

Large-scale storage of Concentrated Solar Power from industrial waste

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Abstract

Deep penetration of renewable energies into the grid relies on the development of large-scale energy storage technologies using cheap, abundant and non-toxic materials. Concentrated Solar Power (CSP) is particularly suitable to massively store thermal energy for dispatchable electricity generation. This is currently accomplished in a few demonstration plants by using molten salts albeit in a not competitive way yet. Process simulation studies indicate that thermochemical energy storage of CSP by means of the Calcium Looping (CaL) technology would reduce the cost of storage and increase the flexibility of energy supply provided that widely available and cheap CaO precursors with high and stable multicycle activity are used. In this work, we investigate the behavior of Calcium rich steel slag at CaL conditions that would expectedly maximize the efficiency of CSP energy storage and power production. When treated with acetic acid, this non-toxic widely abundant waste yields a CaO rich solid with stable conversion near 0.8 over successive carbonation/calcination cycles at these CaL conditions.

Keywords: Steel slag, Thermochemical Energy Storage, Calcium Looping, Concentrated Solar Power, CaO precursor

1. Introduction

Commercial deployment of renewable energy technologies at large scale is urgently needed for limiting global warming to 2.0°C (in 2100) above pre-industrial levels as agreed at the 21st Conference on Climate Change COP21. Main renewable energy technologies (solar and wind) will not achieve a high degree of penetration in the power grid unless large-scale energy storage technologies are developed based on cheap, abundant and non-toxic materials.¹⁻⁴ Concentrated Solar Power (CSP) with central tower technology lends itself to large-scale storage of energy in a primary form as high temperature heat for the efficient generation of electricity on demand.⁵⁻⁶ In this technology, a set of mirrors (heliostats) are distributed on the ground and properly oriented to concentrate solar radiation in a target receiver located in the top of a tower where achievable temperatures can reach up to 1000 °C.⁷⁻⁹ From the perspective of large scale energy storage, a great advantage of CSP is that thermal energy can be stored in low cost materials with high specific heat capacity.

In currently commercial CSP plants with energy storage heat is transferred in the solar receiver to a fluid consisting of a mixture of nitrate salts, mainly sodium nitrate and potassium nitrate (solar salt).¹⁰ Heat storage in solar salts allows typically for power generation for a time period up to 15 hours in the absence of solar radiation with an initial cost estimated at around 5.2 €/Kwh, which makes this technology a relatively inexpensive option as compared to other energy storage technologies such as lithium batteries, with an initial cost over 200 €/Kwh.¹¹ However, the efficiency of thermoelectric conversion in CSP plants with thermal energy storage in solar salts is severely hindered by the degradation of the solar salt at about 550°C. Moreover, high freezing points (~100-220°C) and corrosiveness of solar salts are serious issues that rise capital as well as operation and maintenance costs of the technology.¹²⁻¹³

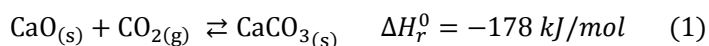
Steel slag has been recently proposed for storing energy in the form of sensible heat in CSP.¹⁴⁻¹⁵ This non-toxic and abundantly available industrial waste presents a similar heat capacity to solar salts as well as other benefits such as a high thermal conductivity and thermal stability up to much higher temperatures as compared with solar salts, which would reduce the cost of energy storage and enhance the efficiency of electric generation. In 2010, the production of slag in the

EU amounted to 21.8 million tons. About 76% of this industrial residue is used in applications such as road construction, cement production and hydraulic engineering. The rest is deposited in landfills.¹⁵⁻¹⁶ According to CSP growth perspectives, the amount of slag deposited in landfills could be enough to be used as thermal energy storage material in CSP plants planned for construction until 2050.¹⁷ Thus, the valorization of steel slag for storage applications of sensible heat in CSP plants has an enormous potential.¹⁵

Another method for heat storage in CSP plants currently investigated at laboratory scale and simulations level is thermochemical energy storage (TCES).¹⁸⁻²¹ TCES is based on the use of the potentially high temperatures achievable in the solar receiver to drive an endothermic chemical reaction. The reaction products are stored separately to be brought together on demand at conditions for the reverse exothermic reaction to occur, which releases the heat previously used to induce the endothermic reaction. The main advantages of TCES as compared to thermal energy storage (TES) are a considerably higher density of stored energy and the possibility of storing energy permanently without losses.

