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1 **Mineral sequestration of CO₂ by aqueous carbonation of**
2 **coal combustion fly-ash**

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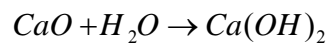
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1 **Abstract**

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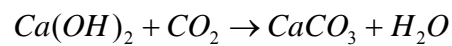
3 The increasing CO₂ concentration in the Earth's atmosphere, mainly caused by fossil fuel
4 combustion, has led to concerns about global warming. A technology that could possibly
5 contribute to reducing carbon dioxide emissions is the in-situ mineral sequestration (long term
6 geological storage) or the ex-situ mineral sequestration (controlled industrial reactors) of CO₂.
7 In the present study, we propose to use coal combustion fly-ash, an industrial waste that
8 contains about 4.1 wt.% of lime (CaO), to sequester carbon dioxide by aqueous carbonation.
9 The carbonation reaction was carried out in two successive chemical reactions, firstly the
10 irreversible hydration of lime:

11



12 secondly, the spontaneous carbonation of calcium hydroxide suspension:

13



14 A high CaO-CaCO₃ chemical transformation (approximately 82%) was estimated by mass
15 balance after two hours of reaction at 30°C. The carbonation of CaO was independent on the
16 initial pressure of CO₂ (10, 20, 30 and 40 bar) and it was slightly affected by the temperature
17 of reaction (30 and 60 °C). The precipitate calcium carbonate was characterized by isolated
18 micrometric particles and micrometric agglomerates of calcite (SEM observations). In
19 addition, the calcite precipitation and lime dissolution were confirmed by comparison of X-
20 ray diffraction spectra. This experimental study demonstrates that one ton of fly-ash could
21 sequester up to 26 kg of CO₂. This confirms the possibility to use the alkaline liquid-solid
22 waste for CO₂ mitigation.

23 **Keywords:** Mineral sequestration of CO₂; Fly-ash; Aqueous carbonation; Calcium
24 oxide; Calcite

25

1 **1. Introduction**

2 The global warming of Earth's near-surface, air and oceans in recent decades is a direct
3 consequence of anthropogenic emission of greenhouse gases into the atmosphere such as
4 CO₂, CH₄, N₂O and CFCs (1). The CO₂ emissions contribute approximately 60% to this
5 climate change. From the time of the industrial revolution that started the 1860's, 75% of CO₂
6 emissions discharged into the atmosphere are caused by the burning of fossil fuels (26.4 ± 1.1
7 Gt CO₂ yr⁻¹ for the 2000-2005 period), and the remaining 25% by land use change (1).
8 Although oceans and terrestrial biosphere can take up high amounts of the CO₂ emitted, about
9 45% remains in the atmosphere as stable specie that may stay for many thousands of years
10 (1). The continuous increase of atmospheric CO₂ might lead to stress on drinking water
11 availability, species extinction, melting of ice sheets and coastal flooding (2).

12 Motivated by concerns about climate change, technical solutions are searched to minimize
13 these harmful consequences. The main actions include: (I) the increase of the efficiency of
14 energy conversion, (II) the reduction of energy demand and (III) the use of carbon free energy
15 sources (nuclear, solar, wind, geothermal and biomass energy) (3). However, fossil fuels
16 account for 85% of world energy needs in the current energy system, and hence, rapid
17 variations of the demand or the prices in the market may seriously harm the global economy.
18 Likewise, the use of fossil fuels will likely continue at the next decades owing to both its low
19 cost and high availability.

20 An alternative to reduce the CO₂ emission without modifying the energy production
21 system is the retention or sequestration of carbon dioxide in stable geological reservoirs (4-7).
22 Such a strategy, so-called geological carbon sequestration, consists of capturing gaseous CO₂
23 from emissions sources and injecting it as a supercritical fluid in terrestrial reservoirs, such as
24 saline aquifers, depleted oil and gas fields or deep coal seams. In geological reservoirs, the
25 supercritical CO₂ could be retained by stratigraphic or structural trapping (physical isolation),

