

Engineering

Special Topic: Energy Storage Technology and Applications

Evolution characteristics of resistance before and after the reaction of thermal chemical energy storage particle clusters in confined spaces

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Abstract: Thermochemical energy storage (TCES) systems based on the reversible $\text{CaO}/\text{Ca}(\text{OH})_2$ reaction offer significant potential for high-density heat storage. However, their long-term performance is often limited by particle agglomeration and structural degradation under confined conditions. In this study, the evolution of resistance characteristics of TCES particle clusters in confined spaces was systematically investigated through a combination of experiments and molecular dynamics (MD) simulations. A closed $\text{CaO}/\text{Ca}(\text{OH})_2$ reactor was developed to evaluate the cyclic heat storage and release behavior under mechanical confinement. Experimental results showed that, although the reactor maintained stable temperature-pressure performance over 10 cycles, progressive particle agglomeration occurred—particularly at the reactor bottom—leading to increased mass transfer resistance and extended hydration duration. Microscopic analysis revealed that 1 repeated hydration-dehydration cycles caused the fusion of $\text{Ca}(\text{OH})_2$ grains and a pronounced reduction in surface area, indicative of sintering-induced pore collapse. MD simulations demonstrated that agglomeration originates from compression-enhanced atomic diffusion and fusion of $\text{Ca}(\text{OH})_2$ particles under confinement, while CaO particles remain structurally rigid with negligible interparticle bonding. These results elucidate the multiscale mechanisms governing the evolution of structural resistance in confined thermochemical systems and provide critical design insights for mitigating agglomeration and ensuring durable cyclic performance. I

Keywords: $\text{CaO}/\text{Ca}(\text{OH})_2$, thermochemical energy storage, confined spaces, particle agglomeration

INTRODUCTION

Thermochemical energy storage (TCES) systems have emerged as a promising technology for large-scale thermal management and renewable energy utilization due to their high energy density, long-term storage capability, and negligible heat losses [1]. Unlike sensible or latent heat storage, TCES relies on reversible chemical reactions to store and release heat, thereby enabling energy storage over extended durations without significant thermal dissipation [2]. Among various candidate materials, the $\text{CaO}/\text{Ca}(\text{OH})_2$ reaction system ($\text{CaO} + \text{H}_2\text{O} \leftrightarrow \text{Ca}(\text{OH})_2 + \Delta H$) stands out because of its high reaction enthalpy ($\sim 104 \text{ kJ mol}^{-1}$), abundant raw materials, low cost, and suitable operating temperature range ($400 \text{ }^\circ\text{C}$ – $550 \text{ }^\circ\text{C}$) [3,4]. These features

make it particularly attractive for applications such as industrial waste heat recovery, solar thermal energy storage, and peak-load balancing in renewable-based power systems [5,6].

However, despite its thermochemical advantages, the long-term cyclic stability of the $\text{CaO}/\text{Ca}(\text{OH})_2$ system remains a major obstacle to practical deployment. During repeated hydration-dehydration reactions, the material often experiences particle agglomeration and macroscopic caking, which degrade the permeability of the packed bed and hinder steam diffusion [7–9]. The resulting increases in mass and heat transfer resistance lead to reduced reaction rates and lower energy storage efficiency over time. These issues are particularly critical under confined reactor conditions, where mechanical stress and limited expansion space intensify interparticle contact. Most previous studies on $\text{CaO}/\text{Ca}(\text{OH})_2$ thermochemical storage have been conducted in small, laboratory-scale reactors, typically under loosely packed or partially confined configurations [10,11]. As a result, the effect of spatial restriction and mechanical confinement on the evolution of particle structure and cluster formation has not been adequately investigated. Moreover, existing research has largely relied on macroscopic experimental characterization, while the microscopic mechanisms governing particle interactions and agglomeration dynamics remain poorly understood [12,13].

To address these challenges, recent research efforts have focused on both reactor design optimization and material modification. On the reactor side, developments have progressed from conventional fixed-bed designs to fluidized beds, mechanically assisted fluidized systems (e.g., ploughshare mixer configurations), and multilayer reactor architectures. These approaches aim to enhance heat and mass transfer through structural optimization—such as the incorporation of fins or layered arrangements—thereby alleviating pressure drop and steam diffusion limitations within the reactive bed [14–17]. From a materials perspective, strategies such as doping with inert supports or constructing core-shell structures have proven effective in suppressing sintering and improving cyclic stability [18,19]. Nevertheless, most of these studies have been carried out under idealized or semi-confined conditions. The evolution of particle agglomeration resistance under strictly confined environments—such as closed, kilogram-scale reactors operating under realistic mechanical stress and steam pressure—remains insufficiently understood, and the underlying microscopic mechanisms have yet to be systematically elucidated.

To address these limitations, this study systematically investigates the evolution of resistance characteristics of TCES particle clusters in confined spaces through a combined experimental and molecular dynamics (MD) approach. A closed, kilogram-scale $\text{CaO}/\text{Ca}(\text{OH})_2$ reactor was designed to replicate realistic mechanical confinement and vapor pressure conditions during cyclic heat storage and release. The evolution of particle morphology and surface structure before and after cycling was characterized using SEM and BET analyses to quantify agglomeration and surface area changes. In parallel, MD simulations were performed to model the nanoscale behavior of CaO and $\text{Ca}(\text{OH})_2$ particles under confined and unconfined conditions, aiming to elucidate the fundamental mechanisms driving agglomeration and its impact on the overall resistance evolution within the reactive bed.

