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**Effect of seawater, aluminate cement and alumina-rich spinel
on pelletised CaO-based sorbents for calcium looping**

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Abstract

Calcium looping (CaL) is considered as an emerging technology to reduce CO₂ emissions in power generation systems and carbon-intensive industries. The main disadvantage of this technology is reactivity decay over carbonation/calcination cycles due to sintering. The main objective of this study was to evaluate the performance of novel sorbents for CaL. Three types of pelletised CaO-based sorbents for CO₂ capture were developed by adding aluminate cement, aluminate cement with seawater or alumina rich spinel to calcined limestone. Different concentrations of seawater in deionised water solutions were tested: 1, 10, 25 and 50 vol%. All samples were tested in a thermogravimetric analyser (TGA) under two different calcination conditions: mild (N₂ atmosphere and 850°C during calcination) and realistic (CO₂ atmosphere and 950°C during calcination). The samples were characterised using SEM and EDX. Aluminate cement CaO-based sorbents exhibited better performance in the TGA tests (25% conversion after 20 cycles achieved by limestone and 35% with aluminate cement CaO-based pellets, under mild conditions, and 11% conversion after 20 cycles with limestone compared to 15% utilising aluminate cement CaO-based pellets, under realistic conditions). However, doping had a negative effect in the reactivity of the sorbent. Moreover, alumina rich spinel CaO-based sorbents showed the worst performance.

Key words: pellets, doping, CO₂ capture, limestone, sorbent pretreatment, sorbent conversion.

1. Introduction

Carbon capture and storage (CCS) is a chain of processes that has been proposed as a potential method to reduce CO₂ emissions from power generation and carbon-intensive industries [1]–[3]. Calcium looping (CaL) is a promising technology for CO₂ capture from the existing power generation systems and many carbon-intensive industries [4], [5]. It was first proposed for post-combustion CO₂ capture by Shimizu et al. [6] in 1999 and has been demonstrated at a megawatt scale [7], [8]. It is based on the reversible reaction of sorbent, such as CaO. During this process, carbonation and calcination reactions take place alternatively over multiple cycles to capture and release CO₂ from the flue gas [6]. A typical scheme of CaL is shown in Figure 1. The flue gas containing CO₂ enters the carbonator, where CaO in the CaO-based sorbent and CO₂ react to form CaCO₃. This reaction occurs typically between 600–700°C and is exothermic. Then, the saturated sorbent is transferred to the calciner where the sorbent is regenerated and CO₂ released at a high temperature (>900°C) [6]. Importantly, the calcination reaction is endothermic. In the conventional CaL configuration, the heat required for sorbent regeneration is provided via direct oxy-combustion of fuel in the calciner. High-purity O₂, which is usually produced in the air separation unit (ASU) [9], is used to ensure that high-purity CO₂ is produced in the calciner.

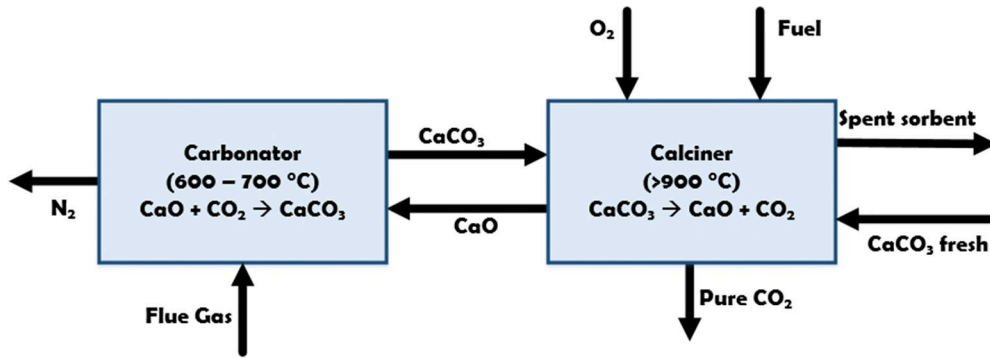


Figure 1: Typical calcium looping process scheme

CaL has been reported to have several advantages compared to mature CO₂ capture technologies, as it will result in low efficiency (around 5–8%) and economic penalties [10]–[12]. Importantly, CaCO₃ is widely available in nature as dolomite and limestone, which makes it relatively inexpensive CO₂ capture material, enabling implementation of CaL [4], [13]. Moreover, both carbonation and calcination reactions occur at high temperatures, allowing for the high-grade heat utilisation for power production [14]. Finally, CaL operates efficiently at an atmospheric pressure that reduces both operating and capital cost [15].

Natural material-based sorbents such as limestone are easy to use and inexpensive solid materials for CO₂ capture due to their availability and potential utilisation of the spent sorbent in the cement industry [13]. Dolomite [16] or animal waste, such as egg shells and sea shells, treated with acetic acid and crushed [17] can also be used as natural materials for CO₂ capture. Enhanced natural materials are modifications of limestone made with the objective of improving its properties maintaining its low cost. Synthetic sorbents are being studied as an improvement of natural existing sorbents. They can be made from organic-acid precursors, sol-gel combustion synthesis, precipitated sodium

carbonate, dry mixing and coating, granulation or nanomaterials, among others [17], [18].

One of the main challenges of CaL is the fast sorbent reactivity decay over carbonation/calcination cycles that is mainly caused by sintering and attrition [7], [17]. Sintering is the mechanism by which solid particles coalesce when heated at temperatures below their melting point [19]. It results in changes of the sorbent surface texture after cycles and it is believed to be one of the more important causes of sorbent deactivation [20]. Although sintering occurs mainly during calcination, it can also occur due to the closure of small pores in the carbonation process that do not reopen afterwards [17], [21].

Pelletisation of CO₂ capture materials is a technique based on the incorporation of support material into CaO-based sorbent (lime) that results in a new material with more resistance to fractionation and attrition. Importantly, several techniques for the preparation of pelletised sorbents have been developed. Manovic et al. [22] fabricated pellets from limestone and cement using the extrusion with the sieve method. They concluded that the pellets prepared using this technique were characterised by high strength, even though strength loss was observed over a high number of calcination cycles. Qin et al. [23] utilised a screw extruder for the fabrication of Ca(OH)₂ and cement particles, concluding that the particles prepared using this technique had reasonable chemical and mechanical properties and that this method can be easily scaled up. Sun et al. [24] prepared pellets for high temperature CO₂ capture using a novel method called extrusion-spheronization that consisted of three main steps: the extrusion of previously mixed powders, the cutting of extrudates and the spheronization of those

particles. They concluded that this method leads to a loss of specific surface area and inferior CO₂ carrying capacity. Finally, Manovic et al. [25], [26] used a granulator for the pelletisation of spent CaO-based sorbents concluding that this method enables the utilisation of the pellets in a fluidised bed reactor and enables the addition of cement to enhance the sorbent strength.

Pelletisation by using calcium aluminate cements was studied by Wu et al. [26], the results showed better carrying capacity over cycles of the pelletised material and higher attrition resistance than the limestone. Attrition tests of calcium aluminate cement pellets modifying the type of limestone used were performed by Ridha et al. [27], they conclude that type of limestone used has no influence in the attrition tendencies. Moreover, doping limestone with certain compounds such as salts (NaCl, Na₂CO₃, KCl, Mn(NO₃)₂, MnCO₃, CaBr₂), halogen dopants or some metal-based materials, decreases the reactivity decay of the sorbent over cycles postponing the sintering phenomenon [17], [21], [28], [29]. The addition of salts showed an improvement in the CO₂ capture capacity due to positive changes in the pore structure of the sorbent where the tests were performed in the Thermogravimetric Analyser (TGA) [28].

Previous studies have proven that the properties of limestone can be improved by adding certain substances; thereby improving the sorbent reactivity and minimising phenomena like sintering and attrition [17], [26], [28], [30], [31]. This work aims to study the effect of aluminate cement, salt and alumina-rich spinel on calcium aluminate pellets. Synthetic materials prepared with lime, calcium-aluminate cement, alumina-rich spinel and different concentrations of seawater were tested to investigate their carbonation conversion in the TGA. Two different calcination conditions were tested to

assess their effect in the prepared materials. Furthermore, the materials produced were characterised using scanning electron microscope (SEM) to evaluate morphological variations. Cement, alumina-rich spinel and sea water were used as modifiers for the preparation of the enhanced materials. Seawater was used as a salt-containing solution due to its availability and ease of use considering further process scale-up.

