Accelerated carbonation by Cement Kiln Dust in aqueous slurries: chemical and mineralogical investigation

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Graphical Abstract

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Accelerated carbonation by Cement Kiln Dust in aqueous slurries: chemical and mineralogical investigation

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Abstract

Cement Kiln Dust accelerated carbonation in aqueous slurries at 25°C and 3 bar PCO₂ was investigated by X-ray **d**Diffraction analysis, solution chemistry, **s**Scanning **e**Electron **m**Microscopy and **e**Energy **d**Dispersive **s**Spectroscopy to better understand chemical and mineralogical processes governing CO₂ uptake. Dissolution of lime, portlandite and ettringite occurs primarily in the carbonation process. These provide Ca²⁺ ions to react with CO₃²⁻ ions leading to calcite bulk precipitation from solution. Concomitantly, the dissolution of Ca-(Al)-silicate grains takes place but it is limited by the formation of a Si-rich and Ca-depleted rim which appears onto the grain surfaces due to an initial hydration step. The Si-rich decalcified rim hinders the diffusion of Ca²⁺ ions from the core of silicate grains to the bulk solution. The diffusion of Ca ions through the rim is then the rate limiting step for the carbonation of Ca-(Al)-silicate, that accounts for up to 4% of the carbonation potential. Achieved results elucidate the processes governing CO₂ uptake by **Cement**

~~Kiln Dusteement kiln dust~~, and are fundamental in the perspective of enhanced CO₂ sequestration by ~~Cement Kiln Dusteement kiln dust~~.

Keywords

Accelerated carbonation, ~~Cement Kiln Dusteement kiln dust~~, Ca-(Al)-silicate, Ca carbonate, CO₂ sequestration

1. Introduction

Carbon dioxide (CO₂) is the most important greenhouse gas resulting from the human activity, and it is responsible for about two-thirds of the enhanced greenhouse effect.¹ The development of ~~eCarbon eCapture, Utilization~~ and ~~sStorage~~ (CCUS) technologies is one of the possible strategies for reducing CO₂ in the atmosphere. Among the CCUS technologies, CO₂ utilization by mineralization as carbonates is often referred as accelerated carbonation technology.^{2,3} Mineral carbonation is a process whereby CO₂ is chemically reacted with Ca and/or Mg containing minerals to form stable carbonate materials. Carbonation can occur naturally during the weathering process of minerals,² consisting in the reaction between natural alkaline silicates and atmospheric CO₂. This process removes CO₂ from the atmosphere by neutralizing the acid gas with mineral alkalinity.⁴ Weathering of Ca and Mg (hydr)oxides and silicates is a major consumer of excess atmospheric CO₂ on a geological timescale.⁵ However, the kinetics of carbonation is very slow at ambient condition due to the relatively low CO₂ concentration, about 0.03-0.06% by volume.^{4,6,7} Accelerated carbonation involves alkaline materials reacting with CO₂ in controlled conditions, aiming to reduce the time required for complete carbonation and to accelerate the reaction to a timescale of a few minutes or hours,^{2,3,8} with the potential to capture billions of tonnes of carbon per year.⁹ Several up-to-date reviews on the state of the art of ~~mMineral eCarbonation~~ (MC) technologies are available, reporting an increasing number of research projects worldwide and thus highlighting the interest and the potentiality of mineral carbonation within CCUS technologies.¹⁰⁻¹² The undeniable benefit of mineral carbon sequestration is being the most permanent and safe method of carbon

storage. However, despite the well documented advantages, the technology is not mature yet. After 20 years of R&D studies since its first proposal as CCUS method,³ the state of development is still at the laboratory demonstration scale and only some MC technologies have recently approached the commercial scale.^{10,12} The main reasons for limited application on a larger scale are the low reaction conversion, the slow kinetics and the energy intensity of the accelerated carbonation processes, which affect the economic viability of the technology.^{10,12} It is well recognized that to reach the highest carbonation efficiency, the major challenges are represented by the identification of the controlling mechanisms and optimal operating parameters. In particular, when carbonation of alkaline materials is performed through aqueous route, the following three mechanisms could be involved: 1) dissolution of Ca and Mg reactive species from the solid matrix; (2) dissolution of CO₂ into the liquid phase and conversion of carbonic acid to bicarbonate/carbonate ions; (3) consequent nucleation and precipitation of carbonates.^{2,13} The material particle size, the temperature, the gas pressure, the liquid/solid (L/S) ratio are important parameters that could differently affect the carbonation mechanisms,^{2,10} and a prediction on a theoretical basis of the main effects and of the joint interactions between the different factors is hard to be derived. At present, the possibility to enhance the reaction kinetics and the extent of the carbonation process, as well as to improve its economic viability, are the focus of several accelerated carbonation experiments being conducted worldwide.^{14,15}

Some of the above-mentioned drawbacks could be avoided when alkaline wastes are used as feedstock instead of mineral resources. In fact, alkaline residues generally contain highly reactive Ca and Mg species, potentially suitable for achieving high and fast carbonate conversions without the need of pre-treatment or energy intensive operating conditions. Moreover, they are available at low cost near CO₂ point source emissions and allow avoiding the exploitation of natural resources. Finally, the resulting pH neutralization and mineral modification induced by carbonation could improve the chemico-physical characteristics of the waste material, allowing for a safer disposal or for a beneficial re-use.^{11,16,17}

Among alkaline industrial residues that can be used as a source of carbonate-forming ions, Cement Kiln Dust (CKD), a by-product from cement industry, appears interesting due to its suitable composition and its availability near CO₂ point source emission. The cement industry generates in fact around 5% of global CO₂ emissions¹⁷ and produces yearly 30 millions of tonnes of CKD.¹⁸ Therefore, accelerated carbonation of CKD could make possible a significant reduction of the cement plant CO₂ emissions. CKD is a potential hazardous waste, in part because of the caustic nature and its potential to be a skin, eye, and respiratory irritant. In addition, contaminants from the raw materials and fuels tend to concentrate in CKD.^{19,20} Previous works on CKD²¹⁻²³ mainly focused on the improvement of the carbonation process by varying operating conditions such as CO₂ pressure, temperature, liquid-to-solid (L/S) ratio, CO₂ humidity, CO₂ flow rate, liquid flow rate, particle size, and solid pre-treatment. Gunning et al.¹⁶ studied the effects of the carbonation of the CKD on the chemistry, microstructure and leaching characteristics of the solid material, whereas Anderson et al.²⁴ investigated the influence that the carbonation of CKD, performed at ambient temperature and pressure, has on the mineral composition and calcite precipitation mechanisms. At the current state of knowledge and in view of a scale-up of the process, further laboratory scale studies are needed with the aim to better elucidate the mechanisms that may limit the rate or the extent of the accelerated carbonation process on CKD.

In a previous work, our research group carried out accelerated carbonation experiments on CKD focused on the assessment of the optimal operating condition in terms of CO₂ sequestration and reaction kinetics.²⁵ The operating parameters such as L/S ratio, CO₂ pressure and temperature were found to differently affect the CO₂ uptake. The higher CO₂ uptake and reactive species conversion were attained at lower temperatures and under slurry-phase conditions. In particular, the optimal water content and the optimal CO₂ pressure were found to be L/S=5 L/kg and PCO₂=3 bar, respectively, allowing to achieve a ~~The higher CO₂ sequestration uptake of capacity (9.80%.~~ However,) was achieved at a L/S=2.5 and at operating pressure of 3 bar, but the maximum theoretical CO₂ sequestration capacity of 13.4% was not reached. Experimental results indicated that during

carbonation of CKD the reaction rate slows down, with an initial rapid conversion of alkaline species into carbonates and a more gradual conversion of residual un-reacted species, without reaching a complete conversion.

In the present study, CKD was carbonated in aqueous suspension (slurry-phase carbonation) at 25°C and CO₂ pressure of 3 bar to elucidate chemical and mineralogical processes limiting the CO₂ sequestration ~~yield-capacity~~ by combining X-ray ~~d~~Diffraction analysis (XRD), ~~s~~Scanning ~~e~~Electron ~~m~~Microscopy (SEM), chemical analysis of solution in contact with the alkaline waste during the carbonation experiment, and speciation and equilibrium calculation. Results can be useful to improve understanding of the governing processes, and allow for better utilization of CKD in CO₂ sequestration.

2. Materials and methods

2.1 Cement Kiln Dust and carbonation experiment

The CKD analysed in this study was collected from a cement plant in the South Sardinia (Italy). The plant adopts a semidry process based on Lepol Grate Technology in which hot gases, coming from the kiln, from an auxiliary burner and, sometimes, from the recovered hot gas of the cooler, are used in two chambers for drying and pre-calcining the raw materials. A total mass sample of 60 kg was collected at the air pollution control devices treating the exhaust gases from the kiln system (electrostatic filter) and stored in airtight containers at room temperature.

A detailed chemical composition of CKD is reported in Table 1. Calcium is the major component by far (CaO, 47%), while Mg (MgO, 2.6%), Na (Na₂O, 0.28%) and K (K₂O, 1.3%) are present in small amounts. This composition is within the typical range reported in literature.^{16,22,26} Among the potential harmful elements, Pb (463 mg/kg), V (363 mg/kg), Zn (177/mg/kg), Cu (163 mg/kg), Ni (97 mg/kg), Mn (39 mg/kg), Tl (25 mg/kg), Cr (22 mg/kg), and As (16 mg/kg) are the most abundant.

The operating conditions to be adopted for the accelerated carbonation experiment, in terms of
temperature, CO₂ pressure and water content, procedure was performed were selected on the basis
of considering the results obtained in a previous study by our research group (Cappai et al.²⁵). The
mentioned study was specifically aimed at evaluating the influence on CO₂ uptake and reaction
kinetics exerted by the operating parameters such as L/S ratio (0.4; 1; 3; 5; 10 L/kg), CO₂ pressure
(1; 3; 5; 10 bar) and temperature (25; 50; 100 °C). HThe higherst CO₂ uptake and reactive species
conversion were attained at lower temperatures (25°C) and under slurry-phase conditions. In
particular, the higherst CO₂ sequestration capacity (9.80%) was achieved at a L/S=5 and at operating
pressure of 3 bar (please see Figure S1 in the Supplementary Material section, reporting the CO₂
uptakes over time obtained at T=25 °C and at the different pressures and L/S ratio adopted). In the
present study, a quantity of 100 g of dry sample was mixed with 500 g of deionized water (slurry-
phase process) and exposed to a 100% CO₂ atmosphere, at a pressure of 3 bar and a temperature of
25°C. Test was performed in a 2 l pressurized reactor equipped with a 1.7 l internal Teflon vessel,
an electric jacket for temperature control, and a stirred shaft. At each set time (0.5, 1, 2, 3, 5, 8 and
24 hours), a dedicated sampling device was used for drawing slurry samples, which were filtered
over a 1.2 µm membrane. Liquid phase was used for chemical analysis (see 2.3 paragraph). Solid
samples were oven dried at 40°C for 24 hours and stored in closed containers for subsequent
analysis. The experiment was performed in triplicate. Obtained results are perfectly in agreement
and observed variations are in the range of the experimental errors. For this reason and the sake of
clarity, in the result and discussion paragraphs, we prefer to present the mean values of chemical
data, and the corresponding standard deviation is indicated by error bars in reported graphics. The
specific curves of each experiment are reported in the Supplementary Materials (Fig. S2, S3, S4 and
S5).