1 solubility trapping (dissolved in the aqueous phase) and/or hydrodynamic trapping (associated
2 to long residence time of dissolved CO₂-bearing fluids in aquifers). However, the main
3 scientific concerns inquiring the geological carbon sequestration applicability are the high
4 pressure and temperature variations caused by the large CO₂ accumulation on the reservoirs.
5 These thermodynamic variations could exert forces that diminish the reservoir confinement
6 due to the formation of cracks and faults either in reservoir itself or in the cap rocks.
7 Moreover, the CO₂ dissolution into the pore water and the consecutive carbonic acid
8 formation can result in the dissolution of several minerals (mainly carbonate, oxides and
9 hydroxide minerals) affecting the long-term confinement properties of the reservoirs (8).

10 In terrestrial reservoirs, the CO₂ pressure can decrease in the long term as a consequence
11 of another retention mechanism: mineral trapping or mineralogical carbon sequestration. The
12 stored CO₂ may transform to stable carbonate minerals by reactions with aqueous ions
13 (mainly calcium, magnesium and iron) resulting from silicate weathering (9-12). Although
14 this mechanism favours the permanent CO₂ sequestration, it is expected to be slow in
15 geological formation (hundreds of years) due to the slow kinetics of silicate mineral
16 dissolution and carbonate mineral precipitation. However, mineralogical carbon sequestration
17 could contribute significantly to CO₂ sequestration in the proximity of the emission source,
18 without the need of storing the gas into a geological reservoir.

19 Soong et al. (13) proposed the use of mineralogical carbon sequestration in controlled
20 reactors as a viable approach to reduce CO₂ emissions into the atmosphere using by-products
21 from coal combustion in power plants (fly-ash) and oil and gas production (brine solutions).
22 Brine solutions act as calcium and magnesium source favouring the CO₂ retention by
23 carbonate precipitation. Fly-ash was used to increase the pH level of the reactant brine and
24 also as an additional source of calcium to enhance reaction efficiency for the carbonation
25 process.

1 Coal combustion in power plants provides approximately 40% of world electricity
2 generation. At present, the coal reserves are estimated around 900 billion ton (14).
3 Considering that coal consumption reached 5 billion tonnes in 2003, coal-energy production
4 will continue, and even increase, in the next centuries due to the energy demand for industrial
5 and domestic uses (15). Therefore, the continuous building of power plants is envisaged to
6 hold this energy production system. This may cause serious disruption to the global climate
7 since each 500 MW coal power plant emits about 3 million tonnes of CO₂ per year. Likewise,
8 the worldwide production of fly-ash, estimated currently at 600 million tonnes per year, will
9 also increase exponentially in the near future. The main producers of fly-ashes are China,
10 Russia and the United States of America.

11 Fly-ash material is used as cement raw material and as a partial replacement for cement in
12 concrete. However, the global production of fly-ash exceeds their potential uses (16), and
13 hence, it is considered a residual by-product. Only around a 30% of the total production is
14 used as a construction material. At present, numerous investigations are focused on the search
15 of new applications for this residue. Three main research lines use fly-ash: i) to synthesize
16 zeolites to be applicable as filter material in water decontamination and gas retention (17,18),
17 ii) as an effective technique in metal retention processes in contaminated soils (19,20) and, iii)
18 for the treatment of mining wastes producers of acid mine drainage (21,22). Although Soong
19 et al. (13) propose the use of fly ash to sequester CO₂, brine solutions were the main agent
20 acting in the carbonation process. Moreover, these authors do not calculate the amount of CO₂
21 sequestered during the process.

22 The objective of integrated waste management is the search for sustainable development,
23 i.e. to balance the fulfilment of human needs with the protection of the natural environment in
24 the present and indefinite future. With this in mind, the main aim of this work is precisely to
25 quantify the CO₂ amount that may be sequestered by calcite precipitation using fly-ash-water

1 dispersion. This study is in our opinion especially attractive since the residual solid by-
2 products from power plants could be used to mitigate the residual gaseous wastes produced by
3 the same plants.