2. Materials and methods

2.1. Materials

Longcal limestone provided by Longcliffe Ltd, UK, was used as natural source of CaCO_3 . Two kinds of commercial calcium aluminate cements (CA-14M and CA-25R) and one alumina-rich spinel (AR 78), manufactured by Almantis Inc., were used as binders in the pelletisation process. Artificial seawater from Complete Aquatics (Sea-Pure, Purified Sea Water for Aquariums) was used to dope the samples. Sea-Pure is sterilized seawater having the same composition as natural seawater. As this water was treated with NaOCl , it only contains a small amount of Na and Cl and 3.5% salinity. Table 1 shows the typical composition of the seawater used in this work. Table 2 shows the composition of the binders provided by Almantis Inc.

Table 1: Sea-Pure seawater composition

Element	ppm
Hydrogen (as H_2O)	110,000
Oxygen (as H_2O)	833,000
Sodium (as NaCl)	10,800
Chlorine (as Cl)	19,400
Magnesium (Mg)	1,290

Table 2: Binders composition

Chemical composition (%)	CA-14M	CA-25R	AR 78
CaO	28	18	0.24
Al ₂ O ₃	71	81	77
MgO	-	-	22.5
Other	-	-	0.26

2.2. Sorbent preparation procedure

Seven types of materials were prepared (Table 3): (i) 10% calcium aluminate cement CA-14M and 90% calcined limestone (LC0); (ii) 10% calcium aluminate cement CA-25R and 90% calcined limestone (LC0*); (iii) 10% calcium aluminate cement CA-14M, 90% calcined limestone and a solution containing 1% seawater and 99% deionised water (LC1); (iv) 10% calcium aluminate cement CA-14M, 90% calcined limestone and a solution containing 10% seawater and 90% deionised water (LC10); (v) 10% calcium aluminate cement CA-14M, 90% calcined limestone and a solution containing 25% seawater and 75% deionised water (LC25); (vi) 10% calcium aluminate cement CA-14M, 90% calcined limestone and a solution containing 50% seawater and 50% deionised water (LC50); (vii) 10% alumina-rich spinel AR 78 and 90% calcined limestone (LA).

Pellets were prepared using a mechanical pelletiser (Glatt TMG 1/6 granulator) (Figure 2), similarly to the previous studies by Manovic et al. [25], [26], as it enables the addition of cement to enhance the sorbent strength. Proportional quantities of the materials according to the samples described above (500 g batches) were introduced into the pelletiser vessel and mixed. The vessel has two blades: the agitator and the chopper that stirred the mixture at a set velocity. The mixing was performed inside the vessel by the

blades and the material was continuously sprayed with deionised water, or solution of seawater and deionised water, until pelletisation occurs. The pellet size was controlled by the speed of the blades (500 rpm for the agitator and 2500 rpm for the chopper). After this process, pellets were sieved to 300–500 μm and dried in open air before storage.

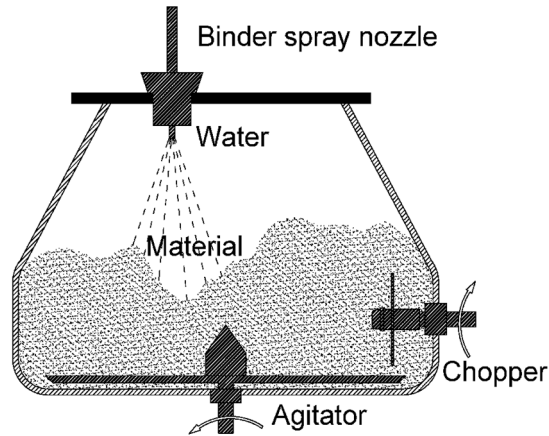


Figure 2: Glatt TMG 1/6 granulator (Developed based on Glatt [32])

Table 3: Materials used in pellet preparation

Sample	Calcined Limestone (wt.%)	Binder	Binder (wt.%)	Water used for pelletisation
LC0	90	CA-14M	10	Deionised water
LC0*	90	CA-25R	10	Deionised water
LC1	90	CA-14M	10	1% seawater, 99% deionised water
LC10	90	CA-14M	10	10% seawater, 90% deionised water
LC25	90	CA-14M	10	25% seawater, 75% deionised water
LC50	90	CA-14M	10	50% seawater, 50% deionised water
LA	90	AR 78	10	Deionised water

2.3. Thermogravimetric analysis of carbonation/calcination cycles

Carbonation conversion of the prepared samples was determined using the Perkin-Elmer Pyris 1 TGA (Figure 3). The samples were tested under two different conditions

(mild and realistic conditions). For the tests under the mild conditions, the calcination was carried out for 3 min at 850°C under 100% N₂ and the carbonation was performed for 15 min at 650°C under 15% CO₂, which corresponds to the typical composition of the flue gas in a coal-fired power plant. Under the realistic conditions, on the other hand, the calcination was carried out for 3 min at 950°C under 100% CO₂ for the first calcination and the carbonation was performed for 15 min at 650°C under 15% CO₂. Subsequent calcinations under realistic conditions occurred in an N₂ atmosphere. It has been previously reported that the first calcination has a slightly important role in the performance of the sorbent because is when sintering mainly occurs [33]. Under both mild and realistic conditions, the heating ramp rate was set to 40°C/min during heating and 20°C/min during cooling. In both cases, the atmosphere was switched to N₂ during the transition between the calcination and carbonation processes to avoid carbonation under undesired conditions [34]. The gas flow rate in all the cases was set at 20 mL/min and controlled by Perkin-Elmer Thermal Analysis Gas Station (TAGS). All the prepared samples undergone 20 cycles in both conditions. During each test, around 30 mg of sample were suspended on a platinum pan. Two series of tests were carried out to obtain conclusive results.

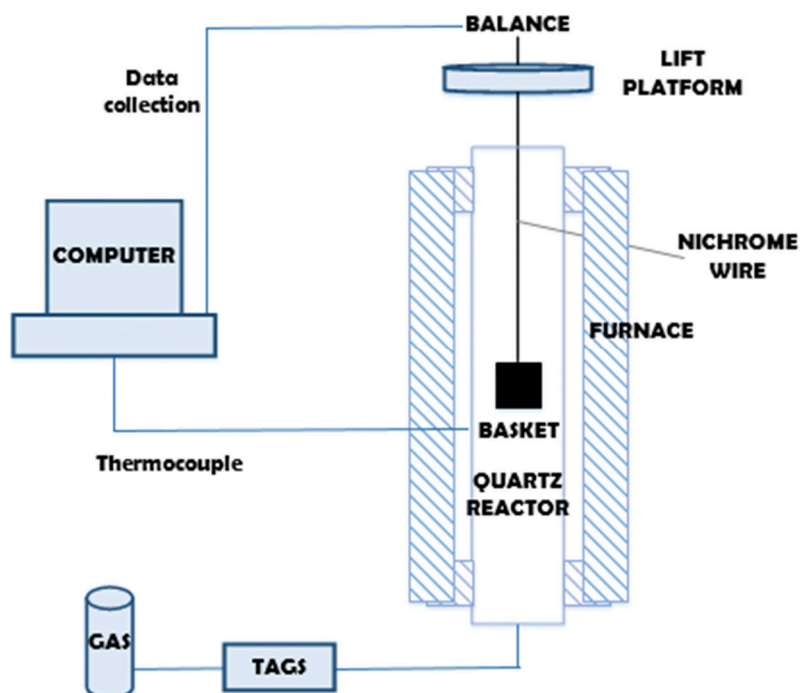


Figure 3: Scheme of Perkin-Elmer Pyris 1 TGA

2.4. Sorbent characterisation

The characterisation of the samples prepared was done with a scanning electron microscope (SEM) and an energy dispersive X-ray analysis (EDX) to study their porosity and component distribution. Analysis conditions are shown in Table 4. Sample morphology and porosity was observed with a Philips XL30ESEM (GSE detector) using an accelerating voltage of 25 kV under high vacuum. A magnification between 2500–5000x was used to show the porosity of the particle, while a magnification of between 120–650x was used to show the morphology of the whole particle. All the samples were coated with gold before introducing them in the scanning electron microscope to prevent them from charging up. EDX was used to determinate the component distribution along the particle. It was done with a Philips XL30ESEM (BSE detector) using an accelerating voltage of 25 kV under high vacuum. Firstly, a spectrum was created using a magnification between 1500–2500x in order to determinate the components

present in the particle. Next, using the same magnification, the components found were mapped to know their position along the sample.