CaL-CSP integration

One of the most promising options to integrate TCES in CSP plants with central tower technology is the Calcium Looping (CaL) process, based on the carbonation/calcination reaction of CaO:²²⁻²⁵



Energy density of the CaO/CO₂ system is around 3.2 GJ/m³ in the solid as compared to 0.8 GJ/m³ for molten salts currently used in commercial plants. An integration scheme recently proposed elsewhere²¹ for coupling the CaL process into CSP tower plants is presented in Figure 1. Basically, the scheme comprises a solar calciner, a CO₂ compression train, a CO₂ storage tank, two solid reservoirs (for CaO and CaCO₃ storage), a carbonator and a power unit. The energy required for the CaCO₃ endothermic decomposition is provided by direct solar radiation

in the calciner under a gas separable from the released CO₂ such as superheated steam or He. The CO₂ produced is then stored in a tank whereas the stream of CaO solids is cooled to room temperature and stored in a reservoir. On demand, the reaction products are circulated into a carbonator reactor in order to release the energy stored in chemical form through carbonation at high temperature and under high CO₂ pressure. The heat of this reaction is delivered to a CO₂ closed loop directly coupled to a gas turbine where the excess CO₂ that does not participate in the carbonation reaction acts as heat carrier and is used through a Joule-Brayton cycle to produce electric power.²¹ High energy integration efficiencies can be achieved according to this scheme by an optimized heat exchanger network. Commercially available tanks can be used to store CO₂ at supercritical conditions and room temperature for a 12 hours daytime 100 MWth CSP plant.²¹ Thus, a minimum pressure of 65 bar would be needed in order to guarantee supercritical CO₂ storage conditions at ambient temperature ($T = 25^{\circ}\text{C}$). To this end, the use of several commercially available tanks would allow the required size of storage volume ($\sim 700 \text{ m}^3$ at 25°C and 65 bar for a 100 MWth CSP plant).²¹ These tanks would occupy a reduced area as compared to the large surface area which is available in a tower CSP plant. One of the main advantages of the CSP-CaL integrated system is that it enables decoupling solar availability and electric power generation, with a thermal-to-electric efficiency of about 45% predicted for a stable CaO conversion $X_r = 0.5$, which may be even improved as the residual value of CaO conversion is further increased.²¹ It must be noted however that efficiency in ref. [21] has been calculated without including some sources of energy loss such as receiver losses or the work needed to separate the gas used in the calciner environment from the CO₂ released by decarbonation. The interested reader is referred to ref. [21] for further details on this CSP-CaL integration scheme.

Regarding the estimated costs for the use of the CaL process in CSP plants, technology and cost objectives for solar field, receiver, thermal storage/HTF, and power block necessary to achieve the US DOE SunShot program target for 2020 (LCOE 0.06\$/kWh) have been shown in ref. [26] This goal would imply a thermal storage cost lower than 15€/KWth, which could be potentially reached by using the CaL process for thermochemical energy storage as reported in ref. [27].

Nevertheless, it must be remarked that the CSP-CaL integration is yet under a concept stage and a techno-economic detailed analysis, which is far beyond the scope of this work, is still lacking. The objective of the present work is to investigate the multicycle performance of Ca rich steel slag pretreated with acetic acid at CaL conditions that maximize the efficiency of energy storage and power production in CSP plants according to the energy integration study reported in ref. [21]. These conditions involve carbonation at high temperature under high CO₂ concentration whereas calcination is performed at relatively low temperature.