4 5 **2. Materials and methods**

6 7 2.1 Fly-ash material

8 The fly-ash used in the present study is a waste residue generated from coal combustion at
9 Los Barrios power station, Cádiz, south Spain. It is a powder composed mainly of spherical
10 microparticles collected from electrostatic precipitators located at the outlet of the chimney
11 where combustion gasses are liberated into the atmosphere. Size distribution analysis indicates
12 that the particles have a median diameter of 40 μm . The specific surface area is 0.63 ± 0.022
13 $\text{m}^2 \text{g}^{-1}$ determined by BET gas adsorption method (MICROMERITICS ASAP 2000
14 instrument). Mineral abundances are similar to those reported by Querol *et al.* (23), and show
15 that fly-ash is composed of mullite (20.8 wt.%), quartz (4.5 %), lime (4.1%), anhydrite
16 (1.3%), K-feldspar (2.5 %), magnetite (0.5 %) and a chalco-aluminosilicate glass phase
17 (66.4%). The chemical composition measured by X-ray fluorescence (XRF, BRUKER
18 PIONEER instrument) shows that Los Barrios fly-ash is a residue rich in Si (41.3 wt.% SiO_2),
19 Al (27.5 wt.% Al_2O_3), C (16 wt.% CO_2), Ca (5 wt.% CaO), and Fe (3.3 wt.% Fe_2O_3) with
20 minor elements (wt.%): Sr (0.3%), Cl (0.02%), Cr (0.01%), Ni (0.02%), Zn (0.01%), V
21 (0.01%), Cu (0.01%), Co (0.01%) and Sc (0.003%). The presence of lime (CaO , 4.1 wt%) in
22 fly-ash accounts for the high potential of both alkalinity and dioxide carbon sequestration as
23 discussed below.

1 2.2 CO₂ sequestration experiments in a stirred reactor

2 One litre of high-purity water with electrical resistivity of 18.2 MΩ cm and 100g of fly-ash
3 were placed in a titanium reactor (autoclave Parr with internal volume of two litres). The fly-
4 ash particles were immediately dispersed by mechanical stirring (450 rpm). The dispersion
5 (solution + solid particles) was then heated to 30 or 60°C using an oven specifically adapted
6 to the reactor. When the dispersion temperature was reached, 10, 20, 30 or 40 bar of CO₂
7 (provided by Linde Gas S.A.) was injected in the reactor (see Fig. 1). This was the initial
8 pressure of CO₂ which was equal to the total initial pressure in the system. Previous
9 experiments showed that after two hours of reaction the pressure drop was close to the
10 thermodynamic equilibrium in the system. For this reason, we considered a reaction time of
11 two hours for all experiments in the present study.

12 Obviously, both the sorption-dissociation of CO₂ in the solution and aqueous carbonation
13 process produce a global pressure drop in the system, $P_{global_pressure-drop}$. In order to estimate
14 the pressure drop produced only by the process of CaO carbonation (noted $P_{carbonation_pressure-}$
15 $drop$), two complementary systems were proposed for each experiment. Firstly, the pressure
16 drop $P_{water_pressure-drop}$ related to the sorption-dissociation of CO₂ into pure water only was
17 measured. Secondly, the pressure drop $P_{Ca-rich_pressure-drop}$ related to the sorption-dissociation of
18 CO₂ in a Ca-rich solution was measured independently. In this second experiment, a
19 concentration of 1g/L of calcium was chosen, that represented the average concentration after
20 fly-ash dispersion in water. These two experiments demonstrated that the Ca-concentration
21 (0-1g/L) has no measurable effect on the sorption-dissociation of CO₂ because the monitored
22 pressure drop in pure water $P_{water_pressure-drop}$ was equivalent to the monitored pressure drop in
23 presence of Ca $P_{Ca-rich_pressure-drop}$. Consequently, the pressure drop produced by the
24 carbonation process of CaO was calculated by a simple pressure balance:

$$25 \quad P_{carbonation_pressure-drop} = P_{global_pressure-drop} - P_{water_pressure-drop} \quad (1)$$

1 Under isothermal conditions, $P_{global_pressure-drop}$ and $P_{water_pressure-drop}$ are proportional to the
2 initial CO₂ pressure.