Table 4: Characterisation conditions

Analysis	Accelerating Voltage (kV)	Spot size	Magnification	Detector
Porosity	25	4	2500–5000x	GSE
Morphology	25	4	120–650x	GSE
Component presence	25	5	1500–2500x	BSE
Component distribution	25	5	1500–2500x	BSE

3. Results and discussion

3.1 Aluminate cement CaO-based pellets

The carbonation conversion over 20 cycles for limestone, modified lime-based pellets with CA-14M (28% CaO, 71% Al₂O₃) cement (LC0) and modified lime-based pellets with CA-25R (18% CaO, 81% Al₂O₃) cement (LC0*) is shown in Figure 4 (mild conditions) and Figure 5 (realistic conditions).

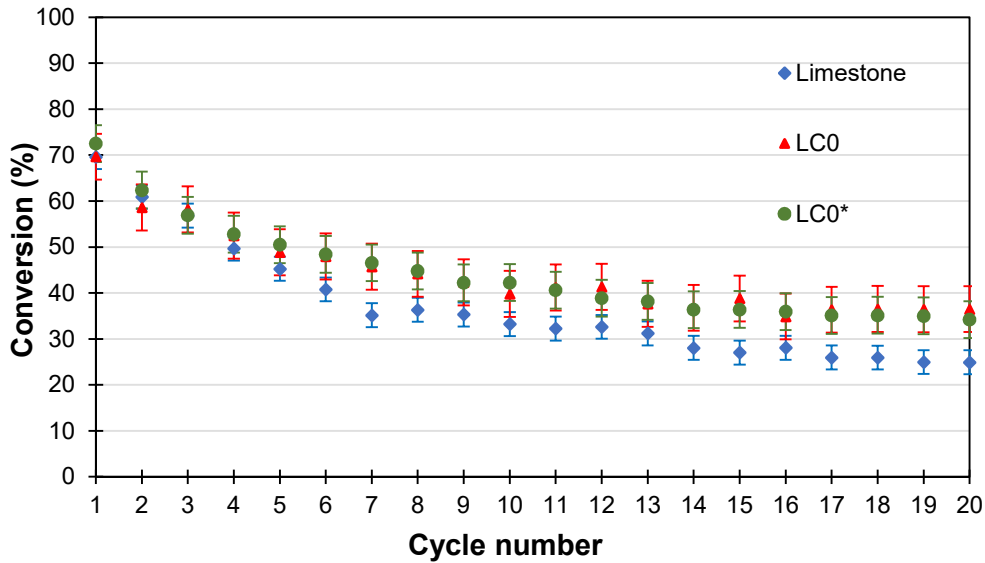


Figure 4: Carbonation conversion of modified lime-based pellets under mild conditions (3 min calcination at 850°C in 100 vol% N₂ and 15 min carbonation at 650°C in 15 vol% CO₂), where error bars refer to standard deviation

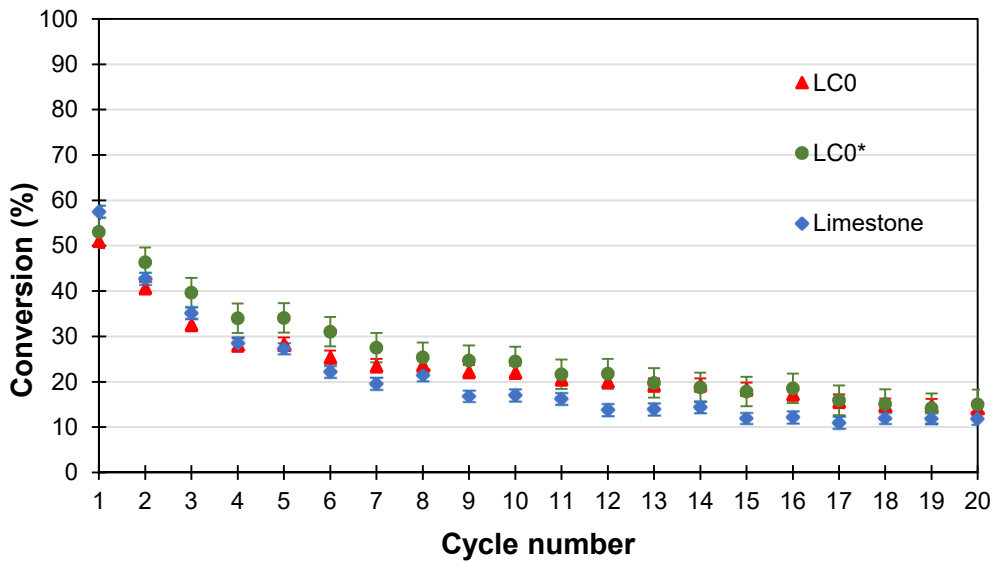


Figure 5: Carbonation conversion of modified lime-based pellets under realistic conditions (3 min calcination at 950°C in 100 vol% CO₂ and 15 min carbonation at 650°C in 15 vol% CO₂), where error bars refer to standard deviation

It can be observed in both Figure 4 and Figure 5 that the use CaO-based pellets supported by calcium aluminate cements improves the carbonation conversion over cycles. Both cements used (CA-14M and CA-25R) showed quite similar behaviour

increasing the carbonation conversion from 25% to 35% after 20 cycles in mild conditions (Figure 4) and from 11% to 15% after 20 cycles under realistic conditions (Figure 5). All the sorbents presented similar conversions in the first cycle, but pellets prepared using cement binders (LC0 and LC0*) appeared to have a more stable carbonation conversion for longer-term cycles (>10), due to a reduction in the activity decay over cycles.

Figure 6 and Figure 7 provide SEM images comparing the pure limestone and the aluminate cement modified lime-based pellets under both mild and realistic conditions, after the first calcination and after 20 cycles.

It can be observed in Figure 6 that the structure of the cement modified lime-based sorbent (6b, 6c, 6d, 6e, 6g, 6h, 6i and 6j) was less sintered when compared to the pure limestone (6a and 6f) under both mild and realistic conditions. The microporosity of all the samples showed in Figure 6 decreased from the first cycle (6d, 6e, 6i and 6j) to the 20th cycle (6a, 6b, 6c, 6f, 6g and 6h) while the macroporosity augmented after 20 calcination/carbonation cycles. The surface of the particle in all considered samples was more irregular after 20 cycles than in the first cycle of calcination due to an increase in macroporosity [25].

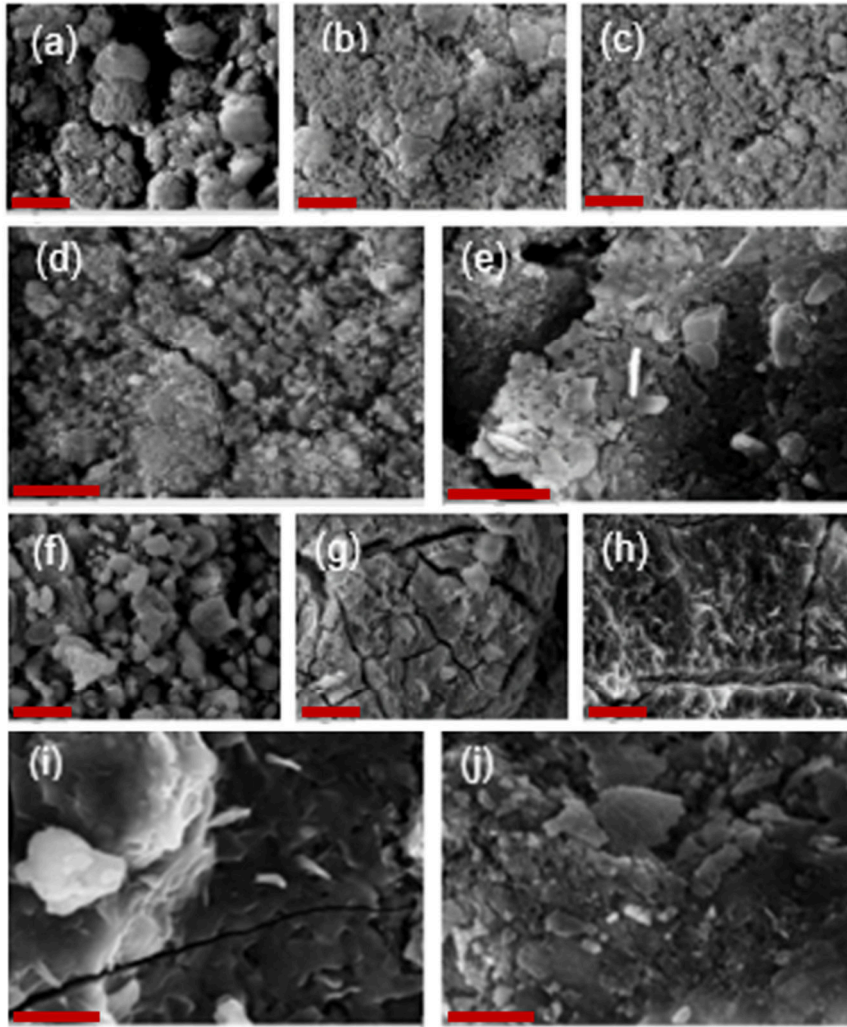


Figure 6: 2500–5000x SEM images of limestone and aluminate cement modified lime-based pellets. (a) limestone, (b) LC0 and (c) LC0* realistic conditions after 20 cycles; (d) LC0 and (e) LC0* realistic conditions first calcination; (f) limestone, (g) LC0 and (h) LC0* mild conditions after 20 cycles; (i) LC0 and (j) LC0* mild conditions first calcination, where red lines represent 5 μm scale bars