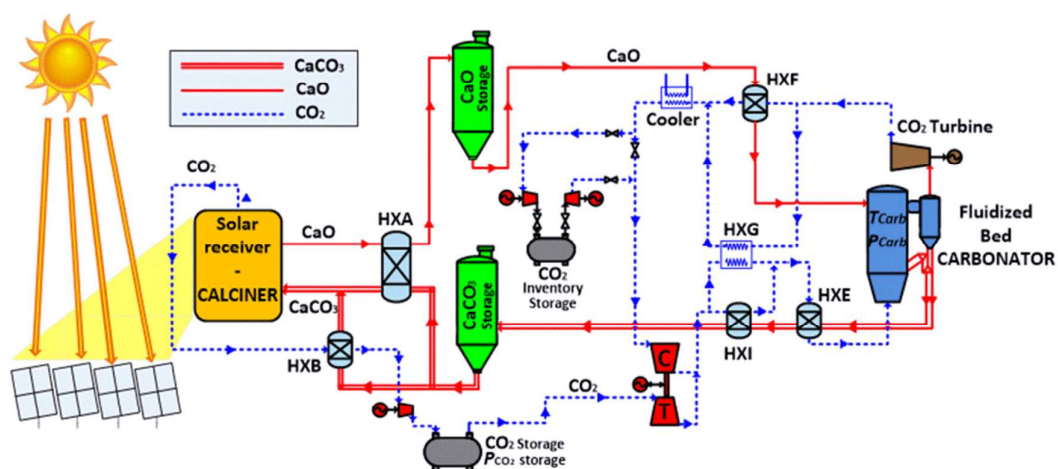


Figure 1. CaL thermochemical energy storage and power production system for concentrated solar power plants with tower technology recently proposed in ref. [21]. The interested reader on technical details about this integration is referred to that work.

2. Experimental

Powdered steel slag from Acerinox Europe S.A.U. (Los Barrios, Spain) has been employed as raw material from which two different samples were prepared. For the first one, powdered steel slag was mixed with dilute acetic acid (VWR Chemicals, 99.9% pure), 25 wt. % in aqueous solution and the mixture (50 mL of diluted acid per gram of slag) was magnetically stirred for 2 hours at room temperature. The mixture was then left to rest and heated at 120°C for 2 h to evaporate the solvent, after which the solids obtained were grinded in an agate mortar.²⁸ After the magnetic stirring and resting, a segregation of two phases was observed consisting of a gel and a liquid. For the preparation of the second sample, an intermediate step was introduced with

the objective of separating the gel phase from the liquid by vacuum filtration. Then the liquid was dried by heating at 120°C for 2 h and the solids grinded in the agate mortar. When the steel slag is subjected to these simple pretreatments, calcium acetate is obtained that decomposes into CaO upon calcination. Table 1 shows the elemental composition of the raw steel slag, the acetic acid treated steel slag and the acetic acid treated steel slag with the intermediate separation step, as obtained from XR fluorescence analysis. XRF analysis shows that the most abundant element in the raw steel slag is Ca followed by Si, Mn, Cr and Mg, with also traces of Al, Fe and Ti. The treated steel slag presents almost the same elemental composition, whereas the sample subjected to the intermediate step of separation exhibits a significant reduction of the amount of Si and Ti, arguably due to the presence of the corresponding oxides in the gel.

Table 1. Elemental composition (weight%) of the steel slag raw powder, the acetic acid treated steel slag and the acetic acid treated steel slag with the intermediate step of separation as obtained from the XR fluorescence analysis.

	Raw Steel Slag	Acetic Acid Treated Steel Slag	Acetic Acid Treated Steel Slag + Separation
Ca	36.93	37.09	54.15
Si	13.48	13.54	0.85
Al	0.70	0.70	0.54
Fe	0.58	0.58	0.93
Mg	1.98	1.99	3.05
Mn	5.04	5.07	7.09
Cr	3.86	3.87	3.53
Ti	0.62	0.62	0.08
O	36.13	36.29	29.35
Other	0.45	0.45	0.84

Calcination/carbonation experiments were performed using a thermogravimetric analyzer (TGA) Q5000IR from TA Instruments. The instrument consists of a high sensitive balance

(<0.1 mg) and a furnace heated by four IR halogen lamps that allow fast heating at controlled rates (300°C/min) and stable isotherms. Quick switch between He and CO₂ atmospheres was achieved by using a gas flow rate of 200 cm³ min⁻¹. The sample is placed inside a SiC enclosure heated by the IR halogen lamps, which minimizes undesired heat transfer phenomena. The tests consisted of 20 carbonation/calcination cycles. Each run was started with a precalcination stage at 675°C during 5 minutes, heating the sample from room temperature at a heating rate of 300°C/min under pure He. In the TGA tests, the temperature was quickly increased (300°C/min) after precalcination to 850°C and the gas switched to pure CO₂ for carbonation, which was maintained during 5 minutes. Once the carbonation stage was ended, the temperature was quickly decreased to 150°C, the gas was changed to pure He and the temperature was maintained for 2 minutes. The sample was calcined again by increasing the temperature (300°C/min) to 675°C for 5 min under pure He. The temperature was then decreased again at 300°C/min to 150°C and maintained during 2 minutes under He, after which a new carbonation stage was started. The intermediate steps at 150°C (under pure He) were introduced in order to mimic the extraction of sensible heat from the solids exiting the carbonator and calciner before storage, which leads to a rapid cooling of the solids.²¹ Samples of small and fixed mass (5.5 mg) were used to ensure an optimum heat and mass transfer during the solid-gas reactions occurring throughout the experiments.²⁹ Particle size distribution was measured for the samples dispersed in 2-propanol by means of laser diffractometry using a Malvern Mastersizer 2000 instrument. Particle size was below 300 μm for both samples. The influence of intraparticle pore diffusion resistance on the carbonation/calcination reactions has been demonstrated in previous works to be negligible for limestone samples with particle sizes in the range 50-1000 μm, including the case for carbonation under high CO₂ concentration and high temperature as corresponds to the conditions of our tests.³⁰⁻³² Moreover, it is well known that acetates show a high surface area and porosity after calcination, which would facilitate further gas diffusion through the pores.³³⁻³⁴ This suggests that the effects of intraparticle pore diffusion resistance on the reaction rate are negligible in the range of particle sizes used in the present work.