3 At the end of the experiment, the reactor was removed from the heating system and was
4 immersed into cold water. The reaction cell was depressurized for 15 minutes during the
5 water cooling period. Then, water cooling at 30°C the reactor was disassembled, and the solid
6 product was separated by centrifugation (30 minutes at 12,000 rpm), decanting the
7 supernatant solutions. Finally, the solid product was dried directly in the centrifugation flasks
8 for 48 h at 65°C. The supernatant solutions were filtered through a 0.2- μ m Teflon filter.
9 Adsorption on the filter and filter holder was considered negligible. The filtered solutions
10 were immediately acidified for measurement of [Ca], [Ni], [Zn], [Cu] and [Sr] by Inductively
11 Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

12

13 2.3 Characterization of the solid phase

14 The mineralogical characterization of the starting material and solid products was carried
15 out by X-ray diffraction (XRD, powder method) using a D501 SIEMENS diffractometer.
16 Working conditions were CoK α monochromatic radiation ($\lambda=1.7902 \text{ \AA}$), 37.5 mA and 40 kV.
17 The experimental measurement parameters were 12s counting time per 0.02° 2 θ step in the 5-
18 80° 2 θ range. The detection is performed by a kevox Si(Li) detector. Morphological analyses
19 were also characterized by means of a scanning electron microscopy (SEM), with a JEOL
20 JSM-5410 instrument, equipped with an energy dispersive system (EDS) for the chemical
21 microanalysis.

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3. Results and discussion

A previous investigation showed that the carbonation of calcium hydroxide suspension at high pressure of CO₂ (initial P_{CO₂}=55 bar) and moderate and high temperature (30 and 90°C) is a potential method to synthesize fine particles of calcite (24). In addition, the reported results have important ecological implications for the ex-situ mineral sequestration of CO₂ by alkaline liquid-solid waste such as fly-ash, bottom ash, Ca/Mg-rich silicates, alkaline waste water, etc. For this reason, the current study was focussed on the mineral sequestration of CO₂ by aqueous carbonation of fly-ash. In the following sub-sections, the chemical reactions of CO₂ sequestration by fly-ash and, the calculation of the sequestered quantity of CO₂ by calcite precipitation and kinetic modelling of sequestered CO₂ in a fly-ash-water suspension are described and discussed.

3.1 Chemical reactions of CO₂ sequestration by fly-ash

The SEM images of solid product (Figure 2), the comparison of x-ray diffraction spectra of the starting material and the solid product (Figure 3) and ICP-AES analysis in the solutions, suggest a simple reaction mechanism for CO₂ mineral sequestration by fly-ash in two successive steps: firstly the irreversible hydration of calcium oxide or lime:



secondly, the spontaneous carbonation of calcium hydroxide suspension:



The precipitate calcium carbonate is characterized by isolated micrometric particles and micrometric agglomerates of calcite (Figure 2). In addition, the calcite precipitation and lime (CaO) dissolution were confirmed by comparison of X-ray diffraction spectra (Figure 3).

1 Finally, the chemical-element concentrations for Ca, Ni, Zn, Cu and Sr in the solution after
2 two hours of fly-ash-pure water-carbon dioxide interactions suggest a preferential and rapid
3 dissolution of lime phase and possibly a slight dissolution of the glass phase ($[Ca] \approx$
4 800mg/L) (22). Concerning, the trace elements (contained initially in the fly-ash) only the
5 strontium was detected in the solution by ICP-AES ($[Sr] \approx 8\text{mg/L}$). Consequently, the
6 concentrations of Ni, Zn and Cu were considered to be smaller than 6 ppb (detection limit).
7 This demonstrates that the fly-ash dispersion into pure water did not favour the liberation of
8 toxic metallic ions after two hours of solid-fluid interaction at moderate temperature. In fact,
9 preliminary experiments show that the carbonation process favours the co-precipitation and/or
10 incorporation of the dissolved impurities into the calcite crystallographic network.