EXPERIMENT AND MATERIALS

In this work, $\text{Ca}(\text{OH})_2$ (purity >99%) supplied by a manufacturer in Shandong, China, was used for pelletization. The initial particle size of the powder was ≥ 0.45 mm. Pelletization was carried out using a disc

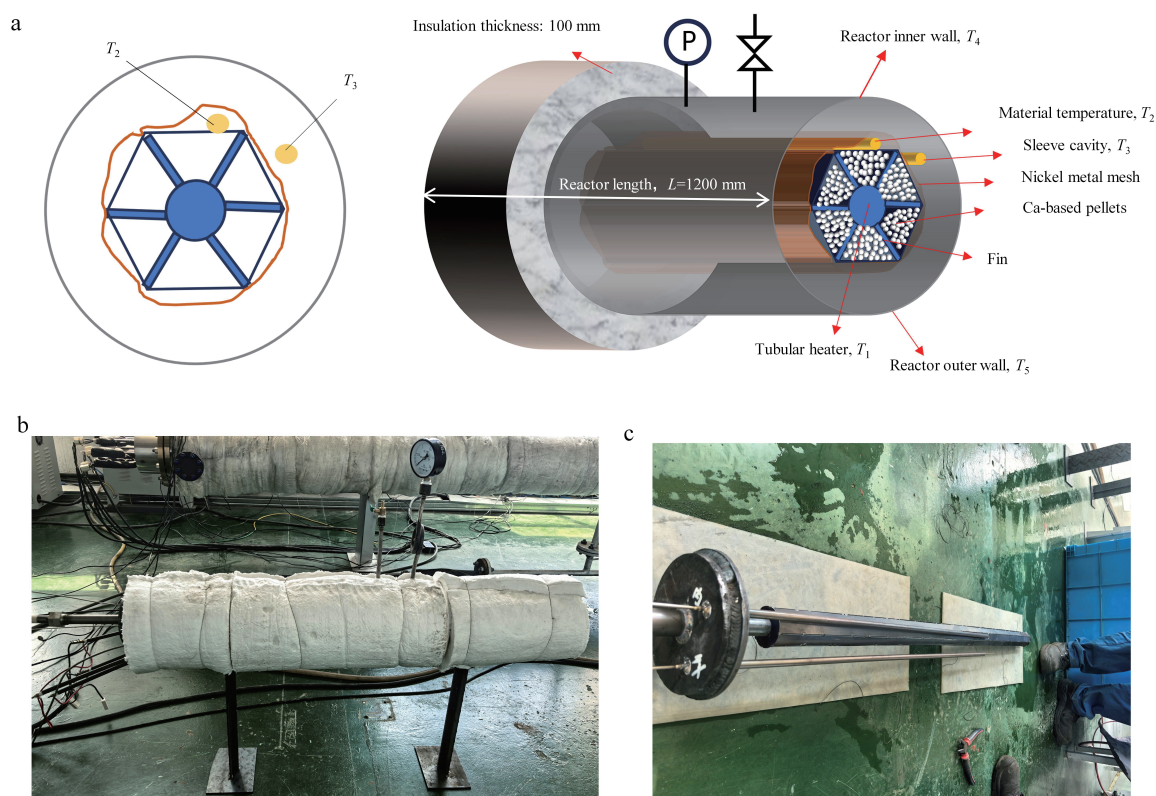


Figure 1 Schematic and photographs of the sealed reactor: (a) 3D structural diagram of the reactor, (b) photograph of the reactor with thermal insulation and instrumentation, (c) photograph of the internal reactor structure before insulation installation.

pelletizer to produce mechanically stable and uniformly sized $\text{Ca}(\text{OH})_2$ pellets. During pelletization, the $\text{Ca}(\text{OH})_2$ powder was continuously fed onto a rotating disc while a fine water mist was sprayed at a controlled rate to promote adhesion and granule growth. The disc rotation speed, inclination angle, and water addition rate were adjusted to ensure stable nucleation and subsequent layering of the powder. Through this growth-agglomeration process, spherical pellets with diameters of 2–3 mm were formed. The resulting pellets were dried at 105 °C for 12 h to remove residual moisture prior to use.