For comparison, TGA tests were also performed at CaL conditions for CO₂ capture. These involve carbonation under 15% CO₂/85% air v/v atmosphere (as typical of flue gas) and calcinations at 900°C under 70% CO₂/30% air v/v at atmospheric pressure with fast transitions between both stages. Calcination in this case must be necessarily carried out under high CO₂ partial pressure in order to avoid the dilution of CO₂, which is extracted from the calciner for compression, transport and storage. Short residence times for both calcination and carbonation stages (5 minutes) were also used as required in practice.³⁵⁻³⁶

X-ray diffraction patterns were collected in a Panalytical X'Pert Pro diffractometer working at 45 kV and 40 mA, using CuK α radiation and equipped with an X'Celerator detector and a graphite diffracted beam monochromator. The microstructure of the samples was also analyzed by scanning electron microscopy (SEM) using a Hitachi S5200 microscope.

3. Results and discussion

3.1. Sample characterization

Figures 2a and 2b show the X-ray diffraction patterns measured for acetic acid treated steel slag without and with the separation step respectively. For both samples, the main phase obtained is partially hydrated calcium acetate (Ca(CH₃COO)₂·½H₂O), with a small amount of calcium magnesium acetate (CaMg₂(CH₃COO)₆). No significant differences are observed from the diffraction patterns. Figure 2c and 2d show SEM micrographs of the pretreated steel slag samples without and with the separation step respectively, where the typical rod-shape microstructures of calcium acetate are clearly observed. Grains of impurities due to metal oxides present in the samples can be also appreciated. The microstructure of both samples is almost identical, which indicates that the reduction of the amount of Si and Ti in the sample caused by the intermediate separation step does not affect the microstructure of the calcium acetate and calcium magnesium acetate formed by the reaction with the acetic acid. Upon calcination the acetates decompose into CaO and MgO.

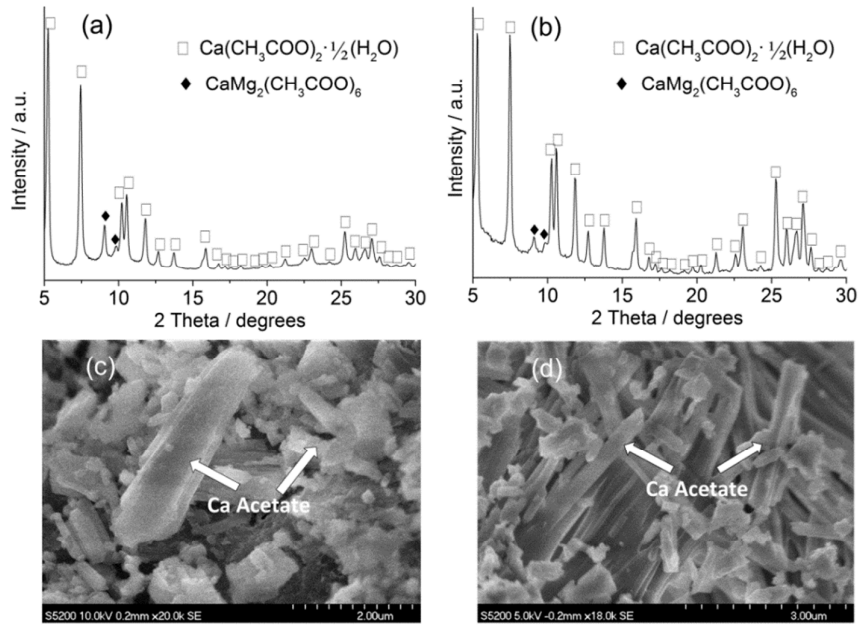


Figure 2. X-ray diffraction patterns of steel slag powder after treatment with diluted acetic acid without (a) and with the separation step (b), respectively. SEM micrographs of the treated steel slag without (c) and with the separation step (d), respectively.