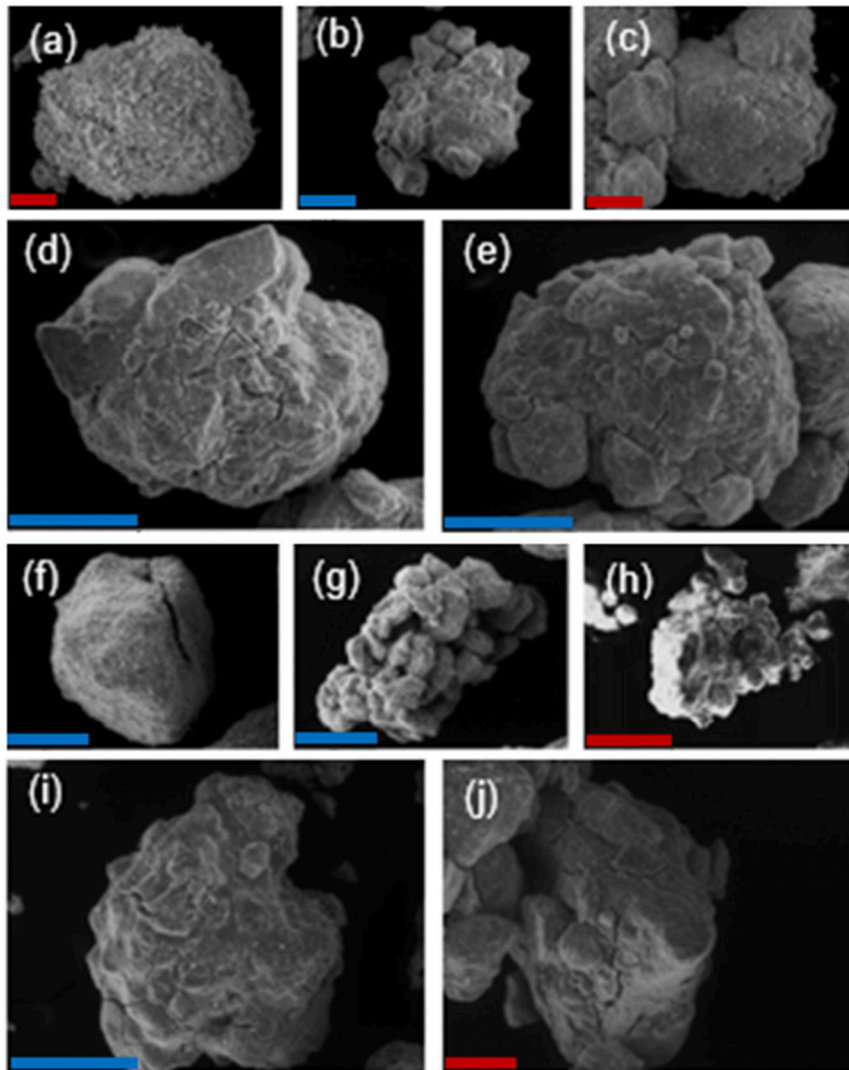


Figure 7: 120–650x SEM images of limestone and aluminate cement modified lime-based pellets. (a) limestone, (b) LC0 and (c) LC0* realistic conditions after 20 cycles; (d) LC0 and (e) LC0* realistic conditions first calcination; (f) limestone, (g) LC0 and (h) LC0* mild conditions after 20 cycles; (i) LC0 and (j) LC0* mild conditions first calcination, where red lines represent 100 μm scale bars and blue lines 250 μm scale bars

The variation in the particle morphology is clearly visible in Figure 7. More cracks can be observed on cement modified lime-based particles (7b, 7c, 7d, 7e, 7g, 7h, 7i and 7j) compared to the pure limestone (7a and 7f). The aluminate cement modified samples presented more irregular surface after 20 calcination cycles (7b, 7c, 7g and 7h) than after the first calcination (7d, 7e, 7i and 7j) as it was also seen in Figure 6.

Cement modified lime-based sorbents prepared performed better in long-term cycles than the limestone (35% compared to 25% conversion for mild conditions and 15% compared to 11% conversion under realistic conditions, after 20 calcination cycles). This result agrees with the results reported in the literature for the use of calcium aluminate cements for high temperature CO₂ capture [17], [22], [26], [35]–[37]. This phenomenon can be attributed to the formation of mayenite (Ca₁₂Al₁₄O₃₃) when Al₂O₃ is present, which results in growth of the pore size, stabilizing the pore structure [22]. Previous studies also concluded that this type of sorbents is characterised with an excellent performance when used in calcination/carbonation cycles for CO₂ capture [38], [39].

Importantly, all considered sorbents presented similar conversions in the first cycle. However, pellets prepared using cement binders (LC0 and LC0*) seemed to have a more stable carbonation conversion from the 10th cycle. This can be related to a decrease in the reactivity decay over cycles according with the previous study conducted by Manovic and Anthony [22], which highlights the beneficial behaviour of CaO originating from Ca(OH)₂ formed during the pelletisation process due to the addition of cement, compared to natural limestone (CaCO₃). During carbonation/calcination cycles, the sorbent structure of the sorbent changes because of the formation of new pores: small pores closed upon carbonation and did not reopen afterwards [17], [21], small pores formed during calcination due to CO₂ release or larger pores that formed because of sintering [33]. From the SEM pictures (Figure 6 and Figure 7) it can be observed that the cement modified lime-based pellets were less sintered due to the formation of such pores (increase in macroporosity) as it was predicted in previous studies [22], [36]. A recent study [30], which were performed at a pilot scale, proved the synergy between

CaL and the cement industry, due to the positive results obtained using calcium aluminate cement modified lime-based pellets as sorbent.

3.2 Seawater effect

Results of carbonation conversion over 20 cycles for aluminate cement modified lime-based pellets (LC0) and aluminate cement modified lime-based pellets doped using the novel approach of adding different concentrations of seawater with deionised water solution (LC1, LC10, LC25 and LC50) are shown in Figure 8 (mild conditions) and Figure 9 (realistic conditions).

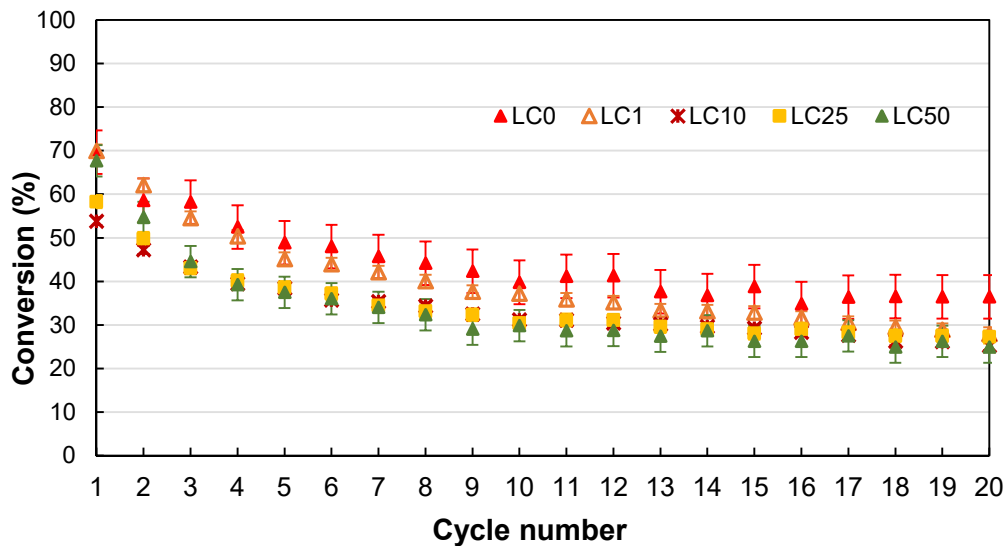


Figure 8: Carbonation conversion of aluminate cement modified lime-based pellets doped with seawater under mild conditions (3 min calcination at 850°C in 100 vol% N₂ and 15 min carbonation at 650°C in 15 vol% CO₂), where error bars refer to standard deviation