2.2 X-ray diffraction and electron microscopy study

An aliquot of ~200 mg of dried powder of untreated CKD, and solid samples collected at each set time during the carbonation experiment were slightly ground in an agate mortar, and subjected to XRD analysis, using conventional θ -2 θ equipment (Panalytical) with Cu K α wavelength radiation ($\lambda = 1.54060 \text{ \AA}$), operating at 40 kV and 40 mA, using the X'Celerator detector.

SEM imaging and EDS (Energy Dispersive Spectroscopy) analysis (before and after the carbonation) were carried out using a field emission (Schottky thermal field emitter) SEM, under high vacuum conditions. In addition, thin sections for SEM imaging were prepared by incorporating CKD in an epoxy resin and subsequently flattening to an appropriate thickness and polishing in order to highlight the rim of the reaction. In order to obtain better quality images, samples were gold coated before observation, using a SEM Coating Unit PS3 (Agar Aids for Electron Microscopy).

2.3 Assessment of CO₂ sequestration

Total carbon content analysis (LECO CHN-1000 Element Analyzer) were performed in duplicate on dried solid residues obtained at the different durations. Mean values from TC (total carbon) content analysis were used to estimate the CO₂ uptake, with an error (difference between mean and real value) always lower than 3% of the average value. The obtained mean values, expressed as weight % of CO₂ (CO₂ carbonated [%]) were used to calculate the CO₂ uptake by applying the equation 1, where CO_{2initial} [%], is the TC content of the untreated CKD, again expressed as weight % of CO₂ (Equation 1).

$$CO_2 uptake[\%] = \frac{CO_{2carbonated}[\%] - CO_{2initial}[\%]}{100 - CO_{2carbonated}[\%]} * 100 \quad \text{Equation 1}$$

The degree of sequestration in terms of reactive species conversion yields was also evaluated, by comparing the amount of CO₂ sequestered in each test to the maximum amount theoretically

possible (Equation 2). The theoretical limit of uptake was calculated based on the Steinour formula (Equation 3),²⁷ which assumes the full stoichiometric conversion to carbonates of the reactive alkaline species-

$$\eta[\%] = \frac{CO_2 \text{ uptake } [\%]}{ThCO_2 \text{ uptake } [\%]} * 100 \quad \text{Equation 2}$$

$$ThCO_2 \text{ uptake } [\%] = 0.785(CaO[\%] - 0.56CaCO_3[\%] - 0.7 SO_3[\%]) + 1.091MgO[\%] + 0.71Na_2O[\%] + 0.468(K_2O[\%] - 0.632KCl [\%]) \quad \text{Equation 3}$$

2.4 Chemical analysis of solutions

The liquid phase was further filtered using a 0.45 µm Millipore filtering system and pH, redox potential, conductivity, alkalinity, trace elements and anions were evaluated on filtered aliquots. pH values were measured by a Ross electrode connected to a pH-meter (Orion, Thermo Fisher Scientific, USA) after calibration against NIST buffer solutions. Redox potential was measured with a platinum electrode, and values were corrected against the Zoëll's solution.²⁸ Conductivity was determined by conductivity meter (Thermo Orion 150 Aplus). Alkalinity was measured on filtered aliquot using both the Gran titration method with hydrochloric acid (indicator: methyl orange), and the Gran function plot method.²⁹ Another aliquot of filtered solution was placed in acid pre-cleaned polyethylene bottles and then acidified to 1% HNO₃ for subsequent analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin-Elmer, Elan DRC-e, USA) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, ARL Fisons ICP Analyzer 3520 B). Anions were determined by Ionic Chromatography (IC, Dionex ICS-3000) in a filtered (0.45 µm) unacidified aliquot. The Detection Limit (DL) for chemical elements was calculated at 10 times the standard deviation of the blank solutions. To evaluate the accuracy and precision of trace elements determination, two reference solutions were used: the NIST SRM 1643e

198 and the EnviroMAT Ground Water ES-L-1. Rhodium was used as an internal standard for ICP-MS
199 analysis to correct for instrument drift. The ionic balance was always better than $\pm 10\%$.

200 2.5 Speciation and equilibrium calculations

201 Speciation and equilibrium calculation were performed using the PHREEQC computer program
202 (llnl database). Saturation indexes (SI) with respect to solid phases were calculated as $SI = \log$
203 (IAP/K_s) , where IAP is the ionic activity product and K_s the solubility equilibrium constant at the
204 specific water temperature.³⁰ pe vs pH diagrams were plotted using the Hydra-Medusa software and
205 its internal database complex.db and complex.elb.³¹

206 3. Results

207 3.1 Mineralogical and microscopic characteristics before and after the carbonation 208 experiment

209 CKD was investigated by XRD (Fig. 1) and SEM analysis (Fig. 2 and 3) before and after the 24-
210 hour carbonation test. Raw CKD (Fig. 1a) are made up of calcite (CaCO_3), quartz (SiO_2), lime
211 (CaO) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). In addition, peaks ascribed to cement minerals such as
212 portlandite ($\text{Ca}(\text{OH})_2$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26 \text{H}_2\text{O}$) were detected. Bixbyite
213 (Mn_2O_3) and, likely, rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$) and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) were also found. SEM
214 analysis (Fig. 2a) of the raw material shows that the grain size ranges from hundreds of nm to
215 hundreds of μm , indicating high heterogeneity for the CKD. EDS spectra show that quartz (Fig. 2b),
216 calcite (Fig. 2c), and dolomite (Fig. 2d) can be easily recognized. Some micrometric crystals have a
217 hexagonal habitus typical of portlandite (images not shown).

218 XRD analysis of CKD after carbonation (Fig. 1b) reveals that the amount of calcite increases after
219 the experiment while lime, portlandite, ettringite, and bixbyite disappear. Besides the presence of
220 quartz, calcite, dolomite, and Ca-silicates (observed already in the raw sample), traces of gypsum
221 | were detected after the carbonation experiment. Gypsum, most likely, derived from ettringite

dissolution, the subsequent release of Ca^{2+} and SO_4^{2-} ions in solution and their precipitation as gypsum and calcite.

To reveal grain surface processes, SEM analysis was performed on CKD sections after the carbonation experiment (Fig. 3a-b). Figure 3a shows the backscattered electron image, and Figures from 3b to 3d show the energy dispersive X-ray maps for Si (b), Ca (c), and Al (d). Micro-analysis and EDS mapping indicate that these grains consist of Ca-Al-silicates, in agreement with XRD analysis (see Fig. 1b) that shows residues of gehlenite in the treated sample. After the carbonation test, residual Ca-silicate grains investigated by SEM appear to be not carbonated, and enveloped by a Si-rich (Fig. 3b) decalcified rim (Fig. 3c). There, Al is homogeneously distributed (Fig. 3d), and elements such as Fe, S, K and V can be recognized by EDS analysis (data not shown).

3.2 CO₂ uptake

Figure 4 shows the CO₂ uptake and the Ca- degree of sequestration in terms of reactive species conversion yields, ~~conversion yields~~ as assessed during the accelerated carbonation test. The time-dependent curve shows a very fast initial conversion of Ca-alkaline reactive species into carbonates. Then, a plateau is reached, at a value lower than the maximum theoretical CO₂ sequestration capacity of 13.4%. As far as the potential of CO₂ sequestration is concerned, the results obtained in this study (9.45% by mass of CO₂) are similar with those reported by Gunning et al.¹⁶ (9% at ambient temperature and 2 bar over 72 h), but lower by ca 4% with respect to maximum sequestration potential observed for this material. Understanding the mechanisms underlying this limit provide us a basis also for comparing the results from different experiments.

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244 3.3 Chemical analysis, thermodynamic driving force and saturation state of the leached 245 solutions

246 XRD analysis reveals that lime, portlandite, ettringite, rankinite and gehlenite are the original
247 phases potentially involved in the carbonation process by providing cations, moving pH value
248 toward slightly basic conditions thus favouring the dissolution of CO₂ and dissociation of carbonic
249 acid to eventually increase concentration of carbonate ion. Actually, the SI respect to the above
250 mentioned minerals are negative (< -10) in the liquid phase, indicating that their dissolution is
251 favoured and, consequently, these are a source of Ca for the carbonation reactions.

252 Table 2 shows pH, redox potential (Eh), electrical conductivity (Cond), and the concentration of
253 selected chemical components of the liquid phase collected during the carbonation experiment. pH,
254 Eh and Cond values were measured immediately after solution collection from the reactor. At the
255 same time, different aliquots were stabilized for chemical analysis. Reported values of Ca, Mg,
256 HCO₃⁻, SO₄²⁻, SiO₂ and Al are the total concentrations of each chemical species measured as
257 described in the paragraph 2.4. Table 3 reports PHREEQC output speciation of selected chemical
258 species (reported as ion activity) deriving from the dissolution of portlandite, ettringite, rankinite,
259 and gehlenite, and of the HCO₃⁻ and CO₃²⁻ species involved in the precipitation of carbonate
260 minerals. Trace elements are reported in Table 4. Set times 0.5, 1, 2, 5, 8, and 24 hours will be
261 referred to hereafter as T1, T2, T3, T4, T5 and T6, respectively. pH values (Table 2) are near
262 neutral and decrease from 7.55 to 6.79, probably initially dominated by the fast dissolution of
263 portlandite and ettringite, then governed by the dissolution of CO₂ in water, the formation of
264 carbonic acid and its subsequent dissociation. In addition, pH values (7.11±0.07), observed between
265 T3 and T6 sampling, reflect the buffering effect of calcite precipitating during accelerated
266 carbonation. Redox potential values (Eh between 342 and 453 mV) indicate oxidizing conditions,
267 and tend to increase during the experiment.

Concentration of Ca and Mg, HCO_3^- and SO_4^{2-} , and SiO_2 and Al vs time in the liquid phase, collected during the carbonation experiment, are shown in Fig. 5a, 5b and 5c, respectively (see also Fig. S3). Ca^{2+} (60-70%) is the most abundant species (Table 3) for the total content of Ca. This tends to increase in the first 2 hours, and reaches the highest concentration (43 mmol/l) at T3. Then, it decreases from T3 to T6 (26 mmol/l). This trend is due to the release of Ca to solution because of the dissolution of lime, portlandite, ettringite and Ca(Al)-silicates between T1 and T3. Then, Ca concentration decreases because of the precipitation of new phases, such as calcite and gypsum (see Fig. 1 and 3.1 paragraph), or to absorption processes that become predominant over the dissolution reactions between T3 and T6. In agreement, equilibrium calculation shows that calcite is oversaturated in solution (Fig. 6a).