11

12 3.2 The sequestered quantity of CO_2 by calcite precipitation

13 A simplified method was developed to estimate the sequestered quantity of CO_2 by carbonate
14 precipitation. This method was partially described in the section 2.2. Herein, the pressure drop
15 produced by the carbonation process of CaO (Eqs. 2 and 3) in the system was calculated by a
16 simple pressure balance (Eq. 1). The carbonation pressure drop, $P_{\text{carbonation_pressure-drop}}$ was
17 equal to 1.5 bar for all experiments (Figure 4b). It was independent on the initial pressure of
18 CO_2 (10, 20, 30, 40 bar) and was slightly affected by the temperature of reaction (30 and
19 60°C). The results of the pressure drop kinetics for 30 bar (as initial pressure of CO_2) are
20 shown on Figure 4a. Here, it was observed that the equilibrium of pressure drop was reached
21 after about five hours of solid-fluid interaction.

22 Considering that CO_2 is an ideal gas, the quantity of CO_2 consumed by the carbonation
23 process can be calculated as follows:

$$24 \quad n_{\text{CO}_2} = \frac{P_{\text{carbonation_pressure_drop}} V}{RT} \quad (4)$$

1 where, the V is the reactor volume occupied with gas (1L), T is the temperature of reaction
 2 ($\approx 303^\circ\text{K}$) and R is the gas constant (0.08314472 L.bar/ $^\circ\text{K}$.mol). Using the measured value
 3 $P_{\text{carbonation_pressure-drop}} = 1.5$ bar, we calculated that 0.05954 mol of CO_2 were consumed by the
 4 carbonation process. Taking into account reactions (2-3) and the fact that the fly-ash contains
 5 4.1wt.% of lime (CaO), the carbonation efficiency CE can be calculated by the following
 6 expression:

$$7 \quad CE = \frac{n_{\text{CO}_2} * M_{\text{CO}_2}}{\frac{w_{\text{CaO}}}{M_{\text{CaO}}} * M_{\text{CO}_2}} * 100 \quad (5)$$

8 where, n_{CO_2} is the mol number of consumed CO_2 , calculated by Eq. 4 (0.05954 mol), M_{CO_2} is
 9 the molar mass of CO_2 (44.01 g/mol), w_{CaO} is the starting mass of CaO in the reactor (4.1g)
 10 and M_{CaO} is the molar mass of CaO (56.077g/mol). The carbonation efficiency was equal to
 11 82% after two hours of solid-fluid interactions at 30 and 60°C.

12 Theoretically one ton of fly-ash containing 4.1% of lime could sequester 32.17kg of CO_2 .
 13 With our experimental protocol, 26.19kg of CO_2 per ton of fly-ash could be successfully
 14 sequestered into stable calcite. Indeed, this is an attractive result concerning the ex-situ
 15 mineral sequestration of CO_2 .

16

17 3.3 Kinetic modelling of sequestered CO_2 in a fly-ash-water suspension

18 The monitoring of the pressure drop for any controlled system under ideal gas conditions
 19 allows the kinetic modelling of sequestered CO_2 after gas injection in a solid-liquid system
 20 (fly-ash-water dispersion for this study). This can be done using a simple correlation function,
 21 $n_{\text{total_CO}_2} = f(t)$, where $n_{\text{total_CO}_2}$ is the total mol quantity of sequestered CO_2 in the fly-ash-water
 22 dispersion and t is the time after gas injection.

23 Several kinetic models including first-order, pseudo-first-order, second-order, pseudo-second-
 24 order, parabolic diffusion and power function kinetic expressions are reported in the literature

1 for fitting the kinetic experimental or calculated data of the solid-fluid interaction processes.
 2 For this study, the kinetic modelling concern the total sequestered quantity of CO₂ in a fly-
 3 ash-water dispersion, i.e. the CO₂ sorption-dissociation in water, possibly the CO₂ adsorption
 4 on the fly-ash and, sequestered CO₂ by carbonation process. For this case, the best fit (attested
 5 by a correlation factor close to 1) of the experimental-calculated data was achieved when
 6 using a pseudo-second-order kinetic model according to the following expression:

$$7 \quad \frac{dn_{total_CO2,t}}{dt} = k_s (n_{total_CO2,max} - n_{total_CO2,t})^2 \quad (6)$$

8 where k_s is the rate constant of sequestered CO₂ [1/mol s] for a given initial pressure of CO₂
 9 in the system, $n_{total_CO2,max}$ is the maximum sequestered quantity of carbon dioxide at
 10 equilibrium [mol], $n_{total_CO2,t}$ is the sequestered quantity of carbon dioxide at any time, t ,
 11 [mol].

