaO/CaCO3 is a material system that has been also investigated since several decades as an energy couple for TCS due to its high energy density (Barker R.,1973). Based on the latter application, a new concept has been suggested more recently involving the usage of CaO/CaCO3 as energy carrier for transregional energy distribution (Pan, Z.H. and Zhao, 2017) while recent research efforts to optimize the CaO-looping technology for TCS show the potential of this application (Alovisio et al 2017).

The reversible reaction scheme takes place at temperatures between 500 and 800oC and can be described by the following equations. The high temperature windows and the high reversibility together with material nature, including abundancy, cost-effectiveness and non-toxicity, and high energy density (3.2 MJ/kg CaO) render this gas-solid system an interesting option for TCS.

$$CaO(s) + CO_2(g) \Rightarrow CaCO3(s) \qquad \Delta H= -178 kJ/mol \quad (1)$$

$$CaCO3(s) \Rightarrow CaO(s) + CO_2(g) \qquad \Delta H= 178 kJ/mol \quad (2)$$

On a material basis, a key characteristic for the effectiveness of CaO/CaCO3 system both as CO2-sorbent and energy carrier lies in the preservation of high reactivity of CaO particles within cyclic operation. However, this suggests a great challenge because cyclic deactivation is an inherent characteristic of pure CaO for this scheme (Abanades, J.C., 2002). Due to the high temperatures applied, CaO particles undergo a sintering mechanism which entails gradual material deactivation by surface area decrease and renders high amounts of non-reactive particles and thus, lower conversion rates and process inefficiency. Therefore, and similarly to the case of CaO/Ca(OH)2 couple, an effective material system for TCS via the cyclic carbonation/calcination reaction scheme should be based on high reactivity for effective TCS operation coupled with chemical and structural stability with sufficient sintering resistance for a stable performance over multiple cycles, as well as good compromise between material performance and production cost.

The low cost and abundancy of CaCO3 could be an easy solution to performance degradation suggesting material replacement periodically. Nonetheless, there are plenty of studies investigating various methods for material improvement including the employment of different CaO-precursors for the preparation of synthetic CaO particles, the preparation of suitable CaO-based materials using additives as chemical stabilization agents or applying periodically steam hydration after a certain number of the carbonation/calcination cycles (Yu et al.2011).

Regarding the preparation of novel sorbents for CO2 under cyclic carbonation/calcination operation, the employment of various elements and/or compounds is applied in order to promote a mechanism of resistance towards intercrystalline sintering. State-of-the-art approaches are related to the employment of different additives or dopants in combination with CaO particles including alkali metals, such as sodium (Na), lithium (Li) and potassium (K) (Reddy et 2004) metal oxides like magnesia (MgO) (Albrecht et al. 2008) and in most cases alumina (Al2O3) (Li et al. 2006) , as well as other elements like zirconium (Zr) (Koirala et al. 2011). The interaction of CaO with these additives usually leads to the formation of mixed phases, which are proved to restrict material deactivation upon cycling. Naturally, the presence of such inert phases reduces the total carbonation capacity to a certain extent depending on the amount they are used, however materials reactivity remains substantially higher in terms of average cyclic CO2 capacity cf. pure CaO when multi-cyclic operation is considered.

A second approach qualified as suitable for enhancing the cyclic performance of CaO by reactivating the material and restoring its CO2 capture capacity involves periodic hydration of CaO particles (Arias et al. 2010) . During cyclic hydration/dehydration, CaO undergoes a swelling- shrinkage mechanism resulting to particle fragmentation. Thus, the development of finer particles with higher surface area can provide a solution to the problematic CaO sintering. Several studies have been reported in the literature examining the application of periodic hydration between multiple carbonation/calcination cycles (Laursen et al. 2001) According to the results obtained, applying hydration either with steam or with liquid water can lead to improved CaO

carbonation performance through partial restoration of its carbonation activity. Being a cost-effective method for CaO particles regeneration, several options are suggested on the process level that should be followed in terms of temperature, flow/atmosphere composition or duration of the reactivation step for an efficient process.

2 MATERIALS METHODOLOGY – PREPARATION AND CHARACTERIZATION

2.1 Core-shell and Composite Pellets Manufacturing

The approach followed for the manufacturing of nearly spherical small pellets is based on two methods including:

a) CaO particles coating with an inert, refractory and mechanically sufficient compound

b) CaO incorporation into an inert and mechanically strong support matrix.