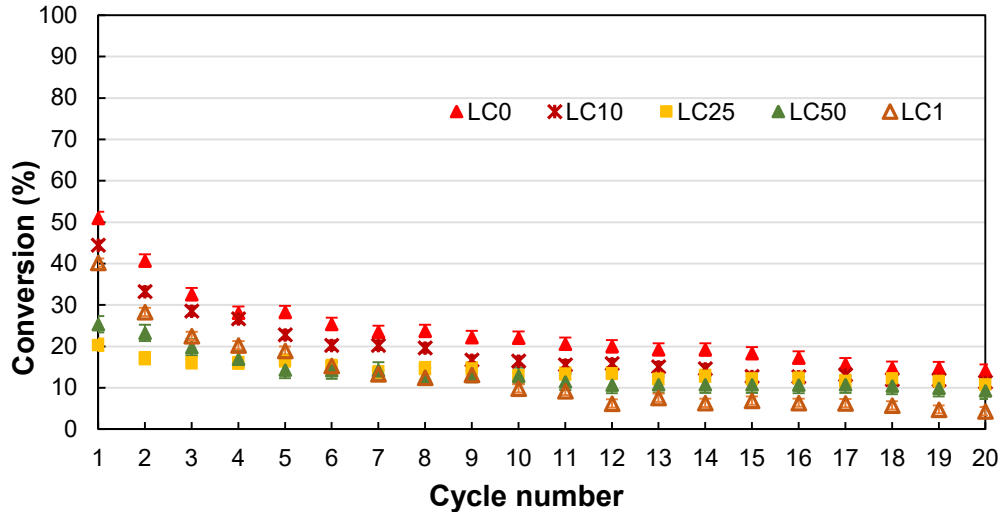


Figure 9: Carbonation conversion of aluminate cement modified lime-based pellets doped with seawater under realistic conditions (3 min calcination at 950°C in 100 vol% CO₂ and 15 min carbonation at 650°C in 15 vol% CO₂), where error bars refer to standard deviation

All the samples doped with different concentrations of seawater (LC1, LC10, LC25 and LC50) behaved poorly when compared to the conversion obtained without the addition of seawater (LC0) under both mild (Figure 8) and realistic (Figure 9) conditions, which indicates that doping with seawater does not improve the performance of the sorbent over cycles. Similar conversions after 20 cycles in both mild (25–27%, Figure 8) and realistic (6–10%, Figure 9) conditions were observed for all considered concentrations of seawater. Therefore, at the proportions used in this study, the salt concentration did not have a significant influence on the carbonation conversion over the cycles. This could be explained by the salinity of the seawater used in this study (3.5%). At such salt concentration, its dilution with water at the considered proportions did not have a significant effect on the sorbent performance. It can be also observed that the worst behaviour under realistic condition was with the sorbent doped with 1% of seawater (LC1) obtaining the lowest conversion, 6% (Figure 9).

Figure 10 and Figure 11 show SEM images comparing the CA-14M cement modified lime-based pellets doped with different concentrations of seawater under both mild and realistic conditions, after the first calcination and after 20 cycles.

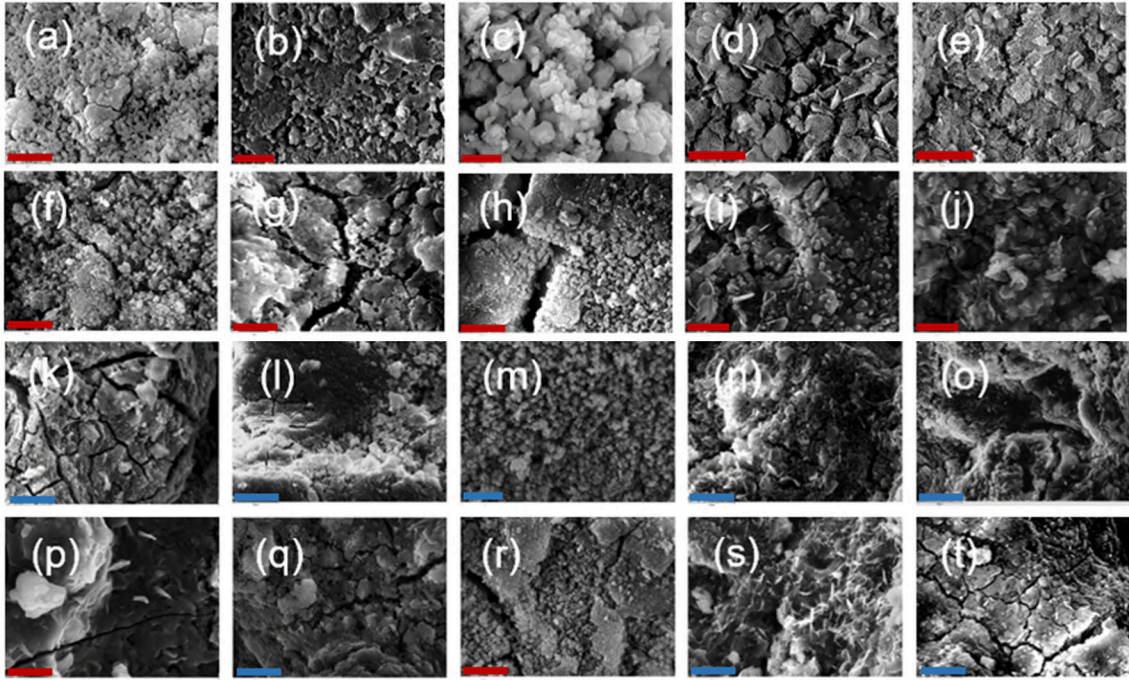


Figure 10: 2500–5000x SEM images of cement modified lime-based pellets doped with different concentrations of seawater. From left to right: LC0, LC1, LC10, LC25 and LC50; from top to bottom: realistic conditions 20 cycles, realistic conditions first calcination, mild conditions 20 cycles, mild conditions first calcination, where red lines represent 5 μm scale bars and blue lines 10 μm scale bars

Comparison of SEM images of the cement modified lime-based pellets doped with different concentrations of seawater (Figure 10), illustrates that the increase in seawater concentration leads to the increment in the number of macropores (from left to right) for both mild and realistic conditions. It can be observed flat surfaces on the grains, which appear more visible with the increase in seawater concentration, indicating sintering or formation of a eutectic melt. This melt sometimes led to plugging the macropores hindering the CO_2 adsorption. The particles were more sintered at higher

concentrations of seawater (LC10, LC25 and LC50) which can be observed in the melted areas caused by the formation of eutectic mixtures (10e, 10d, 10f, 10h, 10i, 10j, 10m, 10n, 10o, 10r, 10s and 10t). Macroporosity of the particle increases with the number of calcination/carbonation cycles.

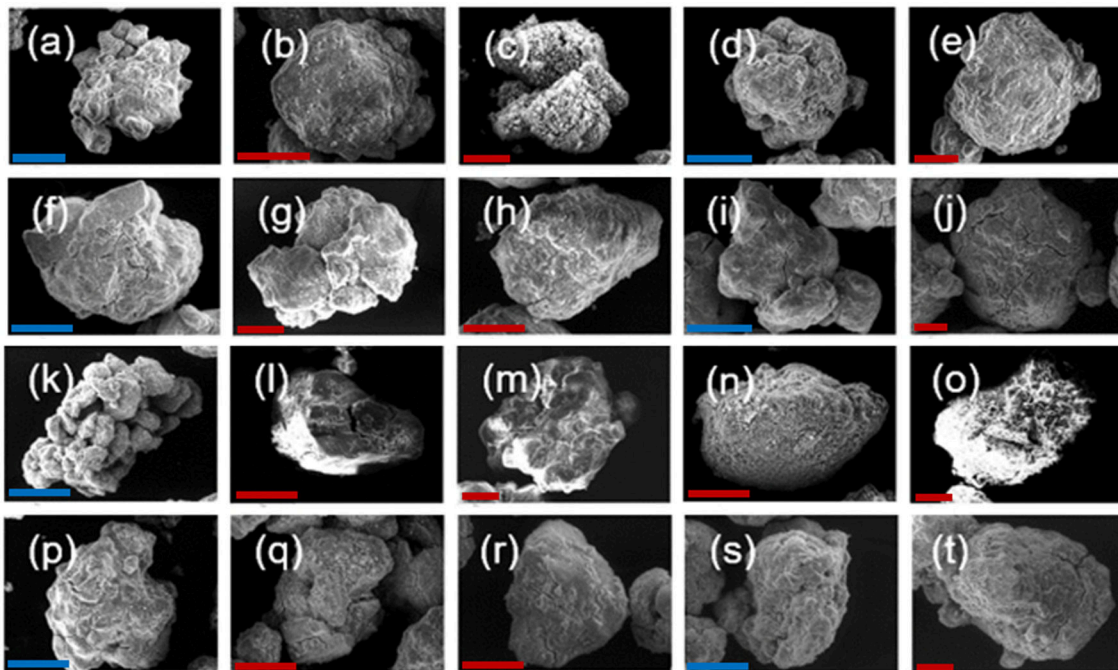


Figure 11: 120–650x SEM images of cement modified lime-based pellets doped with different concentrations of seawater. From left to right: LC0, LC1, LC10, LC25 and LC50; from top to bottom: realistic conditions 20 cycles, realistic conditions first calcination, mild conditions 20 cycles, mild conditions first calcination, where red lines represent 100 μm scale bars and blue lines 250 μm scale bars