Cyclic heat storage and release experiments of the $\text{CaO}/\text{Ca}(\text{OH})_2$ system were conducted in the closed reactor, as shown in Figure 1. The reactor consists of a cylindrical shell with an overall length of 1200 mm, surrounded by a 100 mm-thick thermal insulation layer. The central hexagonal region serves as the reaction zone, which is filled with CaO-based pellet materials (with a maximum filling capacity of 1 kg). This region is enclosed by a nickel metal mesh, providing both mechanical confinement and steam permeability, thereby ensuring structural integrity while allowing vapor transport during hydration and dehydration. A tubular electric heater runs along the reactor axis to provide direct heating. The heater is equipped with metal fins, which enhance heat transfer between the heating element and the packed reactive bed. The annular cavity between the material bed and the reactor wall serves as a steam reservoir, accommodating the steam generated during dehydration and maintaining vapor circulation during hydration. The reactor is designed for a maximum operating pressure of 1 MPa, ensuring safe operation under cyclic heat storage and release conditions. To assist in cold-start operation and minimize heat loss, the outer reactor wall is equipped with

electrical heating tapes (wall-heating bands). Temperature distribution within the reactor is monitored by multiple thermocouples (T_1 – T_5) positioned at representative locations: T_1 near the heater surface, T_2 within the material bed, T_3 in the sleeve cavity, and T_4 – T_5 on the inner and outer reactor walls, respectively.

The procedures for the charging (dehydration) and discharging (hydration) processes are summarized as follows:

(1) Cold-start charging (dehydration) process

At the beginning of the experiment, the reactor was at ambient temperature. The wall-heating system was first activated with a power setting of 4.3 kW (50% of the rated capacity) to rapidly raise the wall temperature to approximately 350 °C (monitored by thermocouples T_4 and T_5). This preheating step was implemented to prevent steam condensation on the reactor walls. Subsequently, the central electric heater was switched on with an initial power of 1.31 kW (20% of the rated capacity). When the temperature at the reactor core (T_1) reached 750 °C, the system was switched to automatic temperature control mode to maintain this temperature (with an effective heating power of about 1.5 kW). During the heating process, Ca(OH)_2 decomposed into CaO and steam. Because the reactor was completely sealed, the accumulation of steam led to a continuous rise in internal pressure. The dehydration reaction was considered complete when the pressure stabilized, indicating that no additional steam was being generated.

(2) Hot-start charging process

The hot-start charging experiment was performed with the reactor already at elevated temperature. Since the wall temperature remained above 350 °C, the wall-heating system was not required. The central heater was set to 1.31 kW, and once T_1 reached 750 °C, the system was again switched to automatic temperature control. The reaction endpoint was determined in the same manner as in the cold-start case, by observing the pressure plateau that indicates completion of the dehydration process.

(3) Hot-state discharging (hydration) process

For the discharging stage, all external heat sources were switched off (both the main heater and the wall heater were set to zero power). The reactor was allowed to cool naturally. When the temperature dropped below the equilibrium point of the hydration, CaO reacted with steam present in the closed system to form Ca(OH)_2 , releasing heat in the process. The consumption of steam led to a gradual decrease in internal pressure. The hydration reaction was considered complete when the system pressure declined to atmospheric level (gauge pressure = 0).

RESULTS AND DISCUSSION

Thermal energy storage performance of CaO-based particles within the confined reactor

Figure 2(a)–(c) illustrates the temporal evolution of the temperature distribution inside the reactor and the corresponding variation in steam pressure during the heat storage process. As shown in Figure 2(a) and (b), the overall charging period lasted approximately 50–60 min. A distinct inflection point was observed at around 10 min, when the material temperature reached roughly 600 °C. According to the equilibrium reaction, Ca(OH)_2 begins to decompose at approximately 550 °C under atmospheric conditions [20]. Once the temperature exceeded 600 °C, the material absorbed additional sensible heat and entered an accelerated decomposition stage. This transition is corroborated by the sharp rise in system pressure after 10 min, as