3.2. Thermogravimetric analysis

The use of steel slag pretreated with acetic acid has been already suggested as CaO precursor in order to use it for post-combustion CO_2 capture by means of the CaL process.³⁷ However, it is important to remark that CaL conditions for post-combustion CO_2 capture radically differ from those of CSP storage. The former involve carbonation at temperatures around 650°C with a low concentration of CO_2 ($\sim 15\%$ vol typical of flue gas) and calcination in short residence times at high temperatures (around $930\text{--}950^\circ\text{C}$) in a high CO_2 concentration environment. In the case of CaL conditions for CSP energy storage that concerns the present work carbonation would be carried out at $\sim 850^\circ\text{C}$ or higher under a high CO_2 partial pressure whereas the calcination reaction would be performed in the solar receiver under an atmosphere of a separable gas from CO_2 and preferably at the lowest possible temperature.²¹

Figure 3a shows the time evolution of temperature and CaO conversion along the multiple calcination/carbonation cycles carried out under CaL-CSP storage conditions for the treated

steel slag with the intermediate separation step: carbonation at 850°C during 5 minutes under pure CO₂, calcination at 675°C for 5 minutes under He and intermediate stages at low temperature. As may be seen in the figure, full calcination is achieved at 675°C from the first cycle in short residence times. Moreover, the conversion of the regenerated CaO after each cycle converges towards a high and stable value (above 0.8) as the number of cycles is increased. Figure 3b shows the curves obtained for multiple calcination/carbonation cycles carried out under CaL-CO₂ capture conditions for the same sample: 5 min calcination at 900°C (70% CO₂/30% air vol/vol) and carbonation at 650°C (15% CO₂/85% air vol/vol) with quick transitions between both stages. As may be seen (Fig. 3b), complete calcination is not attained at 900°C under 70% CO₂/30% air v/v during the first cycle.

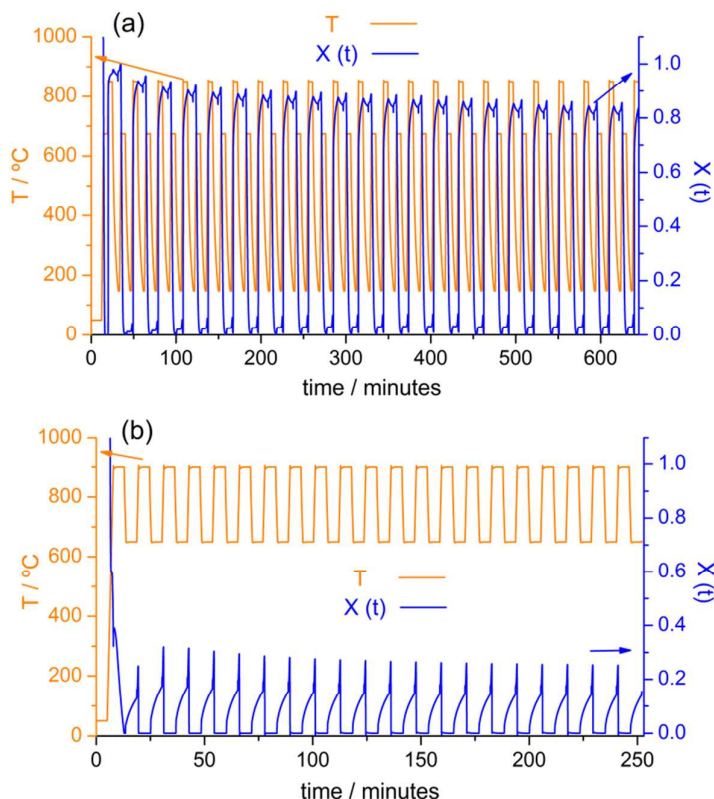


Figure 3. Thermograms for CaO derived from steel slag treated with acetic acid with the intermediate separation step. The thermograms show the time evolution of CaO conversion X (right axis) and temperature T (left axis) during multiple calcination/carbonation cycles. (a) CaL-CSP storage conditions: calcination at 675°C (pure He) for 5 min, carbonation at 850°C (pure CO₂) for 5 min. (b) CaL-CO₂ capture conditions: calcination at 900°C (70% CO₂/30% air vol/vol) for 5 min, carbonation at 650°C (15% CO₂/85% air vol/vol) for 5 min.