The morphology of the particles did not change significantly with the concentration of seawater. All the particles presented cracks and irregular surface for both mild and realistic conditions. Particles after 20 calcination/carbonation cycles (11a, 11b, 11c, 11d, 11e, 11k, 11l, 11m, 11n and 11o) seemed to have more irregular surface than the ones that have been calcined once (11f, 11g, 11h, 11i, 11j, 11p, 11q, 11r, 11s and 11t).

Seawater doped samples behaved poorly when compared to the conversion obtained without the addition of seawater. SEM images of cement modified lime-based pellets doped with different concentrations of seawater (Figure 10 and Figure 11) show how the addition of salt lead to significant increase in the number of macropores. If the pores formed become too large, there will be a loss of surface area [40], which explains the decrease in adsorption capacity when the sample is treated with seawater. Due to the addition of NaCl an eutectic melt is formed indicating sintering of the particles, which has been found in previous work [40]. The addition of NaCl accelerates the rates of sintering and crystal formation during calcination due to the existence of a liquid phase that rises ionic mobility and diffusion [41]. This could explain why the addition of seawater does not have a positive effect in the carbonation capacity of the cement modified CaO-based pellets. In addition, an analysis of the SEM images has revealed how the salt tends to be allocated in the places were the Al_2O_3 was placed hindering the CO_2 adsorption capacity. This phenomenon could also explain why the doped samples performed poorly than the ones prepared without the addition of seawater.

It has been reported previously [17], [21], [28], [29], [42] that the doping of limestone with different salt solutions improves the CO_2 capture capacity of lime due to positive changes in the pore structure. The difference between the results obtained in this work and those reported in the literature could be linked to the concentration of NaCl utilised in the experiments; it is important to notice that the seawater utilised is treated with NaOCl, leaving a small amount of sodium and chlorine on it. Also, those reports showed the effect of doping with salt a non-enhanced limestone, SEM images show how the salt tends to be allocated in the places were the Al_2O_3 was placed hindering the CO_2

adsorption capacity; the negative effect of the salt in the sorbent could be related to the addition of cement during the pellet preparation.

3.3 Alumina-rich spinel CaO-based pellets

Results of carbonation conversion over 20 cycles for limestone, aluminate cement modified lime-based pellets (LC0) and alumina-rich spinel modified lime-based pellets (LA) are shown in Figure 12 (mild conditions) and Figure 13 (realistic conditions).

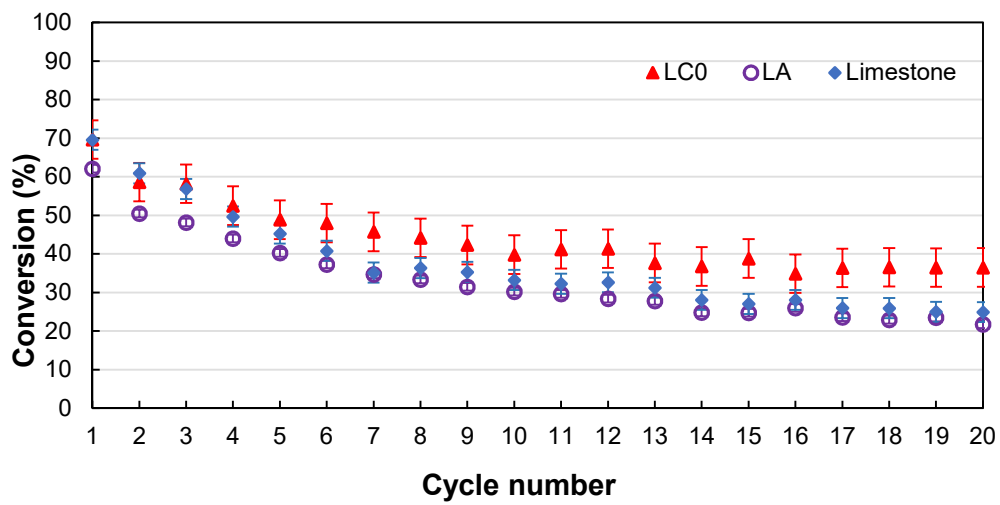


Figure 12: Carbonation conversion of aluminate cement and alumina-rich spinel modified lime-based pellets under mild conditions (3 min calcination at 850°C in 100 vol% N₂ and 15 min carbonation at 650°C in 15 vol% CO₂), where error bars refer to standard deviation

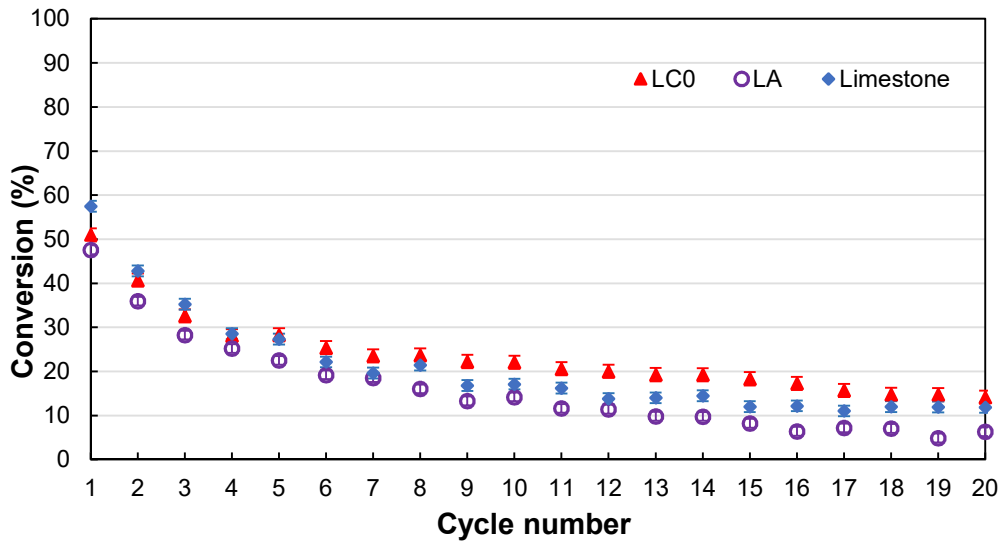


Figure 13: Carbonation conversion of aluminate cement and alumina-rich spinel modified lime-based pellets under realistic conditions (3 min calcination at 950°C in 100 vol% CO₂ and 15 min carbonation at 650°C in 15 vol% CO₂), where error bars refer to standard deviation

Alumina-rich spinel modified lime-based pellets did not exhibit any improvement in the carbonation conversion compared to limestone and cement modified lime-based pellets for both mild (Figure 12) and realistic (Figure 13) conditions.

Figure 14 and Figure 15 provide SEM images comparing the pure limestone, the cement modified lime-based pellets and the alumina-rich spinel modified lime-based pellets under both mild and realistic conditions, after the first calcination and after 20 cycles.