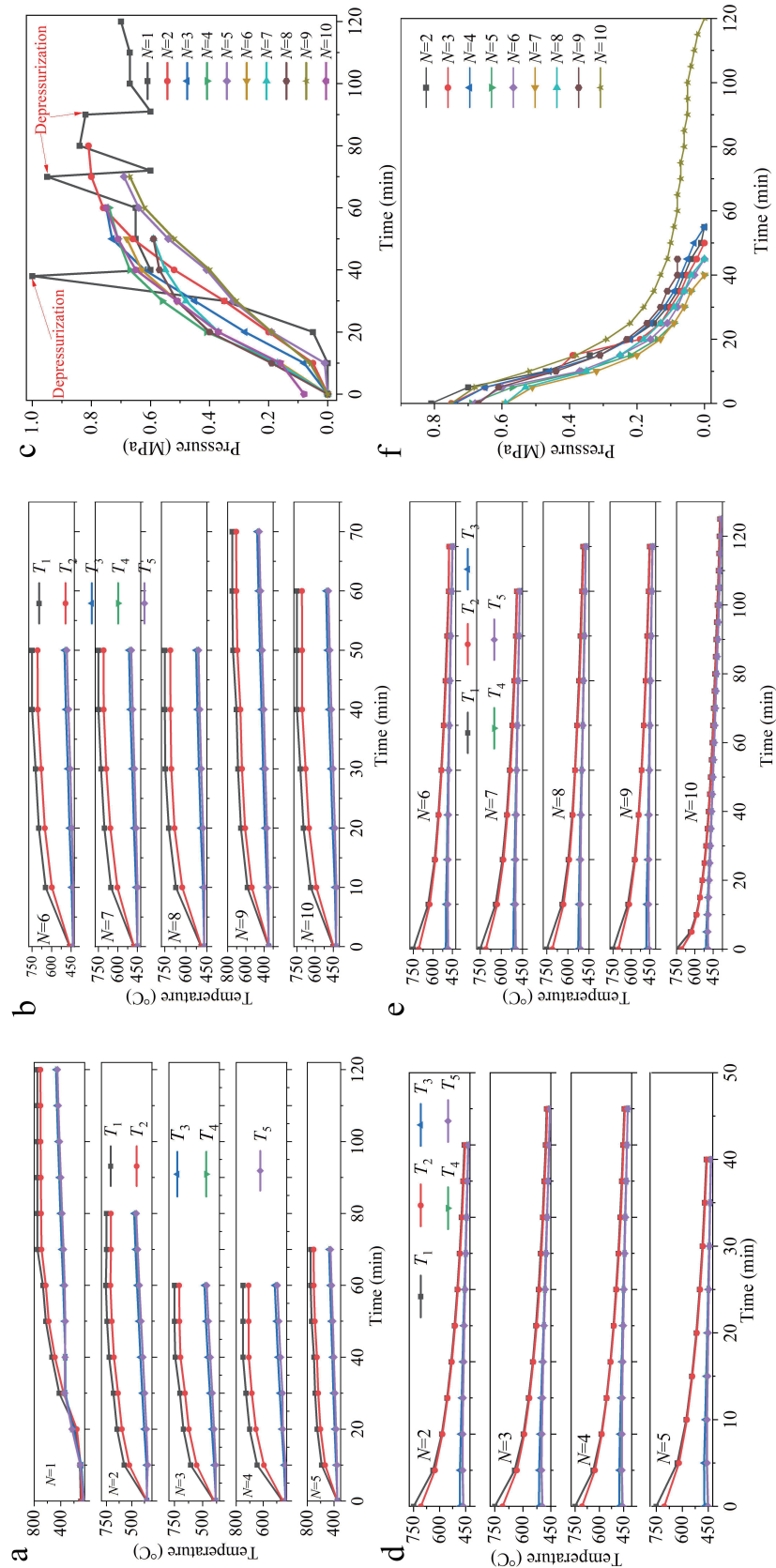


Figure 2 Temperature and pressure in the reactor during the charging/discharging phases: (a) temperature during the 1st–10th charging stages, (b) temperature during the 6th–10th charging stages, (c) pressure during the 6th–10th charging stages, (d) temperature during the 1st–5th discharging stages, (e) temperature during the 2nd–5th discharging stages, (f) pressure during the 6th–10th discharging stages.

depicted in Figure 2(c). During the 1st charging cycle ($N = 1$), the pressure increase inside the reactor was markedly faster than that in subsequent cycles. This behavior is attributed to the thermal expansion of residual air within the reactor and the connecting pipelines during heating. Through controlled venting operations, non-condensable gases were effectively purged, allowing the following cycles to proceed under a nearly pure steam atmosphere. By the 10th charging cycle, the maximum system pressure reached 0.75 MPa at 60 min, nearly identical to the 0.76 MPa recorded during the 2nd cycle. This consistency indicates that the maximum operating pressure remained stable throughout repeated operation, demonstrating the excellent integrity and airtightness of the closed system. Throughout the entire charging process, the electric heating power was maintained steadily at 1.5 kW, corresponding to a specific surface heat flux of approximately 1.5 W cm^{-2} . This level of heat flux confirms that the CaO bed, in combination with the finned-tube heater design, can effectively withstand and transfer heat of this magnitude. These findings provide a valuable technical reference for the scale-up and thermal optimization of future TCES reactors.

The temperature profiles at various measurement points and the corresponding steam pressure evolution during the 10 hydration cycles are shown in Figure 2(d) and (e). As the reactor cooled naturally, the bed temperature reached the equilibrium point of the hydration, initiating the exothermic conversion of CaO to Ca(OH)_2 . As illustrated in Figure 2(e), the hydration reaction lasted for approximately 60 min. During the first 20 min, the internal pressure decreased sharply with falling temperature, indicating a vigorous hydration stage. When the pressure dropped below 0.2 MPa, a clear inflection appeared in the pressure-time curve, signifying a transition to a slower reaction rate as the system approached equilibrium. Consequently, maintaining the reactor pressure above 0.2 MPa during the exothermic stage is essential to sustain a high hydration conversion efficiency. It is noteworthy that, although complete hydration was achieved in all 10 cycles, the reaction duration in the 10th cycle extended to approximately 120 min, which was significantly longer than that in the previous 9 cycles. This slowdown is likely attributed to the gradual expansion of the reactive material during repeated hydration-dehydration cycles, which may have hindered steam diffusion within the packed bed [21].