12 The integrated form of Equation (6) for the boundary conditions $t = 0$ to $t = t$ and $n_{total_CO2,t} =$
 13 0 to $n_{total_CO2,t} = n_{total_CO2,t}$ is represented by a hyperbolic equation:

$$14 \quad n_{total_CO2,t} = \frac{n_{total_CO2,max} * t}{\left(\frac{1}{k_s * n_{total_CO2,max}} \right) + t} \quad (7)$$

15 In order to simplify the fitting of experimental-calculated data, we have defined the constant
 16 $t_{1/2} = 1/k_s * n_{total_CO2,max}$. Physically, $t_{1/2}$ represents the time after which half of the maximum
 17 sequestered quantity of carbon dioxide was reached and is called “half-sequestered CO₂
 18 time”. It can be used to calculate the initial rate of sequestered CO₂, $v_{0,s}$, [mol/s].

$$19 \quad v_{0,s} = \frac{n_{total_CO2,max}}{t_{1/2}} = k_s (n_{total_CO2,max})^2 \quad (8)$$

20 The numerical fit of the experimental-calculated kinetic curve at 30 bar and 30°C ($n_{total_CO2,t}$
 21 vs. t) using Eq. (7) is shown on Figure 5. The parameters $t_{1/2}$ and $n_{total_CO2,max}$ were estimated
 22 by applying a non-linear regression using the least-squares method. The initial rate of

1 sequestered CO₂ was calculated using Eq. 8 ($v_{0,s} = 8.28 \times 10^{-4}$ mol/s) at 30°C. This value
2 indicates that the mass transfer of compressed CO₂ in contact with solid-water dispersion is
3 higher than CO₂ transfer at atmospheric conditions or at low pressure (25-26).

4

5 3.4 Conclusion

6 The results presented in this study showed that the ex-situ mineral sequestration of CO₂ by
7 aqueous carbonation of fly-ash could be an attractive and potential method to reduce the CO₂
8 emission in the atmosphere from power plants. This experimental investigation demonstrated
9 that one ton of fly-ash, an industrial waste that contains about 4.1 wt.% of lime (CaO), could
10 sequester up to 26 kg of CO₂. This confirms the possibility to use the alkaline liquid-solid
11 waste for CO₂ mitigation.