Usually, the calcination temperature to attain full decomposition of limestone typically employed as CaO precursor is above 930°C under high CO₂ partial pressure as required for CO₂ capture.³⁵ Furthermore, as may be seen in Figure 3b, the multicycle conversion of the regenerated sorbent is relatively low (below 0.2) at these conditions in contrast with the result observed for CaL-CSP storage conditions (Figure 3a).

Under the high temperatures of calcination needed at CaL conditions for CO₂ capture, CaO based sorbents generally suffer severe sintering, which leads to a drastic drop of the CaO surface available for carbonation (and therefore of conversion) in just a few cycles. This behavior has been previously reported for CaO based sorbents derived from calcium acetate and calcium magnesium acetate. Thus, successive carbonation/calcination cycles lead to a decay of CaO conversion for these acetates as reported in these previous studies.³³⁻³⁴ Moreover, the presence of CO₂ in the calcination atmosphere enhances CaO sintering,^{34, 38} although severe sorbent sintering has been observed even for the relatively mild calcination conditions in air or inert atmosphere.³⁹⁻⁴¹ It has been also reported that another limiting factor on the carbonation performance of CaO derived from acetates would be the progressive closure of the pores at the external surface of the particles (pore plugging) during repetitive carbonation/calcination cycles.⁴² In our work we observe however that the conversion exhibited by CaO derived from treated steel slag at CaL-CSP conditions is very high and stable. The use of He for calcination enhances fast decarbonation at relatively low temperature due to its high thermal conductivity and the high diffusivity of CO₂ in He. Moreover, CaO reactivity towards carbonation is also promoted at CaL-CSP conditions involving high temperature under pure CO₂. The kinetics of carbonation in the fast reaction controlled phase at this high temperature is promoted while at the same time the enhancement of surface diffusion allows for a thicker layer of CaCO₃ to build up on the particles' surface before the reaction becomes limited by solid-state diffusion.⁴³ In fact, within the context of the CaL process applicability for CO₂ capture, it has been proposed to introduce an enhanced carbonation step (recarbonation) under these conditions (high temperature and high CO₂ concentration) as a method to mitigate the loss of CaO activity.⁴⁴⁻⁴⁶ In

general, it must be emphasized that the multicycle CaO conversion behavior of a given material would depend critically on the calcination/carbonation conditions in the CaL process.

3.3. CaO multicycle conversion

Figure 4 shows data on multicycle CaO conversion at the end of the carbonation stage obtained from the thermograms shown in Figure 3 and also for the treated steel slag without the separation step under CaL-CSP conditions. As anticipated, results for carbonation/calcination cycles performed under CaL-CO₂ capture conditions demonstrate pretty small values of conversion. In contrast, results from the tests performed under CaL-CSP storage conditions show a rather high and stable value of conversion, which would contribute to maximize the thermo-electric global efficiency of the CaL-CSP integration.²¹ CaO conversion data can be fitted using the semi-empirical equation.⁴⁷⁻⁴⁸

$$X_N = X_r + \frac{X_1}{k(N-1) + (1 - X_r/X_1)^{-1}}; \quad (N = 1, 2 \dots) \quad (2)$$

being N the cycle number, X₁ the conversion at the first cycle, k is the deactivation rate constant and X_r is the residual conversion towards which conversion converges asymptotically after a very large number of cycles. For the experiment carried out under CaL-CO₂ capture conditions, the fitting was performed from the third cycle after which CaO was fully regenerated by calcination, and X_r takes a value 0.13. In contrast, for the experiments performed under CaL-CSP storage conditions the residual value of CaO conversion turns out to be as high as X_r = 0.82 for the sample with the intermediate separation step and X_r = 0.63 for the sample without separation.