The morphologies of the particles after 10 cycles are shown in Figure 3. The particles collected from the upper and peripheral regions of the reactor exhibited brownish and greenish discoloration, as shown in Figure 3(d) and (e). Furthermore, the localized corrosion spots were observed on the inner wall near the reactor edges, as depicted in Figure 3(b). The reactor vessel was made of stainless steel (mainly composed of Fe, Cr, and Ni). The discoloration of the particles is therefore presumed to result from metal corrosion and elemental migration from the reactor wall under the steam atmosphere. Energy-dispersive X-ray spectroscopy (EDS) analysis of the samples (Figure 3(f)) confirmed this assumption. The green particle contained 4.21 wt% Cr and 0.30 wt% Ni, whereas the brown particle contained 0.35 wt% Cr and 0.15 wt% Ni. In contrast, the white particles collected from the bottom of the reactor contained only trace amounts of Ni. These findings indicate that CaO can induce corrosion of stainless-steel surfaces during repeated hydration-dehydration cycles. Therefore, corrosion-resistant design and material selection should be carefully considered in future reactor development to ensure long-term durability under high-temperature steam environments.

As shown in Figure 3(c), noticeable particle deformation and agglomeration occurred at the bottom of the reactor after 10 cycles. It has been proven that CaO-based materials tend to undergo sintering and agglomeration during CaO/Ca(OH)_2 TCES processes [22]. Such phenomena can significantly impede steam diffusion within the packed bed and consequently reduce the overall reaction efficiency. The agglomeration

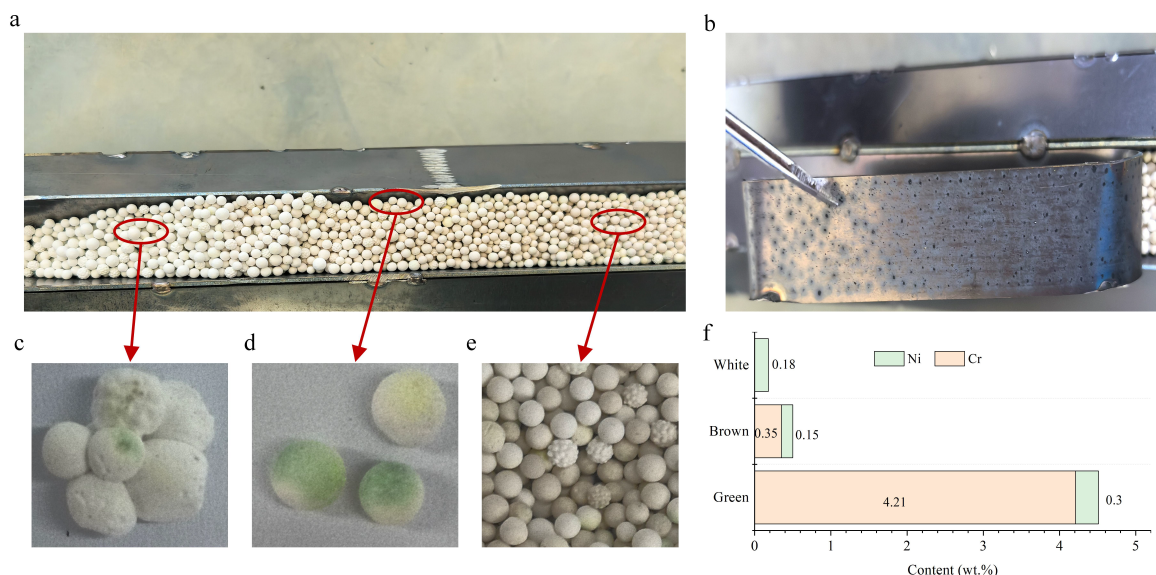


Figure 3 (a) Reactor packed with CaO-based particles, (b) corroded reactor wall, (c) agglomerated particles, (d) green corroded particles, (e) brown corroded particles, (f) elemental composition of the particles.

is closely associated with the cyclic volumetric expansion and contraction of the material during the hydration-dehydration cycles [23]. The molar volume of CaO is approximately $16.7 \text{ cm}^3 \text{ mol}^{-1}$, whereas that of Ca(OH)_2 is $33.5 \text{ cm}^3 \text{ mol}^{-1}$ [12]. In a confined reactor space, the expansion of the material during hydration is constrained by the reactor walls, forcing particles into closer contact. Under high-temperature conditions, this enhanced contact promotes interparticle bonding and sintering, ultimately leading to agglomerate formation. This effect is particularly pronounced at the bottom of the reactor, where particles not only experience radial confinement from the reactor walls but also bear the mechanical load of the overlying bed. Consequently, particle agglomeration is most severe in this region.

Microscopic morphology of Ca-based particles during cycles

As shown in Figure 4, the morphology of Ca(OH)_2 particles undergoes significant evolution after cycles. Before cycling, the particles exhibit well-defined hexagonal prismatic crystals with distinct boundaries and a loosely packed arrangement, indicating high crystallinity and surface openness. After 10 cycles, the originally discrete hexagonal grains fuse together, forming dense agglomerates with blurred grain boundaries. This morphological transition reveals that sintering and recrystallization occur during the repeated phase transformations. As shown in Figure 4(c), the BET surface area decreased dramatically from 18.1 to $3.8 \text{ m}^2 \text{ g}^{-1}$ after 10 cycles, confirming that the fusion of Ca(OH)_2 grains leads to the collapse of pore structures and loss of reactive surface area.

