

CaO/Ca(OH)₂ thermochemical heat storage of carbide slag from calcium looping cycles for CO₂ capture

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ABSTRACT

Carbide slag is an industrial waste generated from ethylene gas production in chlor-alkali plants. Here, a novel system coupling calcium looping and CaO/Ca(OH)₂ thermochemical heat storage using carbide slag were proposed to simultaneously capture CO₂ and store heat. For CaO/Ca(OH)₂ thermochemical heat storage, the hydration/dehydration performance of original carbide slag and carbide slag that experienced calcium looping cycles for CO₂ capture was investigated. The performances of the two types of carbide slag with and without chlorine were compared. The dehydration conversions of carbide slag improved with the increase of dehydration temperature. The chlorine content has no apparent effect on the hydration/dehydration performance of original carbide slag. However, for CO₂ capture, carbide slag with high chlorine content shows lower carbonation conversion than that of carbide slag without chlorine. The hydration/dehydration conversions of carbide slag that experienced CO₂ capture cycles are lower than those of original carbide slag. For carbide slag with chlorine, the hydration conversion can be improved by more than one CO₂ capture cycle. Therefore, carbide slag that experienced various CO₂ capture cycles is still suitable to be used in CaO/Ca(OH)₂ thermochemical heat storage although calcium looping has an adverse effect on the hydration/dehydration performance of carbide slag.

1. Introduction

Solar energy, which is the largest and widely distributed energy source worldwide, has been utilized for decades and has been widely used in concentrated solar power (CSP) plants [1,2]. Heat storage is crucial in CSP plants due to the intermittent and instability of solar radiation [3]. Heat storage can be divided into sensible heat storage (SHS), latent heat storage (LHS), and thermochemical heat storage (THS) [4]. SHS has been widely used in industrial production. However, the low energy densities of materials and high heat loss have seriously hindered its development [5]. Table 1 lists the energy densities of several commonly used materials for heat storage. Table 1 shows that the materials used for THS have higher energy density than the materials used for SHS or LHS. On this basis, THS is a promising heat storage in CSP plants.

Materials used for THS can be divided into six types, namely, metal hydride, redox system, organics, carbonate, ammonia decomposition system, and inorganic hydroxide [10]. The decomposition of inorganic hydroxides occurs at 523–873 K, which is suitable for medium-

temperature heat storage. The commonly used inorganic hydroxides are Ca(OH)₂/CaO, Mg(OH)₂/MgO, Ba(OH)₂/Ba, and Sr(OH)₂/SrO [10]. CaO has been regarded as one of the most promising materials for THS [11]. A cycled CaO/Ca(OH)₂ THS is based on the dehydration reaction of Ca(OH)₂ (as shown in Eq. (1)) to store heat and hydration reaction of CaO (as presented in Eq. (2)) to release heat. Initially, Ca(OH)₂ absorbs solar energy and decomposes into CaO and H₂O in a solar dehydrator. The generated CaO and H₂O are stored in CaO and H₂O storage tanks, respectively. CaO and H₂O are transferred to a hydrator and react with each other to release the stored heat, and Ca(OH)₂ is regenerated. Ca(OH)₂ is stored in a Ca(OH)₂ storage tank and is transported back to the solar dehydrator for the next cycle [12].



However, CaO-based materials used for CaO/Ca(OH)₂ THS have poor mechanical properties. It is reported that CaO/Ca(OH)₂ crystallites tend to suffer from severe fragmentation [13] and attrition [14] after

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Table 1
Energy densities of some materials for heat storage.

Type	Material	Energy density (MJ/m ³)	Reference
SHS	Silicone oil	189	[6]
SHS	Nitrite salts	548	[6]
SHS	Nitrate salts	898	[6]
SHS	Carbonate salts	1512	[6]
SHS	Liquid sodium	287	[6]
LHS	Sodium nitrite	373	[6]
LHS	Sodium nitrate	389	[6]
LHS	Potassium nitrate	561	[6]
LHS	Sodium carbonate	701	[7]
THS	FeO/CO ₂	2600	[8]
THS	CaO/H ₂ O	3000	[6]
THS	CaO/CO ₂	4400	[6]
THS	NH ₄ HSO ₄ /NH ₃	3082	[9]
THS	SrO/CO ₂	3948	[9]

multicycle hydration and dehydration reactions. Given that the CaO-based materials with poor mechanical properties are in contact with a large flow of steam or air in CaO/Ca(OH)₂ THS, they can be entrained by the flow of steam or air, which results in a rapid decrease of their hydration/dehydration performances. Azpiazu et al. [15] confirmed that CaO/Ca(OH)₂ in hydration and dehydration reactions only maintained good activity in the first 20 cycles. This is the main drawback of CaO/Ca(OH)₂ THS. Many researchers have investigated various precursor materials doping in CaO-based materials to enhance the structural integrity of materials, such as aluminum oxide (Al₂O₃) [12], Na₂Si₃O₇ [16], nanoparticles [17,18], and LiOH [19]. In addition, different types of industrial reactors, such as fixed bed and circulating fluidized bed (CFB) reactors, can be used for CaO/Ca(OH)₂ THS. The thermal conductivity improvement of the reactor provides an important foundation for the implementation of CaO/Ca(OH)₂ THS. CFB reactors have better thermal conductivity than fixed bed reactors under the same temperature and atmosphere, which have attracted wide attention [20,21].