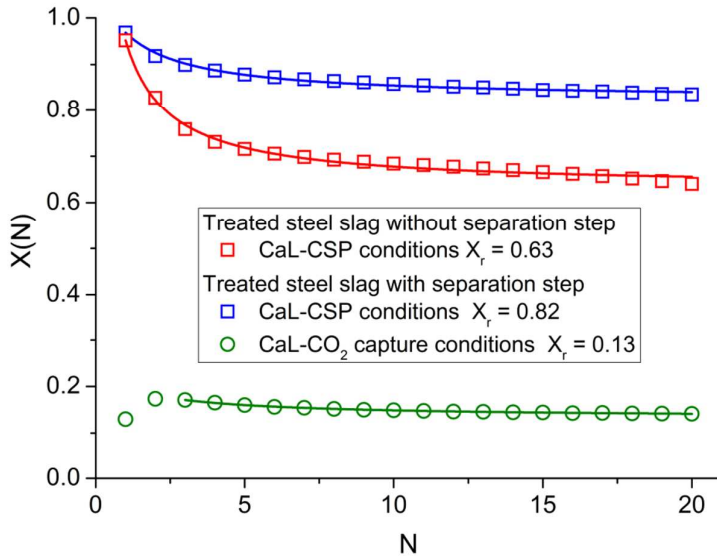


Figure 4. Multicycle conversion of CaO derived from steel slag treated with acetic acid without and with the intermediate separation step. Tests carried out under CaL-CSP storage conditions and CaL-CO₂ capture conditions. Solid lines represent the best fits of equation (1) to experimental data. Values of the residual conversion obtained from the best fittings are shown in the inset.

Figure 5 shows micrographs of treated steel slag, without and with the intermediate separation step, cycled under CaL-CO₂ capture (Figures 5a and 5b) and CaL-CSP storage conditions (Figures 5c and 5d). As may be seen, the samples cycled under CaL-CO₂ capture conditions show CaCO₃ patches of size on the order of 200 nm, along with metallic oxides grains present in the steel slag (M_xO_y) that remain inert along the cycles. Remarkably, for the samples cycled under CaL-CSP storage conditions the CaCO₃ patches are much bigger, with some of them larger than 500 nm, which could be explained by the more favorable conditions for carbonation. Moreover, in the latter case the samples show a higher segregation of the inert metallic oxides grains.

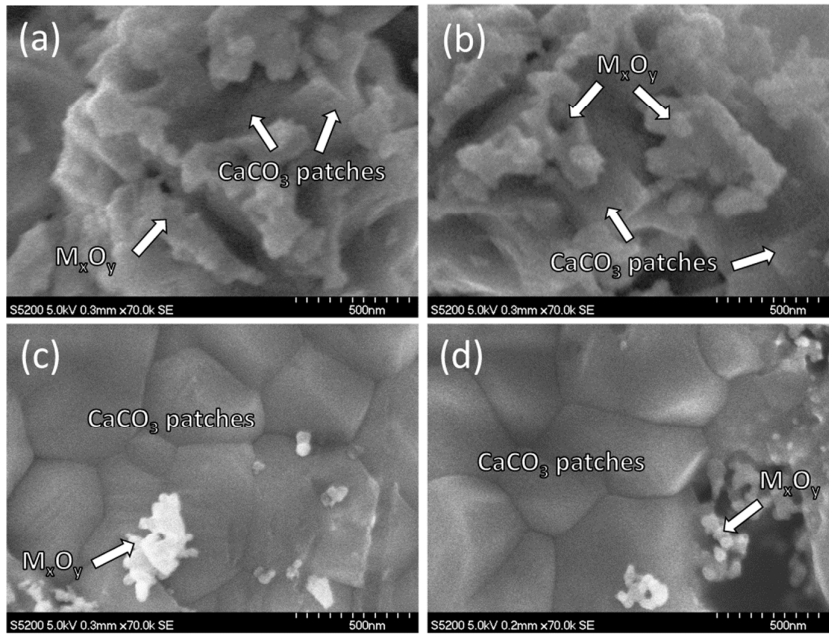


Figure 5. SEM micrographs of modified steel slag (a, c) without and (b, d) with the intermediate separation step after 20 carbonation/calcination cycles under (a, b) CaL-CO₂ capture conditions: calcination at 900°C (70% CO₂/30% air vol/vol) for 5 min, carbonation at 650°C (15% CO₂/85% air vol/vol) for 5 min and (c, d) CaL-CSP storage conditions: calcination at 675°C (pure He) for 5 min, carbonation at 850°C (pure CO₂) for 5 min.