Mg concentration (Table 2, Fig. 5a and Fig. S3a) increases from T1 to T6, despite results of equilibrium calculation (Fig. 6b) indicate that leached solutions are oversaturated with respect to Mg(Ca)-bearing carbonate minerals such as dolomite and magnesite. In fact, although dolomite is oversaturated in studied solutions (SI between 3.1 and 5), dolomite precipitation is driven by kinetic factors. A high $\text{Mg}^{2+}/\text{Ca}^{2+}$ molar ratio (higher than 5–10:1)³² is required to precipitate dolomite because the Mg^{2+} ion has a high hydration energy³³. Leached solutions have a $\text{Mg}^{2+}/\text{Ca}^{2+}$ molar ratio between 0.10 and 0.96, and increase from T1 to T5 (Fig. 5a and Fig. S4) because of calcite precipitation, reaching steady-state values between T5 ($\text{Mg}^{2+}/\text{Ca}^{2+} = 0.92$) and T6 ($\text{Mg}^{2+}/\text{Ca}^{2+} = 0.96$). Moreover, the kinetic of precipitation mechanism of Mg carbonates is controlled by the supersaturation with respect to magnesite.³⁴ In a broad range of PCO_2 and $\text{Mg}^{2+}/\text{Ca}^{2+}$ activity ratio in solution, the composition of precipitated Ca-Mg carbonate depends only on SI respect to magnesite. Under observed values ($\text{SI} < 3$), Mg can be incorporated into Ca carbonate only in few amount by forming low-magnesian calcite. Thus, Mg^{2+} ions remain in solution and do not contribute to CO_2 uptake during the carbonation process. Other than calcite, strontianite (Fig. 6c), and witherite (Fig. 6d) are oversaturated in solution. Although XRD analysis reveals only the presence of calcite, Sr and Ba carbonates could form independent phases coprecipitating with

294 calcite, but sensitivity of XRD technique does not allow their detection. Amorphous phases cannot
295 be detected by XRD as well.

296 Alkalinity (HCO_3^-) increases from T1 to T5 (Fig. 5b [and Fig. S3b](#)), and it reaches a steady-state
297 value between T5 and T6. The observed increase in alkalinity from T1 to T5 is due to the
298 continuous dissolution of CO_2 into the slurry solution and relative dissociation of carbonic acid. The
299 behaviour of SO_4 can be explained considering dissolution mechanism of ettringite. Ettringite is a
300 stable mineral above a pH of 10.7 and dissolves congruently with a $\log K_{\text{sp}}$ of $-111.6 (\pm 0.8)$. At
301 near neutral pH, ettringite undergoes incongruent dissolution to gypsum, Al-hydroxides and Al-
302 hydroxy sulphates, thus controlling Ca^{2+} , Al^{3+} , and SO_4^{2-} activities.³⁵

303 SiO_2 and Al have a similar trend (Fig. 5c [and Fig S3c](#)), showing an initial increase in concentration,
304 from T1 to T2, and a decrease until T6. Actually, SiO_2 ($\text{SI}_{\text{quartz}}$ 0.9-1.3), $\text{Al}(\text{OH})_3$ (SI 2.0-2.8), and
305 Ca-Al-silicate hydrate minerals, such as gismondine ($\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 9\text{H}_2\text{O}$, SI 9-15), scolecite
306 ($\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$, SI 6.6-10) and laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, SI 5.7-9.5) are oversaturated in
307 solution. Moreover, precipitation of Ca-silicate hydrate gel occurs, as observed by SEM analysis.

308 Trace elements behave according to two distinct groups: 1) V, Mo, Li, B, Ni, U and Sb show an
309 increase in concentration during the experiment; 2) Rb, Ba, Cr, Sr, Zn, Mn, Cd, Co, Tl, and As are
310 released immediately in solution and then decrease during the carbonation experiment. The
311 available literature studies focusing on the influence of MC on trace element solubility indicate that
312 carbonation could either increase or reduce trace element mobility from alkaline residues.^{36,37} In
313 particular, an higher release has been observed for oxyanions, according to the fact that they are
314 often incorporated in ettringite-like minerals which dissolve upon carbonation. Other elements such
315 as heavy metals are converted into their less soluble salts or immobilized through sorption onto
316 CaCO_3 and/or co-precipitation into newly formed minerals.

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4. Discussion

4.1 Process chemistry and thermodynamic prediction

To investigate mineralogical processes of dissolution and precipitation governing accelerated carbonation of CKD, we combined chemical data with PHREEQC calculations, XRD and SEM analysis. During the carbonation test, injected CO₂ dissolves into solution proportionally to the PCO₂, in accordance with Henry's law, and hydrates to carbonic acid (H₂CO₃). Then H₂CO₃ dissociates into bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions depending on the solution pH. Simultaneously, phases such as lime and portlandite (Fig. 1a) in contact with water undergo fast dissolution, in agreement with the calculated SI (< -10), leading to a fast increase in Ca²⁺ concentration from T1 to T2 (see Table 2 and Fig. 5a). As indicated by the activity values in Table 3, Ca²⁺ aquo ions react with CO₃²⁻ leading to calcite bulk precipitation from solution. Also, ettringite,^{38,39} rankinite and gehlenite² take part to the carbonation process. During ettringite dissolution, Ca²⁺ and SO₄²⁻ ions are released into solution and then precipitate as gypsum and calcite. In agreement, XRD peaks of gypsum were observed in the carbonated CKD sample (Fig. 1b). Transformation of Ca-silicates to Ca-carbonate is characterized by a slower dissolution kinetics of Ca-silicates than lime and portlandite. SEM analysis (see Fig. 3) shows that the residual non-carbonated grains of Ca-Al-silicates are surrounded by a Si-rich decalcified rim. This can be explained considering that carbonation of Ca silicates is accompanied by hydration³⁶ that leads to the precipitation of a Ca-silicate hydrate gel. During the carbonation process, the Ca-silicate hydrate gel is progressively decalcified.⁴ Accordingly, the Ca²⁺/SiO₂⁰ activity ratio increase in the liquid phase (Fig. 7 and Fig. S3) due to the release of Ca²⁺ ions which become available for calcite precipitation. It was demonstrated^{2,41} that, progressively, the Ca-silicate hydrate gel is transformed into calcite and highly polymerized silicate gel. This process is the so called secondary

carbonation,³⁶ but, being a slow solid state diffusion process, it has limited practical effect for carbonation purposes.

Figures 8a and b show predominance Pourbaix diagrams for the system Ca-Al-C-Si-H-O, plotted considering chemical parameters from speciation calculation for T1 and T6 samplings. Predominance diagrams allow having a synoptic view of physico-chemical evolution of the investigated system and prediction of mineral evolution. It is worth noting that, in Fig. 8, the CaCO₃ stability field increases in time from T1 to T6 indicating conditions more favourable to calcite precipitation. Concomitantly, the stability field of CaSiO₃ disappears in favour of the Ca₂SiO₄ field, corresponding to a decrease of Si activity in solution (see Table 3) that, in turn, likely favours Si storage in amorphous grain coatings. Black circles indicate pH and pe values of the collected liquid phase at T1 (Fig. 8a) and T6 (Fig. 8b). Although black circles fall outside the calcite field, it is worth noting that chemical properties of the liquid film in contact with the alkaline solid waste grains are different from that of the bulk solution. In fact, dissolution of minerals such as lime, portlandite, gehlenite and rankinite leads to the consumption of hydrogen ions and, consequently, to an increase in pH values, especially in the solution in contact with mineral grains.

4.2 Reaction pathways and chemical processes affecting CO₂ uptake

The rate and extent of carbonation of CKD is affected by transport-controlled mechanisms such as CO₂ and Ca²⁺ diffusion to/from reaction sites, boundary layer effects (diffusion across precipitate coatings on particles), dissolution of Ca(OH)₂ at the particle surface, and pore blockage or precipitate coating development.²² Huntzinger et al.²² studied the extent and potential mechanisms and rate behaviour of the carbonation process in CKD at ambient temperatures and pressures by applying X-ray spectrometry, XRD, thermal analysis, and observed dry mass change. The major reactive Ca species identified in CKD samples before carbonation experiments were lime and portlandite. Authors²² stated that CO₂ sequestration appears to follow unreacted core model theory.

As carbonation progresses, the kinetics of the reaction are attenuated by the extent of the reaction due to diffusion control, with the extent of conversion never reaching completion. Anderson et al.^{24,42} investigated the reaction pathways ruling the carbonation processes in CKD by environmental SEM, XRD, thermal gravimetric analysis/differential thermal analysis. PHREEQC was used for modelling CKD reaction using a 10:1 liquid to solid ratio, and a simplified composition of CKD. Authors^{24,42} found that lime and portlandite were the major reactants. A second reaction path was the weathering of Ca-silicates that released Ca^{2+} for carbonation. Three types of CaCO_3 precipitation mechanisms were observed: (1) diffusion of CO_2 into portlandite particles causing precipitation in the pores of the particle and the growth of a CaCO_3 skin from the outside inward, slowing vapor and aqueous diffusion by causing blockages in the pore systems, (2) precipitation onto existing particles, and (3) precipitation from aqueous solution.

In this study, we combined XRD ~~and~~ SEM-EDS analysis performed before and after the carbonation experiment ~~, and with~~ solution chemistry ~~, with~~ speciation and equilibrium calculations performed at each set time (0.5, 1, 2, 3, 5, 8 and 24 hours) to better investigate chemical processes limiting CO_2 uptake. According to mineralogical and chemical investigations, we propose that the investigated accelerated carbonation of CKD follows a pathway of dissolution and precipitation reactions:

1. hydration and/or dissolution of lime, portlandite, and ettringite and release of Ca^{2+} ions in solution:

2. partial dissolution of rankinite and gehlenite, release of Ca^{2+} ions in solution and formation of a Ca(Al)-silicate external rim:

393 3. contemporary dissolution of gaseous CO₂ into solution and formation of bicarbonate ions
 394 according to the observed pH values (7.2±0.2):

396 4. dissociation of bicarbonate ions into carbonate ions in the solution in contact with the
 397 alkaline solid waste:

399 5. calcite precipitation from solution:

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402 In a first stage, a rapid transformation of lime, portlandite and ettringite into Ca-carbonate takes
 403 place. After their consumption, Ca from the Ca-(Al)-silicate phases diffuses toward the surface of
 404 the grains, and Ca²⁺ ions are dissolved into solution and precipitated as calcite. Leaching of Ca from
 405 Ca-(Al)-silicates results in a withdrawing Ca-(Al)-silicate core covered by a Si-rich decalcified rim
 406 (see Fig. 3) that may change the rate and mechanism of dissolution. During decalcification of the
 407 external rim, Ca²⁺ ions are dissolved into solution, while Si remains in the solid state, hindering the
 408 diffusion of Ca²⁺ ions from the grain core, and limiting conversion.^{20,41} Indeed, XRD analysis (see
 409 Fig. 1b) show that Ca silicate grains are still present in carbonated CKD, because formation of the
 410 external rim results in diffusion to be the rate limiting step, then limiting the carbonation process.
 411 This is reflected in the time-dependent curve of CO₂ uptake in Fig. 4 that shows an exponential
 412 shape, suggesting an initial rapid conversion of Ca reactive species into carbonates, and a
 413 subsequent decrease in reaction rate without reaching a complete conversion as estimated by the
 414 maximum theoretical CO₂ sequestration capacity (13.4%). This behaviour indicates that carbonation
 415 process follows an “unreacted core model”.^{22,40} Moreover, in our slurries experiments the rim is not
 416 made of calcite, as observed by Anderson⁴², the latter mineral precipitating from bulk solution.
 417 Thus, we argued that the rim hindering the unreacted core appears to be dependent on the
 418 experimental condition. Specifically, the composition of the rim could depend on the composition

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of the given CKD and also on the liquid-solid ratio. Moreover, CKD material comprise several minerals whose relative abundance is not constant. These findings allow us to assert that a potential optimization of the CO₂ uptake by CKD could be achieved properly selecting specific additives⁴³ to hinder the formation of external layers for improving diffusion of Ca ions through the Ca-Al-silicate grains to enhance carbonation reaction of the unreacted particle core.