MD simulation of CaO-based particle agglomeration in the confined space

MD simulations were performed to investigate the agglomeration behavior of the CaO/Ca(OH)_2 system under confined conditions. In practical systems, particle surfaces are inherently rough, and interparticle

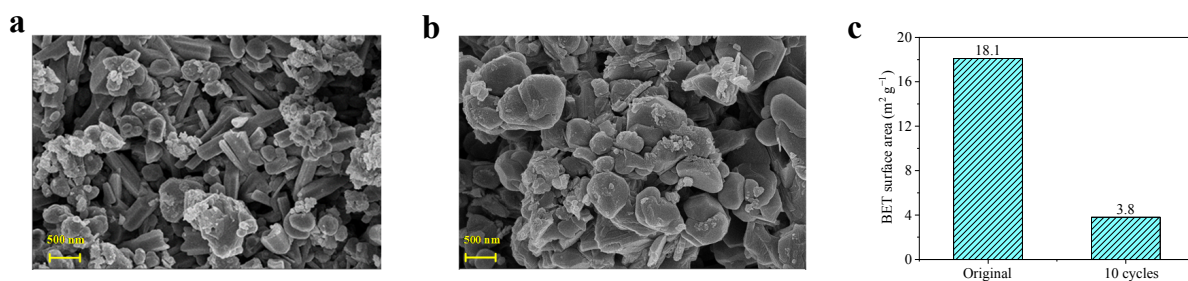


Figure 4 SEM images and BET surface area of particles during 10 cycles: (a) SEM of original particles, (b) SEM of particles after 10 cycles, (c) BET surface area during 10 cycles.

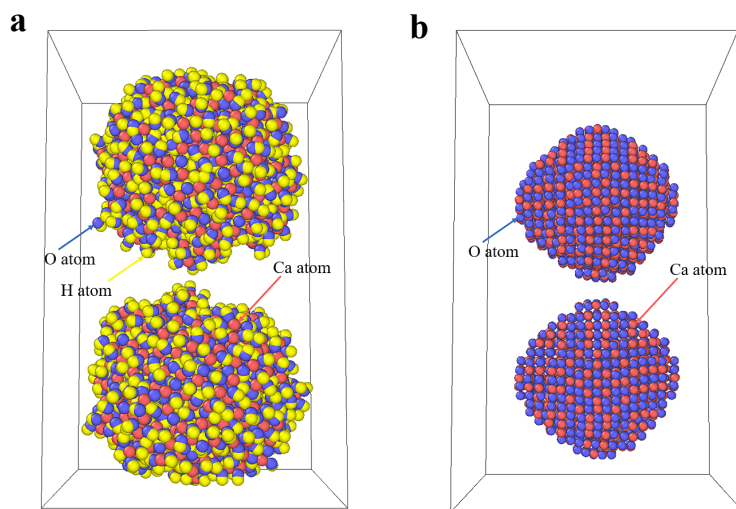


Figure 5 Initial configuration of CaO/Ca(OH)₂ particles: (a) Ca(OH)₂, (b) CaO.

bonding is initiated at the protruding asperities where contact occurs. These surface asperities typically range in size from a few nanometers to several hundred nanometers. To reduce computational cost while preserving the essential physics of the contact process, spherical CaO/Ca(OH)₂ nanoparticles with a diameter of 8 nm were employed to represent these asperities in the simulations. The initial configuration of the particle system is illustrated in Figure 5. To model the mechanical constraint experienced by particles within a confined environment, an inward compressive force was applied to drive the particles toward the center, thereby simulating the external pressure exerted by the reactor walls and surrounding particles in the packed bed. For comparison, simulations were also conducted under free-space conditions, in which the particles were not subjected to external pressure and interacted solely through van der Waals forces.

In this work, the ReaxFF reactive force-field parameters for the Si/Al/Ca/O/H system developed by Pitman and van Duin [24] were employed. This force field has been validated for accurately describing both dehydration and hydration. The computational procedure was as follows: the system was first relaxed in the NVT ensemble at 300 K for approximately 10 Ps with a time step of 0.1 fs to minimize the energy of the initial structure and eliminate any overlap or excessively close contacts. Subsequently, simulations were performed in the NVT ensemble at the target temperature for 100 Ps using the same time step. System trajectories were recorded every 0.1 Ps.

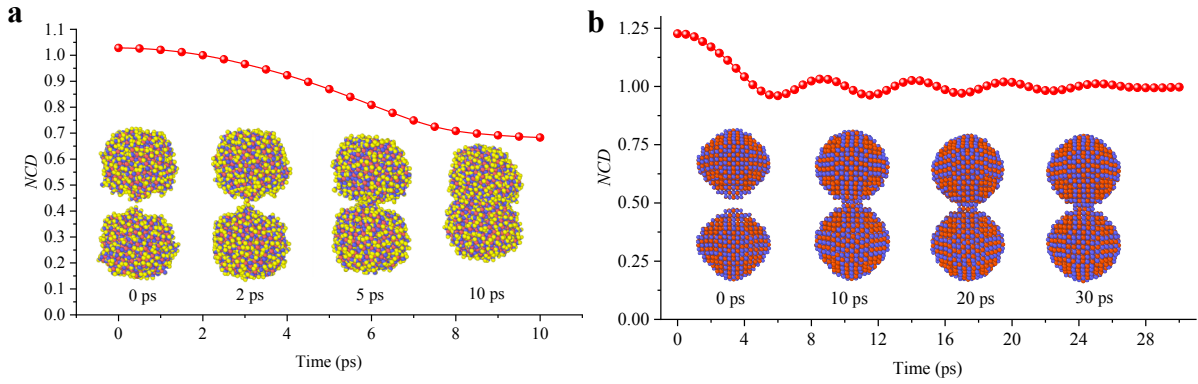


Figure 6 NCD and molecular snapshots of Ca(OH)₂/CaO particles in a confined space: (a) Ca(OH)₂, (b) CaO.