Regarding the first approach, core-shell CaO-based pellets are prepared. Studies in the literature reveal that this method is applied for the enhancement of chemical stability in CaO particles upon cyclic carbonation/calcination operation (Liu et al. 2006). In this work, a CaO-based core is simulated using Ca(OH)2 from natural limestone after calcination and

https://doi.org/10.52202/077185-0187

hydration (in liquid water). Distilled H2O is used as binder for the hydrated powder and nearly spherical formulations with diameters between 1-4 mm can be obtained applying centrifugal forces. Ca(OH)2 pellets are then dried at 100 oC for 1 h and then 1 mL of water is rinsed on the pellets and drying follows again. This procedure is repeated 3 times and the last drying step takes place at ambient conditions. For the coating, slurry of the corresponding refractory compound is prepared adding distilled H2O as binder and it is then applied over the Ca(OH)2 pellets. The resulting core-shell formulations are stabilized via calcination in air flow at various temperatures, as previously mentioned.

Following the second approach, the preparation of composite formulations is achieved via adequate mixing the solid powder precursors, as described in (Sakellariou et al. 2017). For the mixing procedure, two different techniques are applied, including mechanical mixing and suspension of the two (insoluble) precursors in distilled water. In the first case, homogeneous mixing is achieved via solid mechanical mixing in the presence or not of cylindrical zirconia grinders (d= 1 cm, h = 1 cm, powder/grinders = 1/4 in weight). In the second case, the two precursors aresuspended and continuously stirred in distilled water for 24 h, followed by drying of the resulting slurry at 110 oC for 67 h. A nearly spherical shape of the formulations is obtained withthe aid of a rotary mill (Fritsch Pulverisette 6) operated at 600 rpm, while distilled water isadded as binder for the mixed powders. The diameters of the mixed CaO-kaolinite pellets are mostly between 850 mm and 2 mm. Special thermal treatment is then applied for the stabilization of the materials after drying at ambient conditions and the composite pellets were calcined in air flow. Taking into consideration the sensitivity of CaO to ambient moisture (Sakellariou et al. 2015) after each calcination, the formulations are stored in vacuum sealed plastic bags. Figure 3 shows indicative green core-shell and composite pellets in their dry/non- calcined form.

Figure 3. Green nearly spherical formulations:
a. Core-shell pellets (clay coated Ca(OH)2 cores), b.CaO/clay composite pellets

2.2 Monolithic Honeycomb Reactor Preparation

Monolithic honeycomb structures are manufactured in order to be studied as integrated and compact reactors/heat exchangers for the carbonation/calcination reaction scheme. Their preparation is based on the employment of an inert honeycomb structure that is coated with the active material via the slurry (dip) coating technique [105]. The honeycomb substrate used involves cordierite, a magnesium iron aluminium cyclosilicate, obtained by Céramiques Techniques Industrielles/CTI. The small-scale segments employed are of cylindrical shape and are cut from larger/full-scale monoliths. Their main characteristics are presented in Table 1. Due to CaO sensitivity towards ambient moisture, the active materials are used in their hydrated form, which is obtained after calcination at 900oC for 2 h in air and hydration in liquid water at ambient condition

Table 1. Small-scale cylindrical cordierite monoliths specifications

Parameter	**Value**
Length / cm	2.90
Diameter / cm	2.54
Channel size / mm	1.44
Wall thickness / mm	0.27
Cell density / cpsi	221

The coating procedure involves the following steps (also see Figure 4 for the schematic representation):

i. Preparation of the aqueous slurry of the hydrated CaO-based powders with solids content of 40 wt %.
ii. Addition of dispersant: A sodium salt of an acrylic polymer is used for slurry stabilization.
iii. Impregnation of the monolithic cordierite bodies into the prepared slurry.
iv. Removal of the excess slurry from the loaded specimens by blowing air through the honeycomb channels.
v. Drying of the coated monoliths after impregnation step at a temperature of 110 oC for 2 h.
vi. Steps iii, iv and v are repeated several times in order to achieve high powder-loadings required to maximize the volumetric energy storage/release density but also making sure that the channels of the honeycomb are not blocked.
vii. Firing under air at 900oC in order to ensure adequate adhesion of the coating layer on the monolithic substrate.

Figure 4 b and c present the uncoated cordierite monolith and CaO-coated cordierite monolithic structure prepared after its calcination at 900 oC in air flow for 2 h, respectively. A homogeneous coating is achieved following the above mentioned procedure and final loadings between 50 and 60 % are obtained (material mass/mass of ‘clean’ monolith x 100).