5. Conclusions

The carbonation of CKD has been proved to be an effective technology to capture CO₂, and it need to be improved for being applied at a commercial scale. To reach the highest sequestration capacity, the main goals are represented by the identification of the optimal operating parameters and the limiting reaction mechanisms. In order to achieve a better understanding of the chemical and mineralogical processes affecting carbonation and CO₂ uptake efficiency of CKD, a slurry-phase accelerated carbonation was performed at 25°C and 3 bar. The CO₂ uptake by CKD follows an exponential increase, achieving a carbonation capacity of 9.45% in the first hour. XRD analysis indicates that the reactive species in CKD are lime, portlandite, ettringite, rankinite, and gehlenite. Direct observations by XRD and SEM, and geochemical modelling of solution in contact with CKD during the carbonation experiment indicate that CO₂ uptake is limited by the formation of a Si-rich decalcified layer covering the residual Ca-Al-silicates grains. In fact, in the presence of the Si-rich decalcified layer, the solution chemistry reached a stationary state and carbonation ceased before reaching the maximum theoretical uptake (13.4%). Literature studies on CKD observed the formation of a rim made of calcite instead of a Si-rich decalcified layer. Thus, we argued that the knowledge of the specific mechanism active in a given CKD carbonation set-up (reactor and materials) has direct implication for the scaling up to pilot or pre-industrial scale experiment. The findings from the present study indicate that a further process optimization is possible, aimed at avoiding the formation of Si-rich decalcified layer. On the basis of the CO₂ sequestration capacity of 9.45% assessed during the present study, since 0.2 tons of CKD for every ton of clinker are

produced¹⁷ and 0.507 tons of CO₂/ton of clinker are emitted,⁴⁴ the carbonation treatment would have the potential for sequestering 3.7% of the cement plant CO₂ emissions, which would increase to up to 5.27% if the maximum theoretical CO₂ sequestration capacity of 13.4% is exploited. This increase of carbonation efficiency is a crucial aspect in lowering the industrial capture cost, which is still considered too high for the implementation of MC on a large scale. Further studies with slurry accelerated carbonation of CKD would be useful in order to define the optimal conditions for enhanced carbonation process also by using additives to hinder silica rim formation.

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3 571 Figure 1. XRD pattern of CKD before (a) and after the carbonation test (b). Cal (calcite), Qz (quartz), Lime (lime), Dol
4 572 (dolomite), Prt (portlandite), Ettr (ettringite), Bix (bixbyite), Rank (rankinite), Gh (gehlenite), Gyps (gypsum).
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8 574 Figure 2. Scanning ~~e~~Electron ~~m~~Microscopy analysis of raw CKD. a) Overview of the CKD sample grain size; b) image and
9 575 microanalysis of a quartz grain; c) image and microanalysis of a calcite grain; d) image and microanalysis of a dolomite
10 576 grain.
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14 578 Figure 3. ~~Scanning Electron Microscopy~~SEM analysis of a CKD section after the carbonation experiment (T6). Backscattered
15 579 electron image (a) and the results of Si (b), Ca (c), and Al (d) mapping by energy dispersive X-ray on the CKD sample.
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17 580 Arrows indicate the Si-rich decalcified rim that envelops the residual non-carbonated grains of Ca-Al-silicates.
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21 582 Figure 4. CO₂ uptake and ~~degree of sequestration in terms of reactive species~~ the Ca-conversion yields during the accelerated
22 583 carbonation test.
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28 586 Figure 5. ~~Concentration~~Mean concentration of Ca, Mg (a), HCO₃, SO₄ (b), SiO₂ and Al (c) vs time in the liquid phase. Also,
29 587 Mg²⁺/Ca²⁺ molar ratio is shown.
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33 589 Figure 6. SI respect to calcite and Ca²⁺ activity vs time (a); SI respect to dolomite, huntite, magnesite and Mg²⁺ activity vs
34 590 time (a); SI respect to strontianite and Sr²⁺ activity vs time (a); SI respect to witherite and Ba²⁺ activity vs time (a) in the
35 591 liquid phase.
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39 593 Figure 7. ~~Mean~~Ca²⁺/SiO₂⁰ activity ratio concentration vs time in the liquid phase.
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42 595 Figure 8. pe vs pH diagrams for the system Ca-Al-C-Si-H-O for liquid phase collected at T1 (a) and T6 (b). Diagrams are
43 596 drawn by the chemical equilibrium-diagram-tool Hydra/Medusa. Black circles indicate pH and pe values of the collected
44 597 liquid phase at T1 (a) and T6 (b). Concentrations for Ca²⁺ - Al³⁺ - CO₃²⁻ - H₄SiO₄⁰ come from speciation calculation performed
45 598 by PHREEQC.
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602 Table 1. Elemental composition of the CKD (from Cappai et al.²⁵)

Element	(%)	Element	(mg/kg)
Al ₂ O ₃	2.95 ± 0.05	As	16.12 ± 0.79
CaO	46.75 ± 0.91	Ba	185 ± 9
Fe ₂ O ₃	1.94 ± 0.05	Cd	7.08 ± 1.22
K ₂ O	1.30 ± 0.01	Co	5.66 ± 0.89
MgO	2.64 ± 0.08	Cr	22.12 ± 1.34
MnO	0.05 ± 0.00	Cu	163 ± 9
Na ₂ O	0.28 ± 0.10	Mo	38.87 ± 3.13
P ₂ O ₅	N.D.	Ni	97.02 ± 9.59
SiO ₂	18.65 ± 0.21	Pb	463 ± 28.0
TiO ₂	0.12 ± 0.01	Sb	6.82 ± 1.13
LOI	26.80 ± 0.10	Se	13.31 ± 0.10
Soluble anions (mg/kg)		Tl	24.87 ± 1.10
Chloride	3204 ± 93	V	363 ± 7
Sulphate	7382 ± 370	Zn	177 ± 10

Table 2. Mean values of pH, redox potential (Eh), electrical conductivity (Cond), and mean concentration of selected chemical components of the liquid phase collected during the carbonation experiments.

Sample	Time (hour)	pH	Eh (mV)	Cond (mS/cm)	Ca	Mg	HCO ₃ (mmol/l)	SO ₄	SiO ₂	Al (μmol/l)
CKD T1	0.5	7.55	342	6.8	22	3	14	31	3.8	23
CKD T2	1	6.79	374	7.7	40	11	60	34	4.5	30
CKD T3	2	7.18	369	9.1	43	19	81	34	3.7	16
CKD T4	5	7.04	425	9	37	26	93	29	2.4	5
CKD T5	8	7.05	451	8	28	30	103	23	2	4
CKD T6	24	7.18	453	10.3	26	36	106	25	1.6	2

Table 3. ~~Activity~~ Mean activity of Ca^{2+} , HCO_3^- , CO_3^{2-} , SiO_2^0 , SO_4^{2-} and Al^{3+} in the liquid phase collected during the carbonation experiment calculated by PHREEQC.

Sample	Time (hour)	Ca^{2+}	HCO_3^-	CO_3^{2-}	SiO_2^0	SO_4^{2-}	Al^{3+}
		(mol/l)					
CKD T1	0.5	5.66E-03	9.20E-03	1.40E-05	1.78E-03	7.50E-03	8.30E-13
CKD T2	1	9.10E-03	3.90E-02	1.10E-05	2.12E-03	6.20E-03	1.00E-10
CKD T3	2	9.48E-03	5.00E-02	3.40E-05	1.77E-03	5.50E-03	9.70E-12
CKD T4	5	8.11E-03	5.80E-02	2.80E-05	1.14E-03	4.60E-03	1.60E-11
CKD T5	8	6.22E-03	6.50E-02	3.20E-05	9.59E-04	3.70E-03	1.20E-11
CKD T6	24	5.66E-03	6.60E-02	4.40E-05	7.39E-04	3.90E-03	1.80E-12

Table 4. ~~Concentration~~ Mean concentration of trace elements of the liquid phase collected during the carbonation experiment.

Sample	Time	V	Rb	Sr	Mo	B	Li	Ba	Mn	Zn	Cd	Cr	Co	Ni	Pb	Tl	U	Ag	Sb	As
	(hour)	(μmol/l)																		
CKD T1	0.5	122	84	33	7.6	26	39	1.3	3.1	1.3	0.02	4.4	0.11	3	0.006	0.62	0.03	0.003	0.05	0.37
CKD T2	1	253	84	46	8.1	44	53	1.3	20	1.4	0.05	1.6	0.41	12	0.010	0.72	0.11	0.006	0.08	0.41
CKD T3	2	273	77	46	7.9	59	58	1.0	25	0.7	0.02	<0.2	0.51	15	0.006	0.68	0.13	0.005	0.09	0.32
CKD T4	5	304	74	43	8.1	71	69	0.7	15	<0.5	0.01	<0.2	0.49	21	<0.005	0.60	0.14	0.003	0.11	0.20
CKD T5	8	320	71	35	8.3	65	72	0.6	7.2	<0.5	0.01	<0.2	0.39	27	<0.005	0.55	0.13	0.004	0.13	0.19
CKD T6	24	426	66	34	8.8	83	81	0.4	2.5	<0.5	0.01	<0.2	0.25	43	0.008	0.45	0.13	0.006	0.16	0.19

Biographies

682

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684 University of Cagliari (Italy). She has a thorough knowledge of trace metal pollution of waters and
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687

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700 Architecture (University of Cagliari). Her research activity is mainly focused on accelerated
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Accelerated carbonation by Cement Kiln Dust in aqueous slurries: chemical and mineralogical investigation

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Abstract

Cement Kiln Dust accelerated carbonation in aqueous slurries at 25°C and 3 bar PCO_2 was investigated by X-ray Diffraction analysis, solution chemistry, Scanning Electron Microscopy and Energy Dispersive Spectroscopy to better understand chemical and mineralogical processes governing CO_2 uptake. Dissolution of lime, portlandite and ettringite occurs primarily in the carbonation process. These provide Ca^{2+} ions to react with CO_3^{2-} ions leading to calcite bulk precipitation from solution. Concomitantly, the dissolution of Ca-(Al)-silicate grains takes place but it is limited by the formation of a Si-rich and Ca-depleted rim which appears onto the grain surfaces due to an initial hydration step. The Si-rich decalcified rim hinders the diffusion of Ca^{2+} ions from the core of silicate grains to the bulk solution. The diffusion of Ca ions through the rim is then the rate limiting step for the carbonation of Ca-(Al)-silicate, that accounts for up to 4% of the carbonation potential. Achieved results elucidate the processes governing CO_2 uptake by Cement