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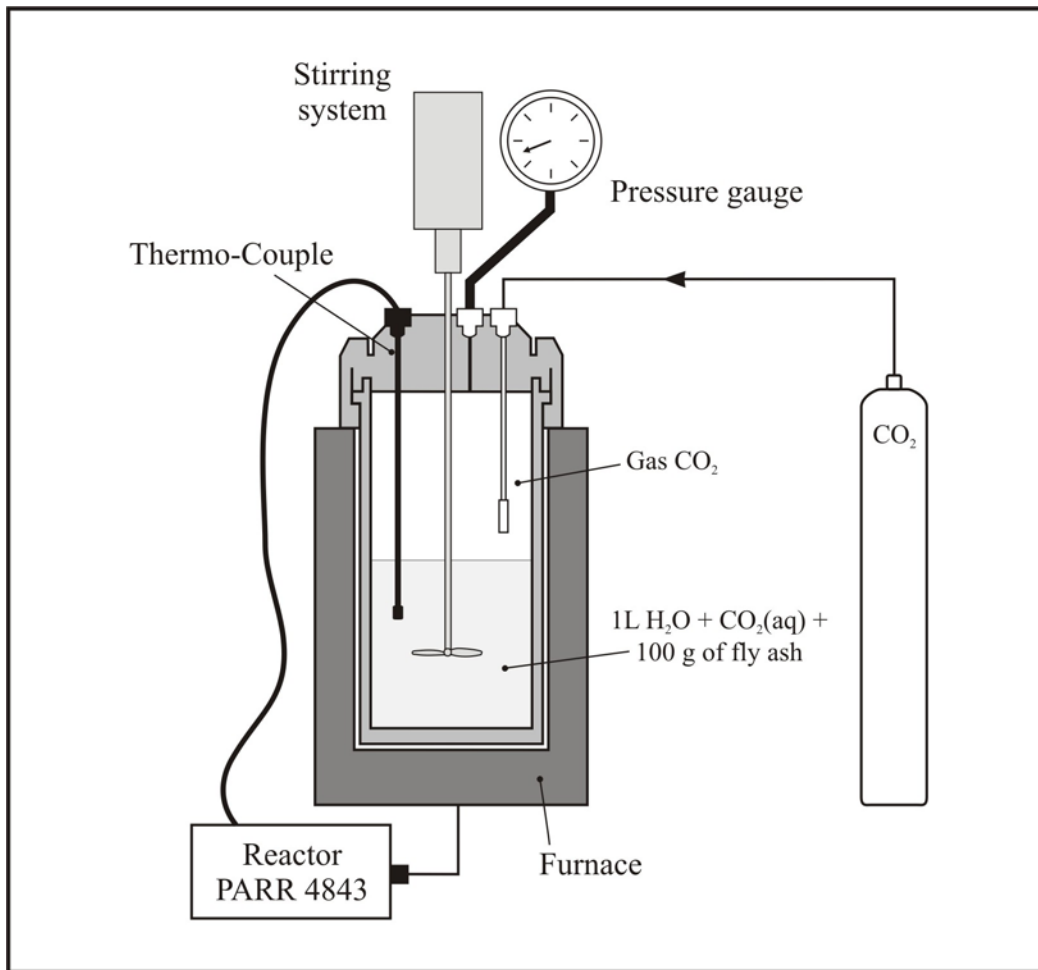
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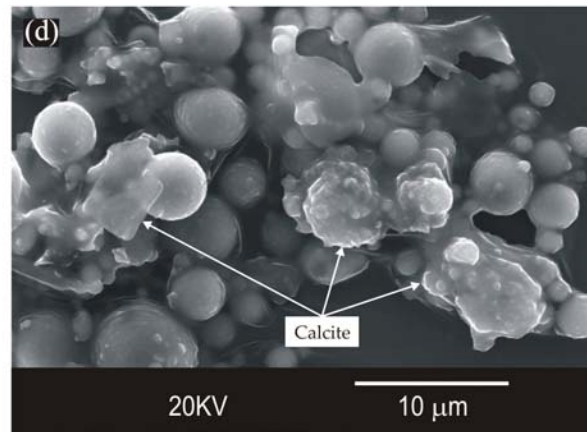
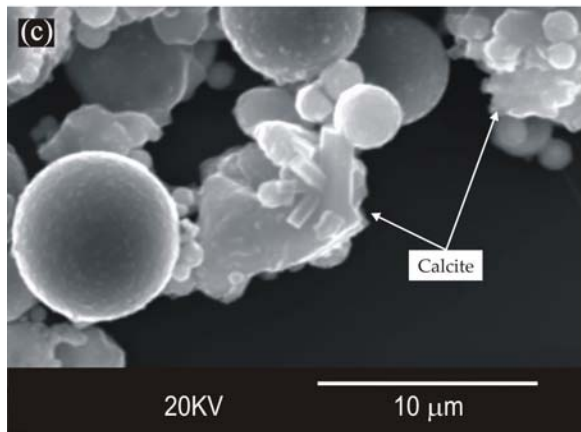
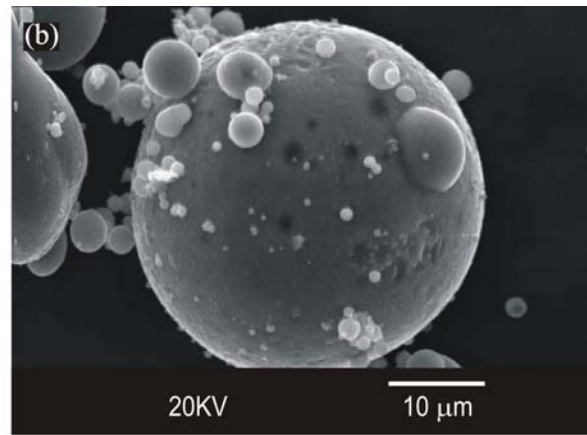
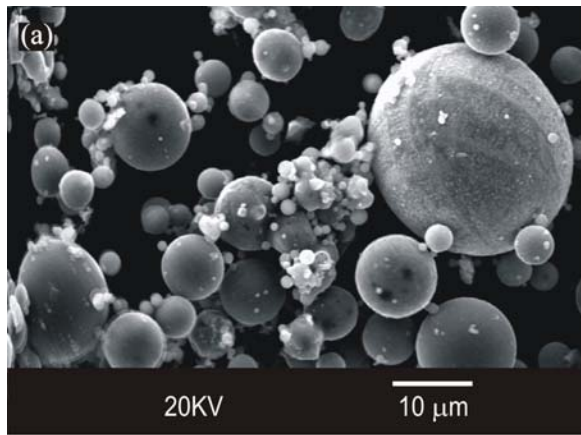