Carbon capture and storage technology has been considered an effective means to reduce the effect of global warming that is caused by CO₂ emissions from coal-fired power plants [22]. Calcium looping,

namely, carbonation/calcination cycles of CaO derived from limestone and dolomite precursors, is considered a promising technology to capture CO₂ from coal-fired power plants [23]. CO₂ in flue gas from coal-fired power plants is transported to a carbonator where CO₂ is captured by CaO at 600–700 °C to form calcium carbonate (CaCO₃) (as shown in Eq. (3)). CaCO₃ is sent to a calciner where it decomposes into CaO and CO₂ at 850–950 °C (as presented in Eq. (4)). Oxy-fuel combustion is usually used to provide the heat for the calciner to achieve high CO₂ concentration (> 95 vol%) in the calciner. The generated CaO in the calciner returns to the carbonator for the next CO₂ capture cycle [24]. Considerable deactivated CaO are discharged from the calciner. Meanwhile, the fresh CaO-based sorbent is added to the calciner.



Carbide slag (denoted by CS) is an industrial waste generated in the production of ethylene gas (C₂H₂). C₂H₂ is the raw material of polyvinyl chloride (PVC). The main composition of CS is Ca(OH)₂. Approximately 1.5–1.9 t of CS is generated by the production of 1 t of PVC in a chlor-alkali plant in China [25]. Most CS is usually landfilled near the chlor-alkali plants, which causes serious environmental pollution and land waste. Perejón et al. [26] reported that the CaO derived from treated steel slag with acetic acid could reach up to a stable carbonation conversion of approximately 0.8 in the successive carbonation/calcination cycles for CaO/CaCO₃ THS. Valverde et al. [27] confirmed that filtration could remarkably mitigate pore plugging which resulted in the high and stable multicycle performance of treated steel slag with acetic acid. Currently, steel slag is only reported for CaO/CaCO₃ THS. Few studies have been reported on CaO/Ca(OH)₂ THS based on steel slag or CS. In fact, several impurities are found in CS, except for Ca(OH)₂, such as Al₂O₃ and SiO₂. Sakellariou et al. [12] determined that the increase of Al content in CaO-based materials could improve the macroscopic integrity. Criado et al. [16] validated that the crushing strength of modified CaO particles with Si-based materials was 3 times higher than that of unmodified CaO particles, which could improve the sustainability of the cyclic hydration/dehydration reactions. These results validate that the existence of Al₂O₃ and Si-based materials in CS maybe contributes to high and stable hydration/dehydration performances.

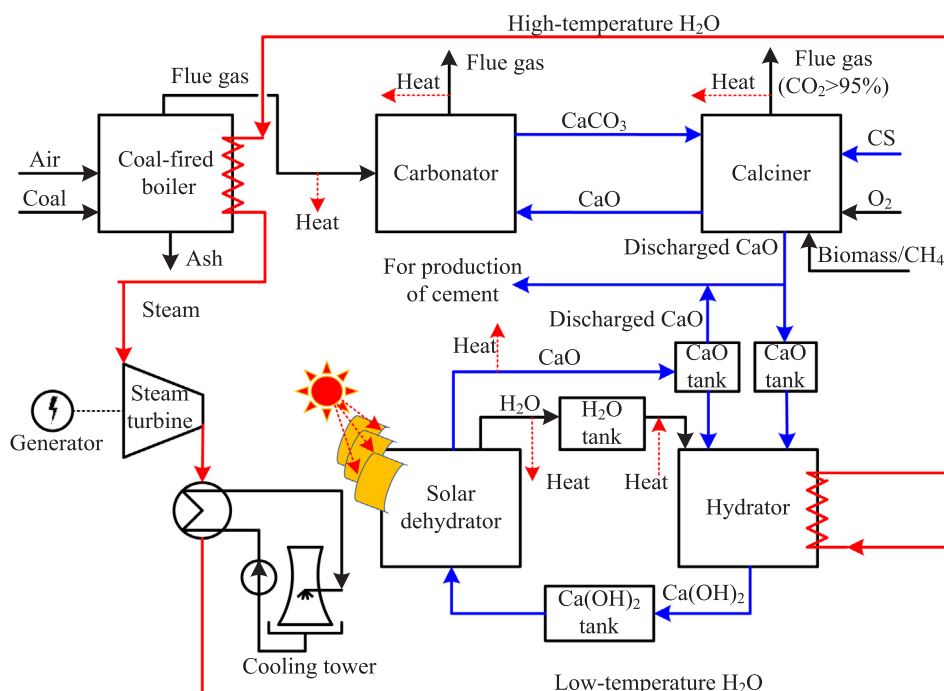


Fig. 1. Schematic diagram of novel system coupling calcium looping process and CaO/Ca(OH)₂ THS process using CS.

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