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3 25 Kiln Dust, and are fundamental in the perspective of enhanced CO₂ sequestration by Cement Kiln
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5 26 Dust.
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8 27 **Keywords**
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10 28 Accelerated carbonation, Cement Kiln Dust, Ca-(Al)-silicate, Ca carbonate, CO₂ sequestration
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13 29 **1. Introduction**
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16 30 Carbon dioxide (CO₂) is the most important greenhouse gas resulting from the human activity, and
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18 31 it is responsible for about two-thirds of the enhanced greenhouse effect.¹ The development of
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20 32 Carbon Capture, Utilization and Storage (CCUS) technologies is one of the possible strategies for
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22 33 reducing CO₂ in the atmosphere. Among the CCUS technologies, CO₂ utilization by mineralization
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24 34 as carbonates is often referred as accelerated carbonation technology.^{2,3} Mineral carbonation is a
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26 35 process whereby CO₂ is chemically reacted with Ca and/or Mg containing minerals to form stable
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28 36 carbonate materials. Carbonation can occur naturally during the weathering process of minerals,²
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30 37 consisting in the reaction between natural alkaline silicates and atmospheric CO₂. This process
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32 38 removes CO₂ from the atmosphere by neutralizing the acid gas with mineral alkalinity.⁴ Weathering
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34 39 of Ca and Mg (hydr)oxides and silicates is a major consumer of excess atmospheric CO₂ on a
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36 40 geological timescale.⁵ However, the kinetics of carbonation is very slow at ambient condition due to
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38 41 the relatively low CO₂ concentration, about 0.03-0.06% by volume.^{4,6,7} Accelerated carbonation
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40 42 involves alkaline materials reacting with CO₂ in controlled conditions, aiming to reduce the time
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42 43 required for complete carbonation and to accelerate the reaction to a timescale of a few minutes or
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44 44 hours,^{2,3,8} with the potential to capture billions of tonnes of carbon per year.⁹
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46 45 Several up-to-date reviews on the state of the art of Mineral Carbonation (MC) technologies are
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48 46 available, reporting an increasing number of research projects worldwide and thus highlighting the
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50 47 interest and the potentiality of mineral carbonation within CCUS technologies.¹⁰⁻¹² The undeniable
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52 48 benefit of mineral carbon sequestration is being the most permanent and safe method of carbon
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54 49 storage. However, despite the well documented advantages, the technology is not mature yet. After
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20 years of R&D studies since its first proposal as CCUS method,³ the state of development is still at the laboratory demonstration scale and only some MC technologies have recently approached the commercial scale.^{10,12} The main reasons for limited application on a larger scale are the low reaction conversion, the slow kinetics and the energy intensity of the accelerated carbonation processes, which affect the economic viability of the technology.^{10,12} It is well recognized that to reach the highest carbonation efficiency, the major challenges are represented by the identification of the controlling mechanisms and optimal operating parameters. In particular, when carbonation of alkaline materials is performed through aqueous route, the following three mechanisms could be involved: 1) dissolution of Ca and Mg reactive species from the solid matrix; (2) dissolution of CO₂ into the liquid phase and conversion of carbonic acid to bicarbonate/carbonate ions; (3) consequent nucleation and precipitation of carbonates.^{2,13} The material particle size, the temperature, the gas pressure, the liquid/solid (L/S) ratio are important parameters that could differently affect the carbonation mechanisms,^{2,10} and a prediction on a theoretical basis of the main effects and of the joint interactions between the different factors is hard to be derived. At present, the possibility to enhance the reaction kinetics and the extent of the carbonation process, as well as to improve its economic viability, are the focus of several accelerated carbonation experiments being conducted worldwide.^{14,15}

Some of the above-mentioned drawbacks could be avoided when alkaline wastes are used as feedstock instead of mineral resources. In fact, alkaline residues generally contain highly reactive Ca and Mg species, potentially suitable for achieving high and fast carbonate conversions without the need of pre-treatment or energy intensive operating conditions. Moreover, they are available at low cost near CO₂ point source emissions and allow avoiding the exploitation of natural resources. Finally, the resulting pH neutralization and mineral modification induced by carbonation could improve the chemico-physical characteristics of the waste material, allowing for a safer disposal or for a beneficial re-use.^{11,16,17}

Among alkaline industrial residues that can be used as a source of carbonate-forming ions, Cement Kiln Dust (CKD), a by-product from cement industry, appears interesting due to its suitable composition and its availability near CO₂ point source emission. The cement industry generates in fact around 5% of global CO₂ emissions¹⁷ and produces yearly 30 millions of tonnes of CKD.¹⁸ Therefore, accelerated carbonation of CKD could make possible a significant reduction of the cement plant CO₂ emissions. CKD is a potential hazardous waste, in part because of the caustic nature and its potential to be a skin, eye, and respiratory irritant. In addition, contaminants from the raw materials and fuels tend to concentrate in CKD.^{19,20} Previous works on CKD²¹⁻²³ mainly focused on the improvement of the carbonation process by varying operating conditions such as CO₂ pressure, temperature, liquid-to-solid (L/S) ratio, CO₂ humidity, CO₂ flow rate, liquid flow rate, particle size, and solid pre-treatment. Gunning et al.¹⁶ studied the effects of the carbonation of the CKD on the chemistry, microstructure and leaching characteristics of the solid material, whereas Anderson et al.²⁴ investigated the influence that the carbonation of CKD, performed at ambient temperature and pressure, has on the mineral composition and calcite precipitation mechanisms. At the current state of knowledge and in view of a scale-up of the process, further laboratory scale studies are needed with the aim to better elucidate the mechanisms that may limit the rate or the extent of the accelerated carbonation process on CKD.

In a previous work, our research group carried out accelerated carbonation experiments on CKD focused on the assessment of the optimal operating condition in terms of CO₂ sequestration and reaction kinetics.²⁵ The operating parameters such as L/S ratio, CO₂ pressure and temperature were found to differently affect the CO₂ uptake. The higher CO₂ uptake and reactive species conversion were attained at lower temperatures and under slurry-phase conditions. In particular, the optimal water content and the optimal CO₂ pressure were found to be L/S=5 L/kg and PCO₂=3 bar, respectively, allowing to achieve a CO₂ uptake of 9.80%. However, the maximum theoretical CO₂ sequestration capacity of 13.4% was not reached. Experimental results indicated that during carbonation of CKD the reaction rate slows down, with an initial rapid conversion of alkaline

species into carbonates and a more gradual conversion of residual un-reacted species, without reaching a complete conversion.

In the present study, CKD was carbonated in aqueous suspension (slurry-phase carbonation) at 25°C and CO₂ pressure of 3 bar to elucidate chemical and mineralogical processes limiting the CO₂ sequestration capacity by combining X-ray Diffraction analysis (XRD), Scanning Electron Microscopy (SEM), chemical analysis of solution in contact with the alkaline waste during the carbonation experiment, and speciation and equilibrium calculation. Results can be useful to improve understanding of the governing processes, and allow for better utilization of CKD in CO₂ sequestration.

2. Materials and methods

2.1 Cement Kiln Dust and carbonation experiment

The CKD analysed in this study was collected from a cement plant in the South Sardinia (Italy). The plant adopts a semidry process based on Lepol Grate Technology in which hot gases, coming from the kiln, from an auxiliary burner and, sometimes, from the recovered hot gas of the cooler, are used in two chambers for drying and pre-calcining the raw materials. A total mass sample of 60 kg was collected at the air pollution control devices treating the exhaust gases from the kiln system (electrostatic filter) and stored in airtight containers at room temperature.

A detailed chemical composition of CKD is reported in Table 1. Calcium is the major component by far (CaO, 47%), while Mg (MgO, 2.6%), Na (Na₂O, 0.28%) and K (K₂O, 1.3%) are present in small amounts. This composition is within the typical range reported in literature.^{16,22,26} Among the potential harmful elements, Pb (463 mg/kg), V (363 mg/kg), Zn (177/mg/kg), Cu (163 mg/kg), Ni (97 mg/kg), Mn (39 mg/kg), Tl (25 mg/kg), Cr (22 mg/kg), and As (16 mg/kg) are the most abundant.

The operating conditions to be adopted for the accelerated carbonation experiment, in terms of temperature, CO₂ pressure and water content, were selected on the basis of the results obtained in a

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3 126 previous study by our research group (Cappai et al.²⁵). The mentioned study was specifically aimed
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5 127 at evaluating the influence on CO₂ uptake and reaction kinetics exerted by the operating parameters
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7 128 such as L/S ratio (0.4; 1; 3; 5; 10 L/kg), CO₂ pressure (1; 3; 5; 10 bar) and temperature (25; 50; 100
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9 129 °C). The highest CO₂ uptake and reactive species conversion were attained at lower temperatures
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11 130 (25°C) and under slurry-phase conditions. In particular, the highest CO₂ sequestration capacity
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13 131 (9.80%) was achieved at a L/S=5 and at operating pressure of 3 bar (please see Figure S1 in the
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15 132 Supplementary Material section, reporting the CO₂ uptakes over time obtained at T=25 °C and at
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17 133 the different pressures and L/S ratio adopted). In the present study, a quantity of 100 g of dry
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19 134 sample was mixed with 500 g of deionized water (slurry-phase process) and exposed to a 100%
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21 135 CO₂ atmosphere, at a pressure of 3 bar and a temperature of 25°C. Test was performed in a 2 l
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23 136 pressurized reactor equipped with a 1.7 l internal Teflon vessel, an electric jacket for temperature
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25 137 control, and a stirred shaft. At each set time (0.5, 1, 2, 3, 5, 8 and 24 hours), a dedicated sampling
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27 138 device was used for drawing slurry samples, which were filtered over a 1.2 µm membrane. Liquid
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29 139 phase was used for chemical analysis (see 2.3 paragraph). Solid samples were oven dried at 40°C
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31 140 for 24 hours and stored in closed containers for subsequent analysis. The experiment was performed
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33 141 in triplicate. Obtained results are perfectly in agreement and observed variations are in the range of
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35 142 the experimental errors. For this reason and the sake of clarity, in the result and discussion
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37 143 paragraphs, we prefer to present the mean values of chemical data, and the corresponding standard
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39 144 deviation is indicated by error bars in reported graphics. The specific curves of each experiment are
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41 145 reported in the Supplementary Materials (Fig. S2, S3, S4 and S5).
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48 **2.2 X-ray diffraction and electron microscopy study**
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50 147 An aliquot of ~200 mg of dried powder of untreated CKD, and solid samples collected at each set
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52 148 time during the carbonation experiment were slightly ground in an agate mortar, and subjected to
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54 149 XRD analysis, using conventional θ -2 θ equipment (Panalytical) with Cu K α wavelength radiation
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56 150 ($\lambda = 1.54060 \text{ \AA}$), operating at 40 kV and 40 mA, using the X'Celerator detector.
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SEM imaging and EDS (Energy Dispersive Spectroscopy) analysis (before and after the carbonation) were carried out using a field emission (Schottky thermal field emitter) SEM, under high vacuum conditions. In addition, thin sections for SEM imaging were prepared by incorporating CKD in an epoxy resin and subsequently flattening to an appropriate thickness and polishing in order to highlight the rim of the reaction. In order to obtain better quality images, samples were gold coated before observation, using a SEM Coating Unit PS3 (Agar Aids for Electron Microscopy).