The normalized centroid distance (NCD) was used to describe the degree of deformation in spheres and was calculated by Eq. (1).

$$\text{NCD} = \frac{\text{MCD}}{(r_1 + r_2)}, \quad (1)$$

where MCD is the centroid distance between spheres, Å; r_1 and r_2 represent the radii of the two spheres, Å.

The agglomeration behavior of Ca(OH)₂ and CaO particles in confined spaces is described by NCD, as illustrated in Figure 6. The NCD between two Ca(OH)₂ particles gradually decreased from 1.05 to 1.00 during the initial 0–2 Ps, indicating that the particles came into physical contact. Between 2–8 Ps, the NCD value dropped rapidly to 0.7, and the accelerated decline suggests that particle fusion occurred rapidly under the applied external pressure. An NCD value below unity confirms the occurrence of particle coalescence. After 8 Ps, the NCD value remained nearly constant, implying that the particles had completely merged and reached structural stability. The corresponding molecular snapshots in Figure 6(a) provide visual confirmation of this process. During 0–2 Ps, the Ca(OH)₂ particles gradually approached each other under compression. At 2 Ps, physical contact occurred, and a neck region began to form at the point of contact. From 2–8 Ps, the neck expanded rapidly, and the two particles fused into a single structure. After 8 Ps, the particles were almost entirely coalesced, indicating complete fusion. Figure 6(b) presents the agglomeration behavior of CaO particles under the same confined conditions. The NCD distance of the CaO particles decreased from 1.23 to 1.00 within 0–5 Ps, indicating initial contact between particles. However, during 5–30 Ps, the NCD value remained approximately constant at 1.0, suggesting that no further fusion occurred. The minor fluctuations observed in the NCD between 4–20 Ps are attributed to elastic collisions and rebound of the CaO particles, rather than agglomeration.

The mean-square displacement (MSD) of an atom is defined as the squared distance it travels over time, providing a quantitative measure of its diffusive motion. The MSD was calculated according to Eq. (2),

$$\text{MSD} = |r(t) - r(0)|^2, \quad (2)$$

where MSD represents the mean-square displacement, Å²; $r(t)$ denotes the atomic position at time t , and $r(0)$ is the initial atomic position. $|r(t) - r(0)|$ corresponds to the displacement of the atom from its initial position at $t = 0$ to time t .

The atomic mobility of Ca(OH)₂ and CaO particles in the confined spaces was further analyzed through their MSD and atomic displacement vector distributions, as shown in Figure 7(a) and (b). As illustrated in

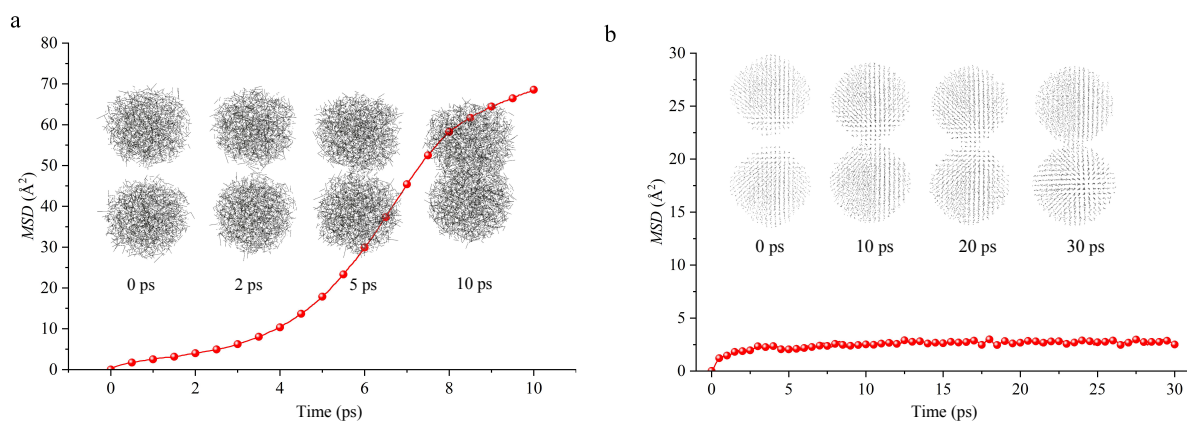


Figure 7 Mean-square-displacement and atomic displacement vector distributions of $\text{Ca(OH)}_2/\text{CaO}$ particles in a confined space: (a) Ca(OH)_2 , (b) CaO .