It must be stressed that the high and stable multicycle CaO conversion obtained at CaL-CSP storage conditions is seen in our tests under conditions that would result in a high efficiency of electricity generation by means of a Brayton cycle using the heat released in the exothermic carbonation reaction and carried on by the excess CO₂ according to ref. [21, 23]. Under these conditions, we observe that steel slag derived CaO is almost fully carbonated in each cycle whereas the CaCO₃ formed is completely calcined at temperatures below 700°C in short residence times. Short residence times would allow in practice the use of a commercial circulating fluidized bed (CFB) reactor for the carbonator operated at high gas velocities (of a few m/s). CFB reactors provide optimum heat and mass transfer and are commonly employed in industrial applications to enhance gas-solid reactions.⁴⁹⁻⁵¹ Carbonator models based on CFBs are being widely studied in recent years for the application of the CaL process to capture CO₂ as

depending on the multicycle CaO conversion and carbonation kinetics. In this regard, an interesting subject for further work would be to adapt these models to the particular behavior of the sorbents for CaL-CSP conditions to obtain relevant parameters for optimum performance such as the solids residence time. Concerning calcination, excessively long solids residence times in the solar receiver would play a detrimental role,⁵² which could be avoided if full calcination is achievable in short residence times as we observe for the material studied in the present work. Several particle receiver concepts have been reported in the literature. For example, Meier et al. have developed a solar multi-tube rotary kiln prototype for carrying out the calcination reaction.⁵³⁻⁵⁵ Other solar calciner concepts proposed use fluidized beds^{54, 56-57} and cyclone atmospheric reactors.⁵⁸ A potentially cheap and simple option would consist of falling particle receivers.⁵⁷ However, the design and coupling of a CFB with a solar receiver is a rather difficult challenge that remains to be addressed. In addition, a main difficulty not solved yet for a CSP plant with central tower technology is the transport of solids to the solar receiver, which would be typically placed at heights above 100 m. This problem has not been investigated to our knowledge in detail in the engineering literature although pneumatic conveying, an already mature technology to transport high temperature granular solids is proposed as a viable solution.²¹ Further R&D must be pursued for the coupling of CFBs to the CSP technology to be realized in practice.

Relatively low calcination temperatures as seen in our work would allow the use of commercial solar receivers based on metal alloys capable of withstanding temperatures up to 850°C,⁵⁹ instead of expensive ceramic based receivers currently under investigation, which would reduce costs.⁵⁹⁻⁶¹ The low calcination temperature achieved in our tests is partly due to the high thermal conductivity of He as well as the high CO₂ diffusivity in He.⁶² Moreover, He can be separated from the CO₂ released during calcination by means of membranes, which would allow in practice CO₂ extraction after calcination to be stored and used on demand in the carbonation step whereas He is recycled for its use in a subsequent calcination stage.⁶³⁻⁶⁶ Nevertheless, the type of membranes and optimum operation conditions to be employed as well as the work required for this separation are critical issues that remain yet to be addressed. A further issue to

be solved for the realization of the integration scheme depicted in Fig. 1 is solid-solid heat exchange since solid-solid heat exchangers are not technologies currently available at commercial scale yet. Possible strategies to deal with this problem are discussed in detail in ref. [21, 23]. The integration of the CaL process and CSP is still in a concept stage and much work is needed to determine more precisely the more appropriate technologies to be employed in the integration as well as economic aspects.

4. Conclusions

This work explores the use of treated steel slag for thermochemical energy storage (TCES) by means of the integration of the calcium looping (CaL) process into concentrated solar power (CSP) plants. Multicycle calcination/carbonation tests demonstrate that CaO derived from the treatment of steel slag with acetic acid has a high and stable multicycle activity at conditions that maximize the efficiency of a CaL-CSP integration scheme based on a CO₂ closed cycle for carbonation and power production reported elsewhere. These conditions involve carbonation at ~850°C or higher temperatures under high CO₂ partial pressure whereas calcination is performed under He, which is separable from CO₂ by means of membranes and enhances quick calcination at a reduced temperature below 700°C thus allowing the use of mature solar receivers technology. The integration of the CaL process into CSP plants using highly reactive CaO derived from treated steel slag would expectedly reduce the cost of electricity generated and increase the flexibility of energy supply to meet demand. A further advantage of this integration is the valorization of steel slag, which is generated as waste in huge amounts by the steel industry. Steel slag is abundant, cheap, and non-toxic, which together with its high and stable multicycle activity demonstrated in the present work makes it a promising choice for thermochemical energy storage in CSP plants with tower technology.

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