2.3 Assessment of CO₂ sequestration

Total carbon content analysis (LECO CHN-1000 Element Analyzer) were performed in duplicate on dried solid residues obtained at the different durations. Mean values from TC (total carbon) content analysis were used to estimate the CO₂ uptake, with an error (difference between mean and real value) always lower than 3% of the average value. The obtained mean values, expressed as weight % of CO₂ (CO₂ carbonated [%]) were used to calculate the CO₂ uptake by applying the equation 1, where CO_{2initial} [%], is the TC content of the untreated CKD, again expressed as weight % of CO₂ (Equation 1).

$$CO_2 uptake [\%] = \frac{CO_{2carbonated} [\%] - CO_{2initial} [\%]}{100 - CO_{2carbonated} [\%]} * 100 \quad \text{Equation 1}$$

The degree of sequestration in terms of reactive species conversion yields was also evaluated, by comparing the amount of CO₂ sequestered in each test to the maximum amount theoretically possible (Equation 2). The theoretical limit of uptake was calculated based on the Steinour formula (Equation 3),²⁷ which assumes the full stoichiometric conversion to carbonates of the reactive alkaline species.

$$\eta [\%] = \frac{CO_2 uptake [\%]}{ThCO_2 uptake [\%]} * 100 \quad \text{Equation 2}$$

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$$ThCO_2\ uptake\ [\%] = 0.785(CaO[\%] - 0.56CaCO_3[\%] - 0.7\ SO_3[\%]) + 1.091MgO[\%] +$$

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$$0.71Na_2O[\%] + 0.468(K_2O[\%] - 0.632KCl\ [\%])$$

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2.4 Chemical analysis of solutions

The liquid phase was further filtered using a 0.45 μm Millipore filtering system and pH, redox potential, conductivity, alkalinity, trace elements and anions were evaluated on filtered aliquots. pH values were measured by a Ross electrode connected to a pH-meter (Orion, Thermo Fisher Scientific, USA) after calibration against NIST buffer solutions. Redox potential was measured with a platinum electrode, and values were corrected against the Zoëll's solution.²⁸ Conductivity was determined by conductivity meter (Thermo Orion 150 Aplus). Alkalinity was measured on filtered aliquot using both the Gran titration method with hydrochloric acid (indicator: methyl orange), and the Gran function plot method.²⁹ Another aliquot of filtered solution was placed in acid pre-cleaned polyethylene bottles and then acidified to 1% HNO₃ for subsequent analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin-Elmer, Elan DRC-e, USA) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, ARL Fisons ICP Analyzer 3520 B). Anions were determined by Ionic Chromatography (IC, Dionex ICS-3000) in a filtered (0.45 μm) unacidified aliquot. The Detection Limit (DL) for chemical elements was calculated at 10 times the standard deviation of the blank solutions. To evaluate the accuracy and precision of trace elements determination, two reference solutions were used: the NIST SRM 1643e and the EnviroMAT Ground Water ES-L-1. Rhodium was used as an internal standard for ICP-MS analysis to correct for instrument drift. The ionic balance was always better than ± 10%.

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2.5 Speciation and equilibrium calculations

Speciation and equilibrium calculation were performed using the PHREEQC computer program (llnl database). Saturation indexes (SI) with respect to solid phases were calculated as SI = log (IAP/K_s), where IAP is the ionic activity product and K_s the solubility equilibrium constant at the

specific water temperature.³⁰ pe vs pH diagrams were plotted using the Hydra-Medusa software and its internal database complex.db and complex.elb.³¹

3. Results

3.1 Mineralogical and microscopic characteristics before and after the carbonation experiment

CKD was investigated by XRD (Fig. 1) and SEM analysis (Fig. 2 and 3) before and after the 24-hour carbonation test. Raw CKD (Fig. 1a) are made up of calcite (CaCO_3), quartz (SiO_2), lime (CaO) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). In addition, peaks ascribed to cement minerals such as portlandite ($\text{Ca}(\text{OH})_2$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26 \text{H}_2\text{O}$) were detected. Bixbyite (Mn_2O_3) and, likely, rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$) and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) were also found. SEM analysis (Fig. 2a) of the raw material shows that the grain size ranges from hundreds of nm to hundreds of μm , indicating high heterogeneity for the CKD. EDS spectra show that quartz (Fig. 2b), calcite (Fig. 2c), and dolomite (Fig. 2d) can be easily recognized. Some micrometric crystals have a hexagonal habitus typical of portlandite (images not shown).

XRD analysis of CKD after carbonation (Fig. 1b) reveals that the amount of calcite increases after the experiment while lime, portlandite, ettringite, and bixbyite disappear. Besides the presence of quartz, calcite, dolomite, and Ca-silicates (observed already in the raw sample), traces of gypsum were detected after the carbonation experiment. Gypsum, most likely, derived from ettringite dissolution, the subsequent release of Ca^{2+} and SO_4^{2-} ions in solution and their precipitation as gypsum and calcite.

To reveal grain surface processes, SEM analysis was performed on CKD sections after the carbonation experiment (Fig. 3a-b). Figure 3a shows the backscattered electron image, and Figures from 3b to 3d show the energy dispersive X-ray maps for Si (b), Ca (c), and Al (d). Micro-analysis and EDS mapping indicate that these grains consist of Ca-Al-silicates, in agreement with XRD analysis (see Fig. 1b) that shows residues of gehlenite in the treated sample. After the carbonation

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test, residual Ca-silicate grains investigated by SEM appear to be not carbonated, and enveloped by a Si-rich (Fig. 3b) decalcified rim (Fig. 3c). There, Al is homogeneously distributed (Fig. 3d), and elements such as Fe, S, K and V can be recognized by EDS analysis (data not shown).

3.2 CO₂ uptake

Figure 4 shows the CO₂ uptake and the degree of sequestration in terms of reactive species conversion yields, as assessed during the accelerated carbonation test. The time-dependent curve shows a very fast initial conversion of alkaline reactive species into carbonates. Then, a plateau is reached, at a value lower than the maximum theoretical CO₂ sequestration capacity of 13.4%. As far as the potential of CO₂ sequestration is concerned, the results obtained in this study (9.45% by mass of CO₂) are similar with those reported by Gunning et al.¹⁶ (9% at ambient temperature and 2 bar over 72 h), but lower by ca 4% with respect to maximum sequestration potential observed for this material. Understanding the mechanisms underlying this limit provide us a basis also for comparing the results from different experiments.

3.3 Chemical analysis, thermodynamic driving force and saturation state of the leached solutions

XRD analysis reveals that lime, portlandite, ettringite, rankinite and gehlenite are the original phases potentially involved in the carbonation process by providing cations, moving pH value toward slightly basic conditions thus favouring the dissolution of CO₂ and dissociation of carbonic acid to eventually increase concentration of carbonate ion. Actually, the SI respect to the above mentioned minerals are negative (< -10) in the liquid phase, indicating that their dissolution is favoured and, consequently, these are a source of Ca for the carbonation reactions.

Table 2 shows pH, redox potential (Eh), electrical conductivity (Cond), and the concentration of selected chemical components of the liquid phase collected during the carbonation experiment. pH,

251 Eh and Cond values were measured immediately after solution collection from the reactor. At the
252 same time, different aliquots were stabilized for chemical analysis. Reported values of Ca, Mg,
253 HCO_3^- , SO_4^{2-} , SiO_2 and Al are the total concentrations of each chemical species measured as
254 described in the paragraph 2.4. Table 3 reports PHREEQC output speciation of selected chemical
255 species (reported as ion activity) deriving from the dissolution of portlandite, ettringite, rankinite,
256 and gehlenite, and of the HCO_3^- and CO_3^{2-} species involved in the precipitation of carbonate
257 minerals. Trace elements are reported in Table 4. Set times 0.5, 1, 2, 5, 8, and 24 hours will be
258 referred to hereafter as T1, T2, T3, T4, T5 and T6, respectively. pH values (Table 2) are near
259 neutral and decrease from 7.55 to 6.79, probably initially dominated by the fast dissolution of
260 portlandite and ettringite, then governed by the dissolution of CO_2 in water, the formation of
261 carbonic acid and its subsequent dissociation. In addition, pH values (7.11 ± 0.07), observed between
262 T3 and T6 sampling, reflect the buffering effect of calcite precipitating during accelerated
263 carbonation. Redox potential values (Eh between 342 and 453 mV) indicate oxidizing conditions,
264 and tend to increase during the experiment.

265 Concentration of Ca and Mg, HCO_3^- and SO_4^{2-} , and SiO_2 and Al vs time in the liquid phase,
266 collected during the carbonation experiment, are shown in Fig. 5a, 5b and 5c, respectively (see also
267 Fig. S3). Ca^{2+} (60-70%) is the most abundant species (Table 3) for the total content of Ca. This
268 tends to increase in the first 2 hours, and reaches the highest concentration (43 mmol/l) at T3. Then,
269 it decreases from T3 to T6 (26 mmol/l). This trend is due to the release of Ca to solution because of
270 the dissolution of lime, portlandite, ettringite and Ca(Al)-silicates between T1 and T3. Then, Ca
271 concentration decreases because of the precipitation of new phases, such as calcite and gypsum (see
272 Fig. 1 and 3.1 paragraph), or to absorption processes that become predominant over the dissolution
273 reactions between T3 and T6. In agreement, equilibrium calculation shows that calcite is
274 oversaturated in solution (Fig. 6a).

275 Mg concentration (Table 2, Fig. 5a and Fig. S3a) increases from T1 to T6, despite results of
276 equilibrium calculation (Fig. 6b) indicate that leached solutions are oversaturated with respect to

277 Mg(Ca)-bearing carbonate minerals such as dolomite and magnesite. In fact, although dolomite is
278 oversaturated in studied solutions (SI between 3.1 and 5), dolomite precipitation is driven by kinetic
279 factors. A high Mg^{2+}/Ca^{2+} molar ratio (higher than 5–10:1)³² is required to precipitate dolomite
280 because the Mg^{2+} ion has a high hydration energy³³. Leached solutions have a Mg^{2+}/Ca^{2+} molar
281 ratio between 0.10 and 0.96, and increase from T1 to T5 (Fig. 5a and Fig. S4) because of calcite
282 precipitation, reaching steady-state values between T5 ($Mg^{2+}/Ca^{2+} = 0.92$) and T6 ($Mg^{2+}/Ca^{2+} =$
283 0.96). Moreover, the kinetic of precipitation mechanism of Mg carbonates is controlled by the
284 supersaturation with respect to magnesite.³⁴ In a broad range of PCO_2 and Mg^{2+}/Ca^{2+} activity ratio
285 in solution, the composition of precipitated Ca-Mg carbonate depends only on SI respect to
286 magnesite. Under observed values ($SI < 3$), Mg can be incorporated into Ca carbonate only in few
287 amount by forming low-magnesian calcite. Thus, Mg^{2+} ions remain in solution and do not
288 contribute to CO_2 uptake during the carbonation process. Other than calcite, strontianite (Fig. 6c),
289 and witherite (Fig. 6d) are oversaturated in solution. Although XRD analysis reveals only the
290 presence of calcite, Sr and Ba carbonates could form independent phases coprecipitating with
291 calcite, but sensitivity of XRD technique does not allow their detection. Amorphous phases cannot
292 be detected by XRD as well.