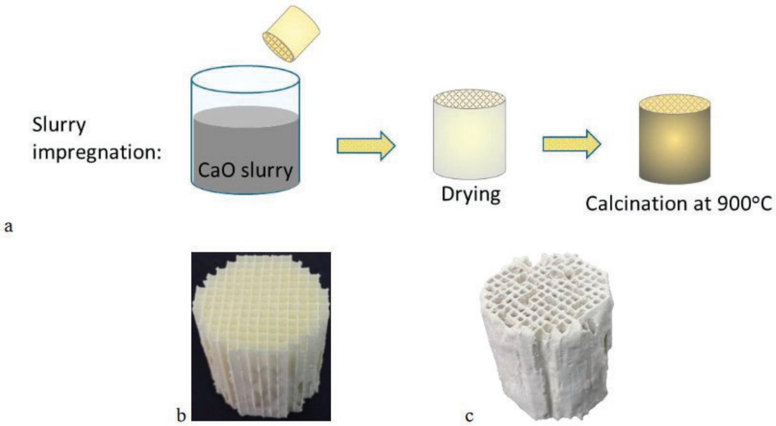


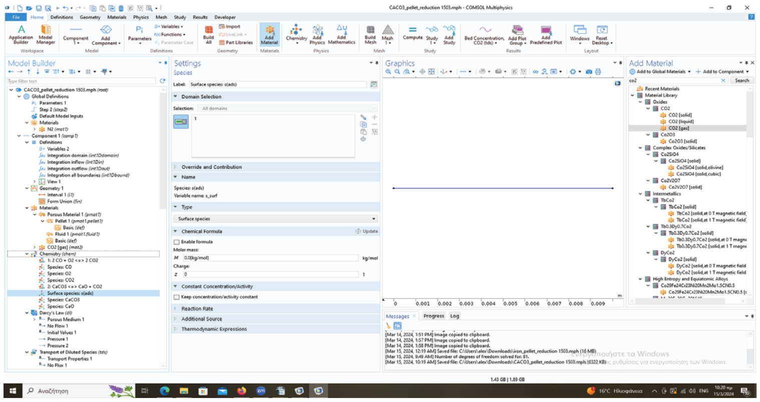
Figure 4. a. Schematic depiction of honeycomb substrates coating procedure, b. Uncoated cordierite monolith, c. Green (before calcination) coated cordierite monolith

3. SIMULATION

This application uses the shrinking core model to study the reduction of $CaCO_3$ core pellets. A 1D model of a packed bed containing CaCO3 pellets is modeled. The bed filling pellets initially consists of solid phase CaCO3. The pellets are reduced by heating process with the flow of N_2 during which the solid core shrinks leaving a porous $CaCO_3$/CaO matrix and producing CO_2 gas. The gas phase transport through the bed is modeled using Darcy's Law. The reduction mechanism is defined in the Chemistry interface including both a surface reaction for the $CaCO_3$ reduction and a gas phase reaction occuring in the reduced pellet part. The Shrinking Core Model is enabled in the Pellets subnode of the Packed Bed feature in the included Transport of Diluted Species interface.

Table 2. Simulation Parameters

Parameter	Value or range of values or description
Carbonation temperature	600, 750 ºC
Calcination temperature	800ºC
Gas for carbonation step	CO_2, CO_2/N_2
Gas for calcination step	N_2
Gas flowrate	8 L min^{-1} (std)
CO_2 content in carbonation stream / total pressure	12.5 – 100 % / 1 bar



Label: Surface species: s(ads)

Domain Selection

Selection: All domains

1

Override and Contribution

Name

Species: s(ads)

Variable name: s_surf

Type

Surface species

Chemical Formula

☐ Enable formula

Molar mass:

M 0.0[kg/mol] kg/mol

Charge:

z 0 1

Constant Concentration/Activity

☐ Keep concentration/activity constant

Reaction Rate

Additional Source

Thermodynamic Expressions

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Figure 5. Simulation software

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4. RESULTS AND DISCUSSION

In the followig figures results are shown regarding the conditions inside the porous medium. Figure 6 depicts the pressure inside the control arc. As can be seen for a given position the inlet (x=0) is at $3x10^5$ Pa and as the flow moves towards the outlet it decreases to $2.2x10^5$Pa in the middle (x=0.5). Finally at the outlet pressure is 1bar . It is apparent form the green line that we have a continuous speed increase moving from inlet (high pressure) U=0.15m/s to outlet (low pressure) U=0.3m/s .