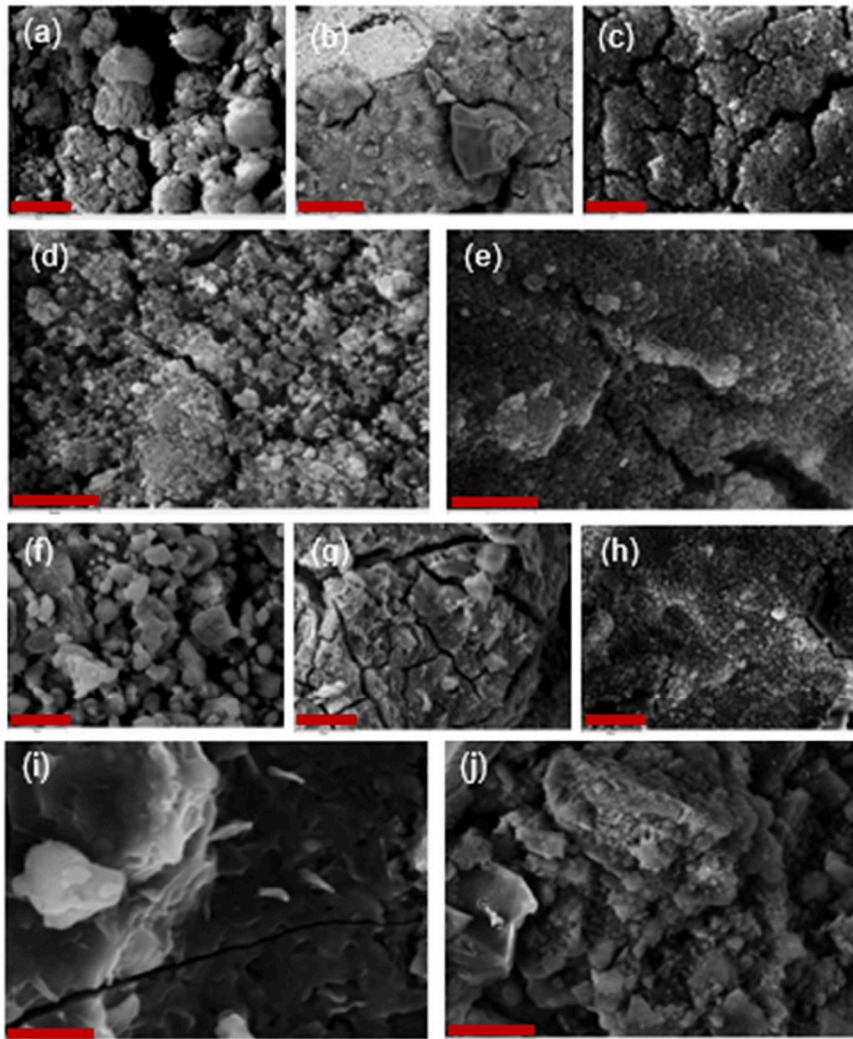


Figure 14: 2500–5000x SEM images of limestone, cement modified lime-based pellets and alumina-rich spinel modified lime-based pellets. (a) limestone, (b) LC0 and (c) LA realistic conditions after 20 cycles; (d) LC0 and (e) LA realistic conditions first calcination; (f) limestone, (g) LC0 and (h) LA mild conditions after 20 cycles; (i) LC0 and (j) LA mild conditions first calcination, where red lines represent 5 μm scale bars

Comparison of SEM images of the pure limestone, cement modified lime-based pellets and alumina-rich spinel modified lime-based pellets (Figure 14), illustrated that modified lime-based pellets (LC0 and LA) were less sintered when compared to the pure limestone in both mild and realistic conditions. Pellets prepared using the novel technique of adding Alumina-rich spinel for their modification (14c, 14f, 14h and 14j) showed melted areas in the particle surface that may be caused because of deposits of

Al₂O₃ and MgO, which can derive in obstruction in the pores hindering the adsorption of CO₂. The surface of the particle in all the samples showed in Figure 14 was more irregular after 20 calcination/carbonation cycles than in the first cycle of calcination due to the increase in macroporosity.

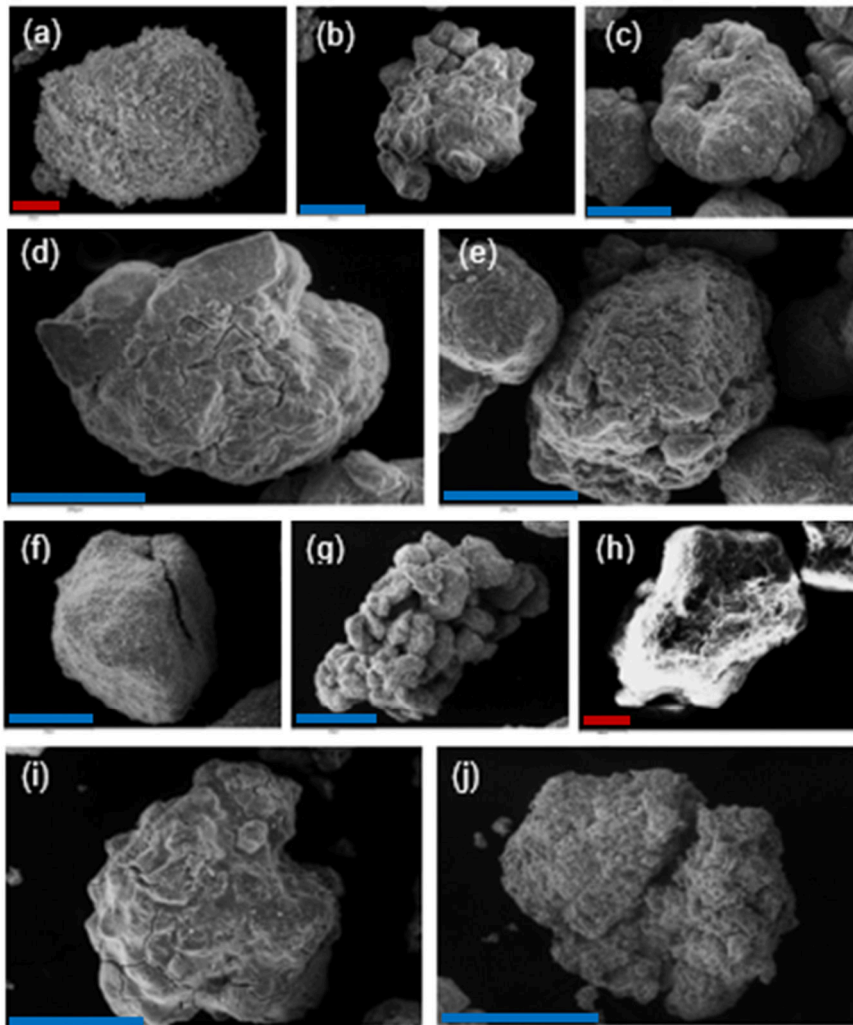


Figure 15: 120–650x SEM images of limestone, cement modified lime-based pellets and alumina-rich spinel modified lime-based pellets. (a) limestone, (b) LC0 and (c) LA realistic conditions after 20 cycles; (d) LC0 and (e) LA realistic conditions first calcination; (f) limestone, (g) LC0 and (h) LA mild conditions after 20 cycles; (i) LC0 and (j) LA mild conditions first calcination, where red lines represent 100 μm scale bars and blue lines 250 μm scale bars

The particle morphology (Figure 15) showed more cracks on cement and alumina-rich spinel modified lime-based samples (15b, 15c, 15d, 15e, 15g, 15h, 15i and 15j) compared to the pure limestone (15a and 15f). The modified lime-based pellets presented more irregular surface after 20 calcination cycles (15b, 15c, 15g and 15h) than after the first calcination (15d, 15e, 15i and 15j) as it was also observed in Figure 14.

Alumina-rich spinel CaO-based pellets did not exhibit any improvement in the carbonation capacity compared to limestone and cement CaO-based pellets in any of the conditions studied. Previous studies [32, 33] concluded that the use of alumina compounds as binders in CO₂ capture improves the performance of the sorbent over cycles. SEM images (Figure 14 and Figure 15) and EDX images (Figure 16, 17, SI-28, SI-29 and SI-30) showed that some Al₂O₃ and MgO deposited in the surface of the particle were blocking the pores. This could be due to the differences in density with the other elements present in the particles. This phenomenon and the amount of alumina-rich spinel used during pelletisation process could explain the difference between the results obtained and earlier results [32, 33].

3.3 Component distribution

Figures 16 and 17 show examples of the EDX analysis done during the experiments. It can be observed how the amount of Na and Cl increases with the increment in seawater concentration used due to the presence of salt; only a small portion (in some cases undetectable) can be found in LC1 and LC10, and they appeared more significantly in LC25 and LC50 for each of the conditions studied. Maps show how the Al₂O₃ was deposited in certain zones of the modified lime-based pellets surface (both cement and alumina-rich spinel) particles blocking the pores and hindering the CO₂ absorption. This

phenomenon intensified when the particles were treated with seawater because salt tended to be deposited in the same position as Al_2O_3 . When there was no presence of alumina in the portion of the particle studied, Na and Cl distributed arbitrarily around the sample. Ca and O always distributed uniformly along the particle. In the alumina-rich spinel modified lime-based pellets, MgO deposited with the Al_2O_3 contributing to pore obstruction. In order to represent the full spectrum of the considered materials, the EDX maps for all the samples have been provided in Supporting Information. This information includes the distributions of O, Na, Cl, Ca, Al and Mg along the different particles (limestone, LC0, LC0*, LC1, LC10, LC25, LC50 and LA) under mild and realistic conditions after 20 cycles and after the first calcination.