293 Alkalinity (HCO_3^-) increases from T1 to T5 (Fig. 5b and Fig. S3b), and it reaches a steady-state
294 value between T5 and T6. The observed increase in alkalinity from T1 to T5 is due to the
295 continuous dissolution of CO_2 into the slurry solution and relative dissociation of carbonic acid. The
296 behaviour of SO_4 can be explained considering dissolution mechanism of ettringite. Ettringite is a
297 stable mineral above a pH of 10.7 and dissolves congruently with a $\log K_{sp}$ of $-111.6 (\pm 0.8)$. At
298 near neutral pH, ettringite undergoes incongruent dissolution to gypsum, Al-hydroxides and Al-
299 hydroxy sulphates, thus controlling Ca^{2+} , Al^{3+} , and SO_4^{2-} activities.³⁵

300 SiO_2 and Al have a similar trend (Fig. 5c and Fig S3c), showing an initial increase in concentration,
301 from T1 to T2, and a decrease until T6. Actually, SiO_2 (SI_{quartz} 0.9-1.3), $Al(OH)_3$ (SI 2.0-2.8), and
302 Ca-Al-silicate hydrate minerals, such as gismondine ($Ca_2Al_4Si_4O_{16} \cdot 9H_2O$, SI 9-15), scolecite

($\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$, SI 6.6-10) and laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$, SI 5.7-9.5) are oversaturated in solution. Moreover, precipitation of Ca-silicate hydrate gel occurs, as observed by SEM analysis. Trace elements behave according to two distinct groups: 1) V, Mo, Li, B, Ni, U and Sb show an increase in concentration during the experiment; 2) Rb, Ba, Cr, Sr, Zn, Mn, Cd, Co, Tl, and As are released immediately in solution and then decrease during the carbonation experiment. The available literature studies focusing on the influence of MC on trace element solubility indicate that carbonation could either increase or reduce trace element mobility from alkaline residues.^{36,37} In particular, an higher release has been observed for oxyanions, according to the fact that they are often incorporated in ettringite-like minerals which dissolve upon carbonation. Other elements such as heavy metals are converted into their less soluble salts or immobilized through sorption onto CaCO_3 and/or co-precipitation into newly formed minerals.

4. Discussion

4.1 Process chemistry and thermodynamic prediction

To investigate mineralogical processes of dissolution and precipitation governing accelerated carbonation of CKD, we combined chemical data with PHREEQC calculations, XRD and SEM analysis. During the carbonation test, injected CO_2 dissolves into solution proportionally to the PCO_2 , in accordance with Henry's law, and hydrates to carbonic acid (H_2CO_3). Then H_2CO_3 dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions depending on the solution pH. Simultaneously, phases such as lime and portlandite (Fig. 1a) in contact with water undergo fast dissolution, in agreement with the calculated SI (< -10), leading to a fast increase in Ca^{2+} concentration from T1 to T2 (see Table 2 and Fig. 5a). As indicated by the activity values in Table 3, Ca^{2+} aquo ions react with CO_3^{2-} leading to calcite bulk precipitation from solution.

Also, ettringite,^{38,39} rankinite and gehlenite² take part to the carbonation process. During ettringite dissolution, Ca^{2+} and SO_4^{2-} ions are released into solution and then precipitate as gypsum and

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3 328 calcite. In agreement, XRD peaks of gypsum were observed in the carbonated CKD sample (Fig.
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5 329 1b).
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7 330 Transformation of Ca-silicates to Ca-carbonate is characterized by a slower dissolution kinetics of
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9 331 Ca-silicates than lime and portlandite. SEM analysis (see Fig. 3) shows that the residual non-
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11 332 carbonated grains of Ca-Al-silicates are surrounded by a Si-rich decalcified rim. This can be
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13 333 explained considering that carbonation of Ca silicates is accompanied by hydration³⁶ that leads to
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15 334 the precipitation of a Ca-silicate hydrate gel. During the carbonation process, the Ca-silicate hydrate
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17 335 gel is progressively decalcified.⁴ Accordingly, the $\text{Ca}^{2+}/\text{SiO}_2^0$ activity ratio increase in the liquid
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19 336 phase (Fig. 7 and Fig. S3) due to the release of Ca^{2+} ions which become available for calcite
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21 337 precipitation. It was demonstrated^{2,41} that, progressively, the Ca-silicate hydrate gel is transformed
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23 338 into calcite and highly polymerized silicate gel. This process is the so called secondary
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25 339 carbonation,³⁶ but, being a slow solid state diffusion process, it has limited practical effect for
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27 340 carbonation purposes.
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29 341 Figures 8a and b show predominance Pourbaix diagrams for the system Ca-Al-C-Si-H-O, plotted
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31 342 considering chemical parameters from speciation calculation for T1 and T6 samplings.
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33 343 Predominance diagrams allow having a synoptic view of physico-chemical evolution of the
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35 344 investigated system and prediction of mineral evolution. It is worth noting that, in Fig. 8, the CaCO_3
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37 345 stability field increases in time from T1 to T6 indicating conditions more favourable to calcite
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39 346 precipitation. Concomitantly, the stability field of CaSiO_3 disappears in favour of the Ca_2SiO_4 field,
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41 347 corresponding to a decrease of Si activity in solution (see Table 3) that, in turn, likely favours Si
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43 348 storage in amorphous grain coatings. Black circles indicate pH and pe values of the collected liquid
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45 349 phase at T1 (Fig. 8a) and T6 (Fig. 8b). Although black circles fall outside the calcite field, it is
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47 350 worth nothing that chemical properties of the liquid film in contact with the alkaline solid waste
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49 351 grains are different from that of the bulk solution. In fact, dissolution of minerals such as lime,
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51 352 portlandite, gehlenite and rankinite leads to the consumption of hydrogen ions and, consequently, to
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53 353 an increase in pH values, especially in the solution in contact with mineral grains.
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355 4.2 Reaction pathways and chemical processes affecting CO₂ uptake

356 The rate and extent of carbonation of CKD is affected by transport-controlled mechanisms such as
357 CO₂ and Ca²⁺ diffusion to/from reaction sites, boundary layer effects (diffusion across precipitate
358 coatings on particles), dissolution of Ca(OH)₂ at the particle surface, and pore blockage or
359 precipitate coating development.²² Huntzinger et al.²² studied the extent and potential mechanisms
360 and rate behaviour of the carbonation process in CKD at ambient temperatures and pressures by
361 applying X-ray spectrometry, XRD, thermal analysis, and observed dry mass change. The major
362 reactive Ca species identified in CKD samples before carbonation experiments were lime and
363 portlandite. Authors²² stated that CO₂ sequestration appears to follow unreacted core model theory.
364 As carbonation progresses, the kinetics of the reaction are attenuated by the extent of the reaction
365 due to diffusion control, with the extent of conversion never reaching completion. Anderson et
366 al.^{24,42} investigated the reaction pathways ruling the carbonation processes in CKD by
367 environmental SEM, XRD, thermal gravimetric analysis/differential thermal analysis. PHREEQC
368 was used for modelling CKD reaction using a 10:1 liquid to solid ratio, and a simplified
369 composition of CKD. Authors^{24,42} found that lime and portlandite were the major reactants. A
370 second reaction path was the weathering of Ca-silicates that released Ca²⁺ for carbonation. Three
371 types of CaCO₃ precipitation mechanisms were observed: (1) diffusion of CO₂ into portlandite
372 particles causing precipitation in the pores of the particle and the growth of a CaCO₃ skin from the
373 outside inward, slowing vapor and aqueous diffusion by causing blockages in the pore systems, (2)
374 precipitation onto existing particles, and (3) precipitation from aqueous solution.

375 In this study, we combined XRD and SEM-EDS analysis performed before and after the
376 carbonation experiment with solution chemistry, speciation and equilibrium calculations performed
377 at each set time (0.5, 1, 2, 3, 5, 8 and 24 hours) to better investigate chemical processes limiting
378 CO₂ uptake. According to mineralogical and chemical investigations, we propose that the

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investigated accelerated carbonation of CKD follows a pathway of dissolution and precipitation reactions:

1. hydration and/or dissolution of lime, portlandite, and ettringite and release of Ca^{2+} ions in solution:

2. partial dissolution of rankinite and gehlenite, release of Ca^{2+} ions in solution and formation of a Ca(Al)-silicate external rim:

3. contemporary dissolution of gaseous CO_2 into solution and formation of bicarbonate ions according to the observed pH values (7.2 ± 0.2):

4. dissociation of bicarbonate ions into carbonate ions in the solution in contact with the alkaline solid waste:

5. calcite precipitation from solution:

In a first stage, a rapid transformation of lime, portlandite and ettringite into Ca-carbonate takes place. After their consumption, Ca from the Ca-(Al)-silicate phases diffuses toward the surface of the grains, and Ca^{2+} ions are dissolved into solution and precipitated as calcite. Leaching of Ca from Ca-(Al)-silicates results in a withdrawing Ca-(Al)-silicate core covered by a Si-rich decalcified rim (see Fig. 3) that may change the rate and mechanism of dissolution. During decalcification of the external rim, Ca^{2+} ions are dissolved into solution, while Si remains in the solid state, hindering the

diffusion of Ca^{2+} ions from the grain core, and limiting conversion.^{20,41} Indeed, XRD analysis (see Fig. 1b) show that Ca silicate grains are still present in carbonated CKD, because formation of the external rim results in diffusion to be the rate limiting step, then limiting the carbonation process. This is reflected in the time-dependent curve of CO_2 uptake in Fig. 4 that shows an exponential shape, suggesting an initial rapid conversion of Ca reactive species into carbonates, and a subsequent decrease in reaction rate without reaching a complete conversion as estimated by the maximum theoretical CO_2 sequestration capacity (13.4%). This behaviour indicates that carbonation process follows an “unreacted core model”.^{22,40} Moreover, in our slurries experiments the rim is not made of calcite, as observed by Anderson⁴², the latter mineral precipitating from bulk solution. Thus, we argued that the rim hindering the unreacted core appears to be dependent on the experimental condition. Specifically, the composition of the rim could depend on the composition of the given CKD and also on the liquid-solid ratio. Moreover, CKD material comprise several minerals whose relative abundance is not constant. These findings allow us to assert that a potential optimization of the CO_2 uptake by CKD could be achieved properly selecting specific additives⁴³ to hinder the formation of external layers for improving diffusion of Ca ions through the Ca-Al-silicate grains to enhance carbonation reaction of the unreacted particle core.

5. Conclusions

The carbonation of CKD has been proved to be an effective technology to capture CO_2 , and it need to be improved for being applied at a commercial scale. To reach the highest sequestration capacity, the main goals are represented by the identification of the optimal operating parameters and the limiting reaction mechanisms. In order to achieve a better understanding of the chemical and mineralogical processes affecting carbonation and CO_2 uptake efficiency of CKD, a slurry-phase accelerated carbonation was performed at 25°C and 3 bar. The CO_2 uptake by CKD follows an exponential increase, achieving a carbonation capacity of 9.45% in the first hour. XRD analysis indicates that the reactive species in CKD are lime, portlandite, ettringite, rankinite, and gehlenite.