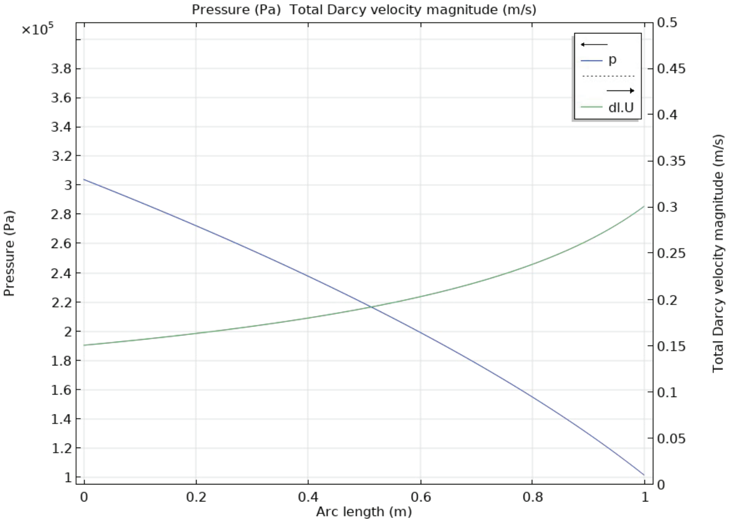

Figure 6. Pressure (Pa)

Figure 7 illustrates CO_2 concentration (mol/m^3) in the pellets located in the control space. At the beginning the concentration of CO_2 on the pellets is minimum and all pellets are big in size. As the $CaCO_3$ pellets are heated ,the calcination process begins. CO_2 is released on the pellet surface and the pore volume. This leads to an increased concentration near the inlet , the smaller the particle radius the greater it is . Furthermore, as the heat transfer progresses, big diameter particles start to break up and release $CO_{2.}$ Leading to an increase of the smaller nad finer particles . It is at the end of the process t=600s that the particle radius has reduced significantly . No more big pellets are left , only small diameter ones with increased CO_2 concentration (mol/m^3) .

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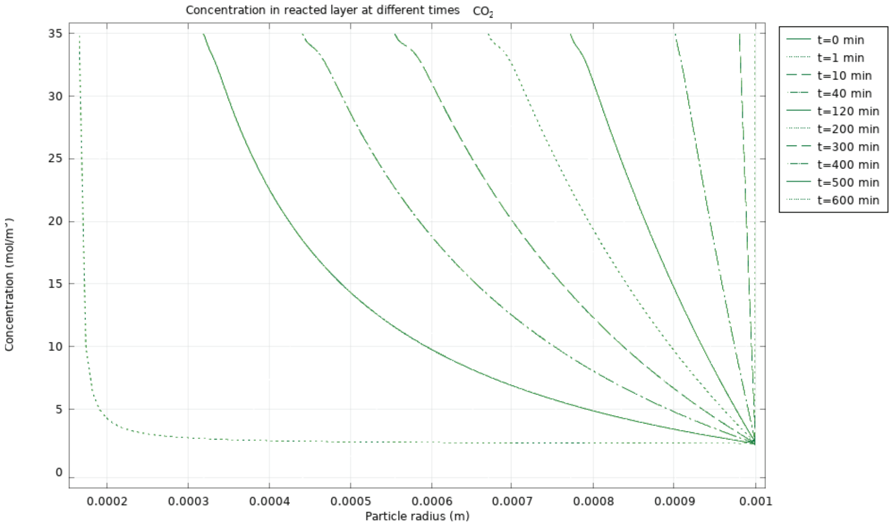

Figure 7. Pellet Concentration in reacted layer x=0.5 at different times

Figure 8 depicts the CO_2 concentration according to the Arc length for different times. As it can be seen for t=0 sec CO_2 concentration is zero. Given time CO_2 concentration(C) starts to rise as we get closer to the outlet carried through N_2 flow. At x=0.2 we have C=10mol/m^3 for t=10sec which rises to 18mol/m^3 for t=500 sec. Finaly after 700 sec it reaches 38mol/m^3 and stabilises indicating the end of the process.