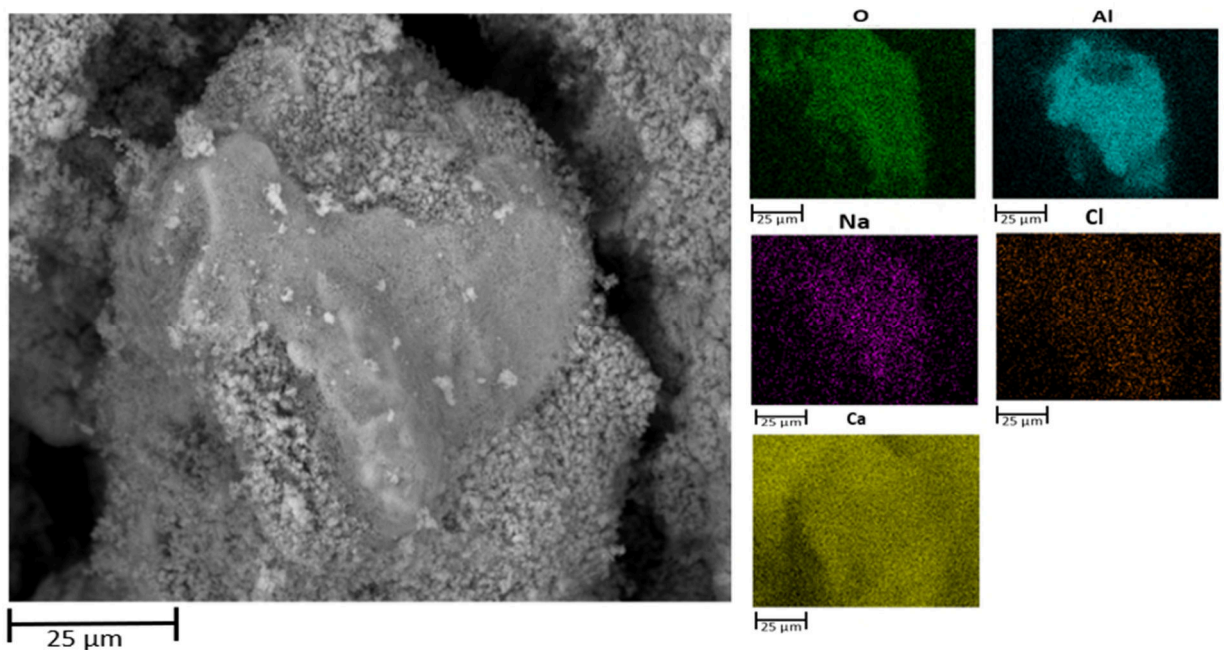


Figure 16: EDX map example - LC10 realistic conditions after 20 cycles

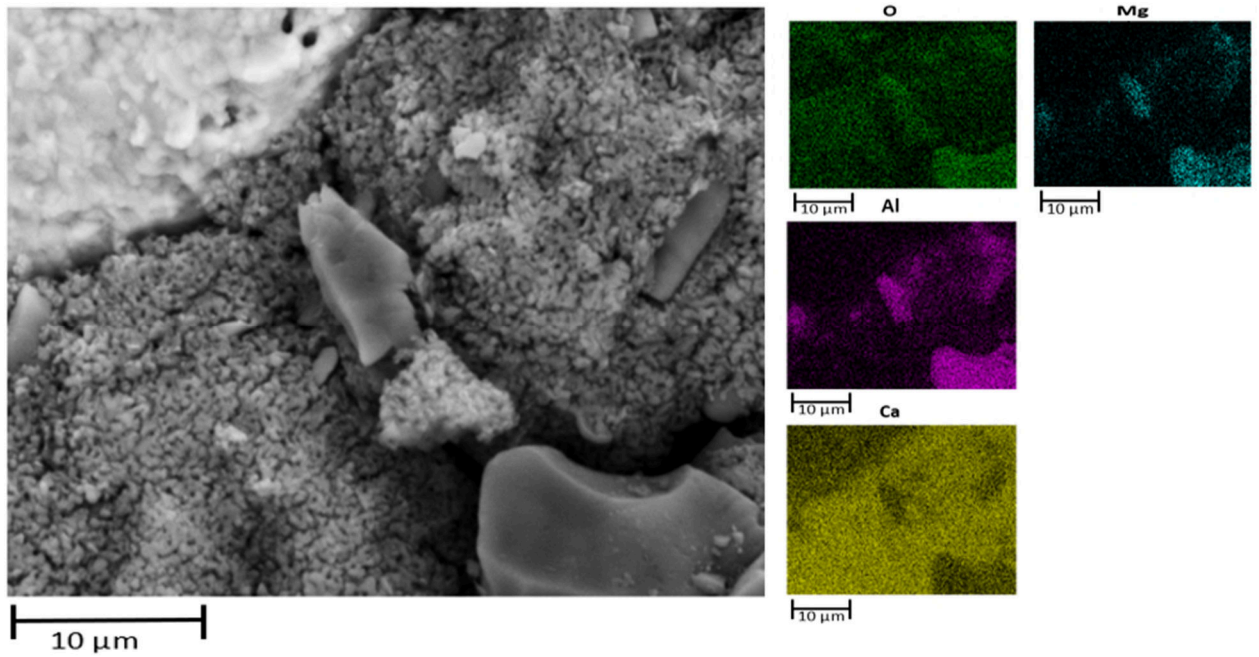


Figure 17: EDX map example - LA realistic conditions after 20 cycles

4 Conclusions

An improvement in carbonation conversion over cycles of calcium aluminate cement CaO-based pellets has been observed (25% conversion after 20 cycles achieved by limestone and 35% with aluminate cement CaO-based pellets, under mild conditions, and 11% conversion after 20 cycles with limestone compared to 15% utilising aluminate cement CaO-based pellets, under realistic conditions). It has been shown that the type of cement utilised in the pelletisation process has negligible influence in the carbonation conversion, obtaining very similar conversions for both aluminate cements utilised, CA-25R and CA-14M. It has been also found that the seawater-doped aluminate cement CaO-based pellets behaved poorly compared to the aluminate cement CaO-based pellets without seawater. The influence of the salt concentration on the carbonation capacity of the sorbent is negligible; almost the same conversion has been obtained after 20 cycles in all the cases studied (LC1, LC10, LC25 and LC50). Deposits of Al_2O_3 and

salt has been observed in the surface of the particles; these deposits can lead to blockage of the pores hindering the CO₂ adsorption when both, cement and seawater, have been combined. Alumina-rich spinel CaO-based sorbents performed poorly over cycles when compared to pure limestone, reaching less conversion after 20 cycles. Al₂O₃ and MgO tend to deposit in the surface of the CaO-based sorbents hindering the CO₂ adsorption.

As the salt seems to deposit in the same place as alumina blocking the pores and hindering CO₂ adsorption, it may be interesting to dope pure natural sorbents, such as limestone and dolomite, with seawater to evaluate if its utilisation without cement improves the sorbent performance. Further research needs also to be performed with different concentrations of alumina-rich spinel to further evaluate its performance.

Supporting Information containing the EDX maps for all the samples studied in this work is available along with this manuscript. It includes the distributions of O, Na, Cl, Ca, Al and Mg along the different particles (limestone, LC0, LC0*, LC1, LC10, LC25, LC50 and LA) after 20 cycles and the first calcination under both mild and realistic conditions.

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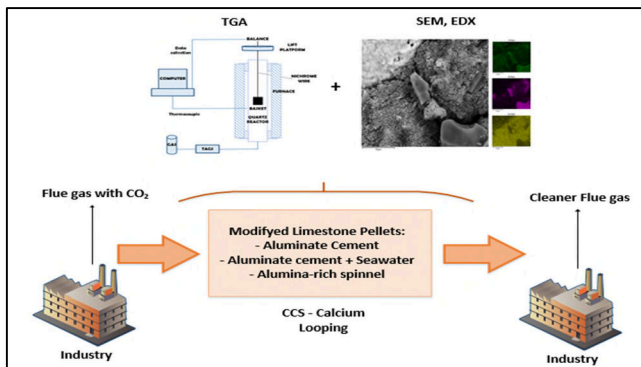
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