Figure 7(a), the MSD of Ca(OH)_2 increased slowly during the initial 0–2 Ps, indicating limited atomic diffusion within the particles. At this stage, the particles were merely approaching each other under external compression without significant atomic exchange. However, the MSD rose sharply in 2–8 Ps, signifying accelerated atomic migration. This behavior corresponds to the formation and rapid growth of a neck region at the particle contact point, where interdiffusion of atoms across the interface leads to progressive particle fusion. After 8 Ps, the MSD growth rate decreased, suggesting that the fusion process had reached completion, and further diffusion was primarily associated with local atomic rearrangements within the newly formed fused grain. Analysis of the atomic displacement vectors reveals that atoms within the Ca(OH)_2 particles exhibit random, fluid-like diffusion during compression. This enhanced atomic mobility allows the material to deform plastically, promoting close interparticle contact and subsequent fusion once the particles touch. As a result, Ca(OH)_2 exhibits a strong tendency toward coalescence and agglomeration in confined spaces.

In contrast, Figure 7(b) shows that the MSD of CaO particles remains extremely low throughout the simulation. Even when the particles come into close contact, no significant atomic diffusion or fusion is observed. The atomic displacement vectors indicate that atoms within CaO primarily oscillate near their lattice sites, reflecting a rigid crystalline structure with limited atomic mobility. Consequently, CaO particles exhibit negligible agglomeration or coalescence under similar confinement conditions. These findings highlight the fundamental difference between the two phases: the agglomeration of CaO -based thermochemical materials arises predominantly from the compression-induced atomic diffusion and fusion of Ca(OH)_2 particles, rather than from CaO . The higher atomic mobility and plasticity of Ca(OH)_2 enable the formation of interparticle necks and eventual particle coalescence, whereas the rigid lattice of CaO prevents such diffusion-driven bonding. This distinction provides important mechanistic insight into the microstructural evolution of $\text{CaO}/\text{Ca(OH)}_2$ systems during repeated hydration–dehydration cycles and underscores the need for structural and operational strategies to mitigate agglomeration in thermochemical reactors.

The agglomeration behavior of Ca(OH)_2 particles in free space was further investigated, as shown in Figure 8. During the initial 0–30 Ps, the NCD between the two particles decreased from 1.13 to 1.00, indicating that the particles gradually approached each other under the influence of van der Waals attraction. However, compared with the confined condition, the approach and contact process was significantly slower, ap-

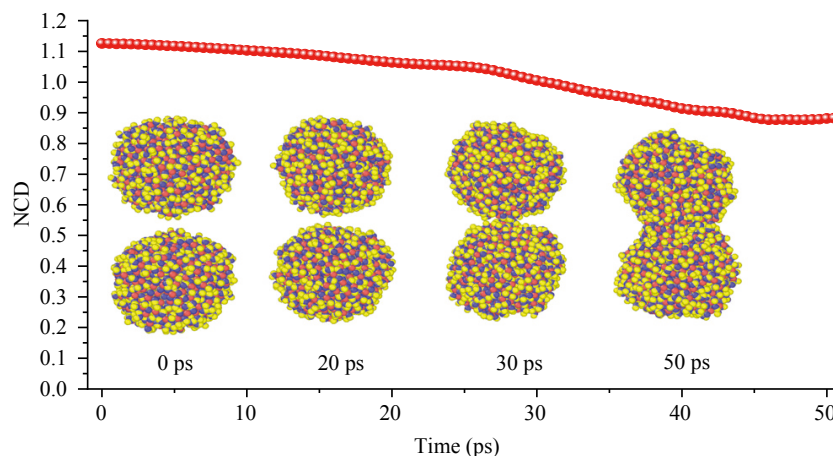


Figure 8 NCD and molecular snapshots of $\text{Ca}(\text{OH})_2$ particles in free space.

proximately 15 times longer before physical contact occurred. Moreover, the subsequent fusion process was also delayed, with the particle coalescence slowing markedly after around 50 ps. These results demonstrate that the absence of confinement substantially reduces the frequency and intensity of interparticle collisions, resulting in weaker compression and slower atomic diffusion at the contact interface. Consequently, spatial confinement plays a key role in accelerating the agglomeration and fusion of $\text{Ca}(\text{OH})_2$ particles.

CONCLUSION

In this study, the cyclic heat storage and release experiments were performed using a closed $\text{CaO}/\text{Ca}(\text{OH})_2$ reactor system, complemented by MD simulations to elucidate the mechanisms of particle agglomeration under confined conditions. The results demonstrate that mechanical confinement plays a decisive role in promoting particle agglomeration and caking, leading to increased mass transfer resistance and extended reaction duration during long-term operation. Morphological characterization confirmed the progressive fusion of $\text{Ca}(\text{OH})_2$ grains and the associated loss of surface area, while MD simulations revealed that the confinement-induced compression enhances atomic diffusion and interparticle adhesion of $\text{Ca}(\text{OH})_2$, in contrast to the structural rigidity and non-cohesive nature of CaO . These findings provide fundamental insight into the mechanisms governing the evolution of structural resistance in confined thermochemical systems and offer practical guidance for the design of high-stability reactors and operation strategies to mitigate agglomeration and maintain durable energy storage performance.

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