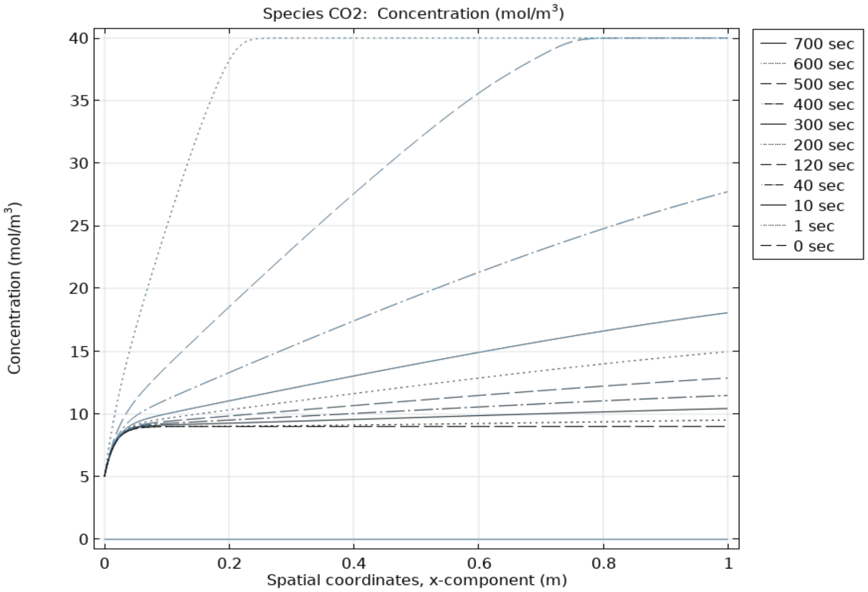

Figure 8. Bed CO_2 concentration(mol/m^3)

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Figure 8 exhibits Solid Core Radius of pellets associated with the Arc length for different times . It is clearly shown that as we get closer to the inlet pellets are exposed first and thus for longer time to the incoming heat (carried through N_2). They have started decomposing earlier which leads to greater shrinking. So at x=0.2 we have a Solid Core Radius (SCR)=0.00075m. In contrast, moving along the Arc towards the outlet, we find pellets of grater diameter due to their later exposre and less time to decompose so at x=0.8 we have Solid Core Radius=0.0008m. Finally for t=700sec when all pellets have reached same temperature and equal exposure the SCR is normallized .

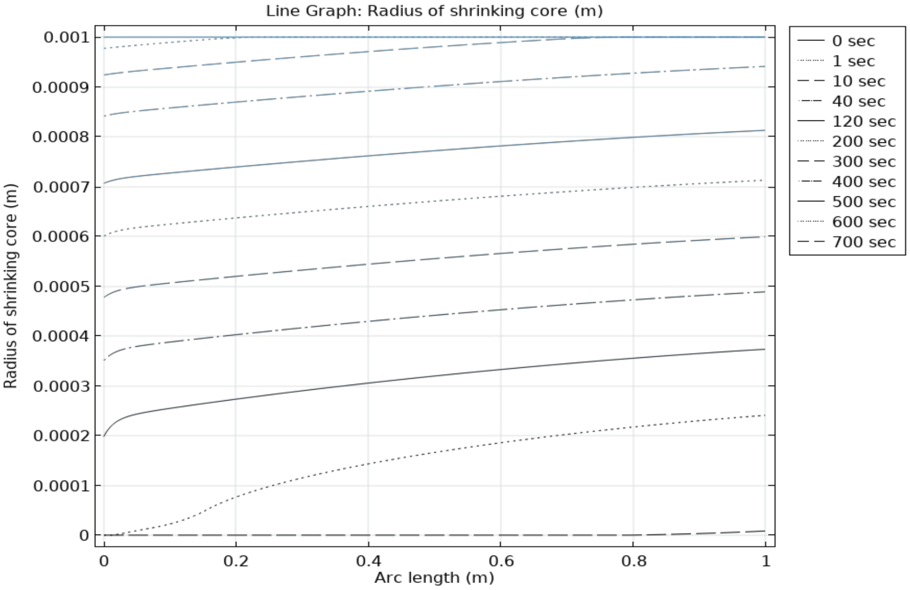

Figure 9. Solid Core Radius (m)

4 CONCLUSIONS

The goal of the present paper is the review of materials which are used to operate CaCO3/CaO thermochemical energy storage systems and the simulation of core pellet reduction during operation. The Simulation was done using Comsol. This application uses the shrinking core model to study the reduction of $CaCO_3$ core pellets using a 1D model of a packed bed containing CaCO3 pellets . Pellets forming the bed initially consist of solid phase spherical material CaCO3. The calcination takes place by heating process with the flow of N_2 during which the solid core shrinks leaving a porous $CaCO_3$/CaO matrix and producing CO_2 gas. Having a software model can leed to more efficient design ,since it allows for design optimization before experiments or construction.This can lead to lower development cost and optimal material sizes selection.

- The presure and flow speed in the packed bed was shown.
- Solid core radius according to time was investigated.
- Bed concentration was shown .

In the future, there is a need to investigate the impact of different temperature levels, geometries particle size and also the carbonization process can be examined .

NOMENCLATURE

A	Area	(m2)
C	Specific heat capacity	(J/kg/K)
h	Specific enthalpy	(J/kg)
m	Mass flow rate	(kg/s)
Q	Heat rate	(W)
T	Temperature	(°C)
SCR	Solid Core Radius	(m)

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