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3 430 Direct observations by XRD and SEM, and geochemical modelling of solution in contact with CKD
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5 431 during the carbonation experiment indicate that CO₂ uptake is limited by the formation of a Si-rich
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7 432 decalcified layer covering the residual Ca-Al-silicates grains. In fact, in the presence of the Si-rich
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9 433 decalcified layer, the solution chemistry reached a stationary state and carbonation ceased before
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11 434 reaching the maximum theoretical uptake (13.4%). Literature studies on CKD observed the
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13 435 formation of a rim made of calcite instead of a Si-rich decalcified layer. Thus, we argued that the
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15 436 knowledge of the specific mechanism active in a given CKD carbonation set-up (reactor and
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17 437 materials) has direct implication for the scaling up to pilot or pre-industrial scale experiment. The
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19 438 findings from the present study indicate that a further process optimization is possible, aimed at
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21 439 avoiding the formation of Si-rich decalcified layer. On the basis of the CO₂ sequestration capacity
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23 440 of 9.45% assessed during the present study, since 0.2 tons of CKD for every ton of clinker are
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25 441 produced¹⁷ and 0.507 tons of CO₂/ton of clinker are emitted,⁴⁴ the carbonation treatment would
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27 442 have the potential for sequestering 3.7% of the cement plant CO₂ emissions, which would increase
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29 443 to up to 5.27% if the maximum theoretical CO₂ sequestration capacity of 13.4% is exploited. This
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31 444 increase of carbonation efficiency is a crucial aspect in lowering the industrial capture cost, which is
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33 445 still considered too high for the implementation of MC on a large scale. Further studies with slurry
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35 446 accelerated carbonation of CKD would be useful in order to define the optimal conditions for
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37 447 enhanced carbonation process also by using additives to hinder silica rim formation.
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Figure 1. XRD pattern of CKD before (a) and after the carbonation test (b). Cal (calcite), Qz (quartz), Lime (lime), Dol (dolomite), Prt (portlandite), Ettr (ettringite), Bix (bixbyite), Rank (rankinite), Gh (gehlenite), Gyps (gypsum).

Figure 2. Scanning Electron Microscopy analysis of raw CKD. a) Overview of the CKD sample grain size; b) image and microanalysis of a quartz grain; c) image and microanalysis of a calcite grain; d) image and microanalysis of a dolomite grain.

Figure 3. Scanning Electron Microscopy analysis of a CKD section after the carbonation experiment (T6). Backscattered electron image (a) and the results of Si (b), Ca (c), and Al (d) mapping by energy dispersive X-ray on the CKD sample. Arrows indicate the Si-rich decalcified rim that envelops the residual non-carbonated grains of Ca-Al-silicates.

Figure 4. CO₂ uptake and degree of sequestration in terms of reactive species conversion yields during the accelerated carbonation test.

Figure 5. Mean concentration of Ca, Mg (a), HCO₃, SO₄ (b), SiO₂ and Al (c) vs time in the liquid phase. Also, Mg²⁺/Ca²⁺ molar ratio is shown.

Figure 6. SI respect to calcite and Ca²⁺ activity vs time (a); SI respect to dolomite, huntite, magnesite and Mg²⁺ activity vs time (a); SI respect to strontianite and Sr²⁺ activity vs time (a); SI respect to witherite and Ba²⁺ activity vs time (a) in the liquid phase.

Figure 7. Mean Ca²⁺/SiO₂⁰ activity ratio concentration vs time in the liquid phase.

Figure 8. *pe* vs *pH* diagrams for the system Ca-Al-C-Si-H-O for liquid phase collected at T1 (a) and T6 (b). Diagrams are drawn by the chemical equilibrium-diagram-tool Hydra/Medusa. Black circles indicate *pH* and *pe* values of the collected liquid phase at T1 (a) and T6 (b). Concentrations for Ca^{2+} - Al^{3+} - CO_3^{2-} - H_4SiO_4^0 come from speciation calculation performed by PHREEQC.

Table 1. Elemental composition of the CKD (from Cappai et al.²⁵)

Element	(%)	Element	(mg/kg)
Al_2O_3	2.95 ± 0.05	As	16.12 ± 0.79
CaO	46.75 ± 0.91	Ba	185 ± 9
Fe_2O_3	1.94 ± 0.05	Cd	7.08 ± 1.22
K_2O	1.30 ± 0.01	Co	5.66 ± 0.89
MgO	2.64 ± 0.08	Cr	22.12 ± 1.34
MnO	0.05 ± 0.00	Cu	163 ± 9
Na_2O	0.28 ± 0.10	Mo	38.87 ± 3.13
P_2O_5	N.D.	Ni	97.02 ± 9.59
SiO_2	18.65 ± 0.21	Pb	463 ± 28.0
TiO_2	0.12 ± 0.01	Sb	6.82 ± 1.13
LOI	26.80 ± 0.10	Se	13.31 ± 0.10
Soluble anions (mg/kg)		Tl	24.87 ± 1.10
Chloride	3204 ± 93	V	363 ± 7
Sulphate	7382 ± 370	Zn	177 ± 10

Table 2. Mean values of pH, redox potential (Eh), electrical conductivity (Cond), and mean concentration of selected chemical components of the liquid phase collected during the carbonation experiments.

Sample	Time (hour)	pH	Eh (mV)	Cond (mS/cm)	Ca	Mg	HCO ₃ (mmol/l)	SO ₄	SiO ₂	Al (μmol/l)
CKD T1	0.5	7.55	342	6.8	22	3	14	31	3.8	23
CKD T2	1	6.79	374	7.7	40	11	60	34	4.5	30
CKD T3	2	7.18	369	9.1	43	19	81	34	3.7	16
CKD T4	5	7.04	425	9	37	26	93	29	2.4	5
CKD T5	8	7.05	451	8	28	30	103	23	2	4
CKD T6	24	7.18	453	10.3	26	36	106	25	1.6	2

Table 3. Mean activity of Ca^{2+} , HCO_3^- , CO_3^{2-} , SiO_2^0 , SO_4^{2-} and Al^{3+} in the liquid phase collected during the carbonation experiment calculated by PHREEQC.

Sample	Time (hour)	Ca^{2+}	HCO_3^-	CO_3^{2-}	SiO_2^0	SO_4^{2-}	Al^{3+}
		(mol/l)					
CKD T1	0.5	5.66E-03	9.20E-03	1.40E-05	1.78E-03	7.50E-03	8.30E-13
CKD T2	1	9.10E-03	3.90E-02	1.10E-05	2.12E-03	6.20E-03	1.00E-10
CKD T3	2	9.48E-03	5.00E-02	3.40E-05	1.77E-03	5.50E-03	9.70E-12
CKD T4	5	8.11E-03	5.80E-02	2.80E-05	1.14E-03	4.60E-03	1.60E-11
CKD T5	8	6.22E-03	6.50E-02	3.20E-05	9.59E-04	3.70E-03	1.20E-11
CKD T6	24	5.66E-03	6.60E-02	4.40E-05	7.39E-04	3.90E-03	1.80E-12

Table 4. Mean concentration of trace elements of the liquid phase collected during the carbonation experiment.

Sample	Time (hour)	V	Rb	Sr	Mo	B	Li	Ba	Mn	Zn	Cd	Cr	Co	Ni	Pb	Tl	U	Ag	Sb	As
CKD T1	0.5	122	84	33	7.6	26	39	1.3	3.1	1.3	0.02	4.4	0.11	3	0.006	0.62	0.03	0.003	0.05	0.37
CKD T2	1	253	84	46	8.1	44	53	1.3	20	1.4	0.05	1.6	0.41	12	0.010	0.72	0.11	0.006	0.08	0.41
CKD T3	2	273	77	46	7.9	59	58	1.0	25	0.7	0.02	<0.2	0.51	15	0.006	0.68	0.13	0.005	0.09	0.32
CKD T4	5	304	74	43	8.1	71	69	0.7	15	<0.5	0.01	<0.2	0.49	21	<0.005	0.60	0.14	0.003	0.11	0.20
CKD T5	8	320	71	35	8.3	65	72	0.6	7.2	<0.5	0.01	<0.2	0.39	27	<0.005	0.55	0.13	0.004	0.13	0.19
CKD T6	24	426	66	34	8.8	83	81	0.4	2.5	<0.5	0.01	<0.2	0.25	43	0.008	0.45	0.13	0.006	0.16	0.19

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702 **Biographies**

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704 Daniela Medas is a research assistant at the Department of Chemical and Geological Sciences,
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706 soils. Main research activities are aimed to understand the geo-bio interactions in polluted and not
707 polluted soils and waters.

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710 Civil-Environmental Engineering and Architecture of the University of Cagliari. Her current
711 research activity mainly concerns accelerated carbonation of alkaline residues and remediation of
712 contaminated sites.

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714 Giovanni De Giudici is a senior lecturer at the Department of Chemical and Geological Sciences,
715 University of Cagliari (Italy). He has a thorough knowledge of mineral dissolution processes and
716 trace metal pollution of waters and soils. Main research activities are aimed to understand the
717 biomineralization processes in heavy metals polluted systems.

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719 Martina Piredda is a Ph.D. in Geoengineering and Environmental Technologies and senior
720 technician of the chemical laboratory at the Dept. of Civil-Environmental Engineering and
721 Architecture (University of Cagliari). Her research activity is mainly focused on accelerated
722 carbonation of alkaline residues.

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724 Simona Podda received her Ph.D. degree in electronics and informatics engineering from the
725 University of Cagliari in 2004. She is a senior researcher at CRS4 - Microscopy Laboratory
726 (Microlab) and is mainly involved in advanced electron microscopy techniques applied to
727 nanotechnologies, environmental sciences and the new materials development.

XRD pattern of CKD before (a) and after the carbonation test (b). Cal (calcite), Qz (quartz), Lime (lime), Dol (dolomite), Prt (portlandite), Ettr (ettringite), Bix (bixbyite), Rank (rankinite), Gh (gehlenite), Gyps (gypsum).

41x21mm (300 x 300 DPI)

Scanning Electron Microscopy analysis of raw CKD. a) Overview of the CKD sample grain size; b) image and microanalysis of a quartz grain; c) image and microanalysis of a calcite grain; d) image and microanalysis of a dolomite grain.

134x116mm (300 x 300 DPI)

Scanning Electron Microscopy analysis of a CKD section after the carbonation experiment (T6). Backscattered electron image (a) and the results of Si (b), Ca (c), and Al (d) mapping by energy dispersive X-ray on the CKD sample. Arrows indicate the Si-rich decalcified rim that envelops the residual non-carbonated grains of Ca-Al-silicates.

219x173mm (96 x 96 DPI)

CO₂ uptake and degree of sequestration in terms of reactive species conversion yields during the accelerated carbonation test.

162x83mm (72 x 72 DPI)

Mean concentration of Ca, Mg (a), HCO_3^- , SO_4^{2-} (b), SiO_2 and Al (c) vs time in the liquid phase. Also, Mg^{2+}/Ca^{2+} molar ratio is shown.

132x322mm (120 x 120 DPI)

SI respect to calcite and Ca^{2+} activity vs time (a); SI respect to dolomite, huntite, magnesite and Mg^{2+} activity vs time (a); SI respect to strontianite and Sr^{2+} activity vs time (a); SI respect to witherite and Ba^{2+} activity vs time (a) in the liquid phase.

329x275mm (96 x 96 DPI)

Mean $\text{Ca}^{2+}/\text{SiO}_2^0$ activity ratio concentration vs time in the liquid phase.

105x91mm (120 x 120 DPI)

pe vs pH diagrams for the system Ca-Al-C-Si-H-O for liquid phase collected at T1 (a) and T6 (b). Diagrams are drawn by the chemical equilibrium-diagram-tool Hydra/Medusa. Black circles indicate pH and pe values of the collected liquid phase at T1 (a) and T6 (b). Concentrations for Ca²⁺- Al³⁺- CO₃²⁻ - H₄SiO₄⁰ come from speciation calculation performed by PHREEQC.

80x184mm (300 x 300 DPI)