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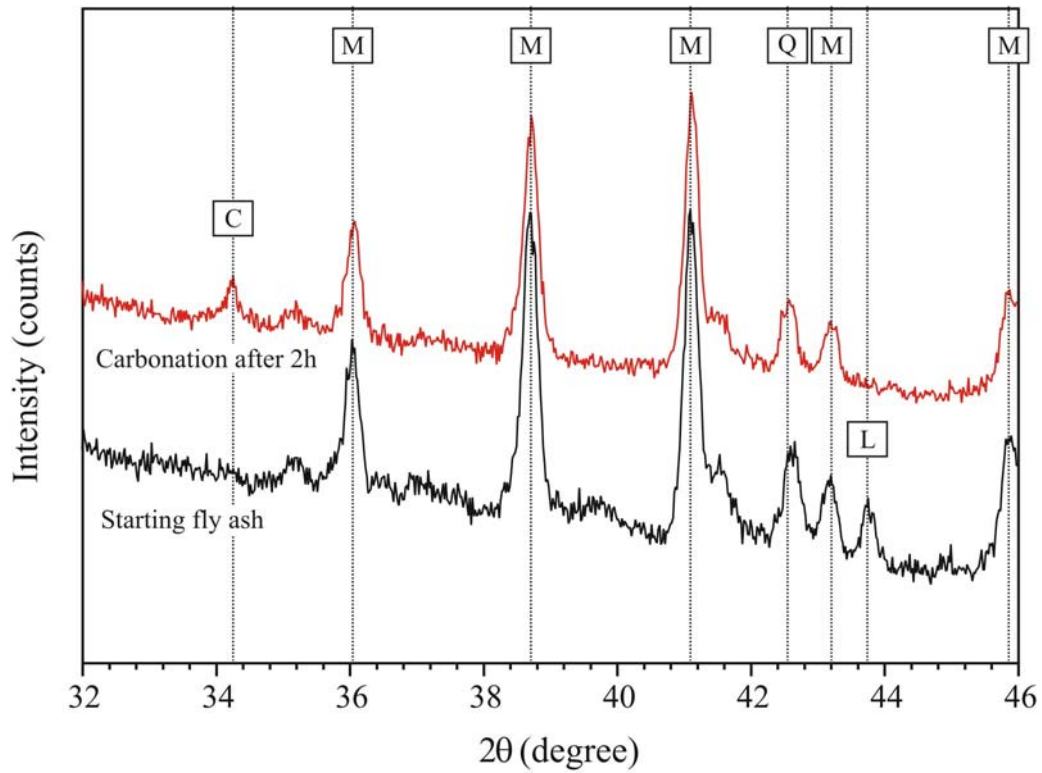
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Figure 1. Schematic experimental system for mineral sequestration of CO₂ by aqueous carbonation of fly-ash in a stirred reactor.



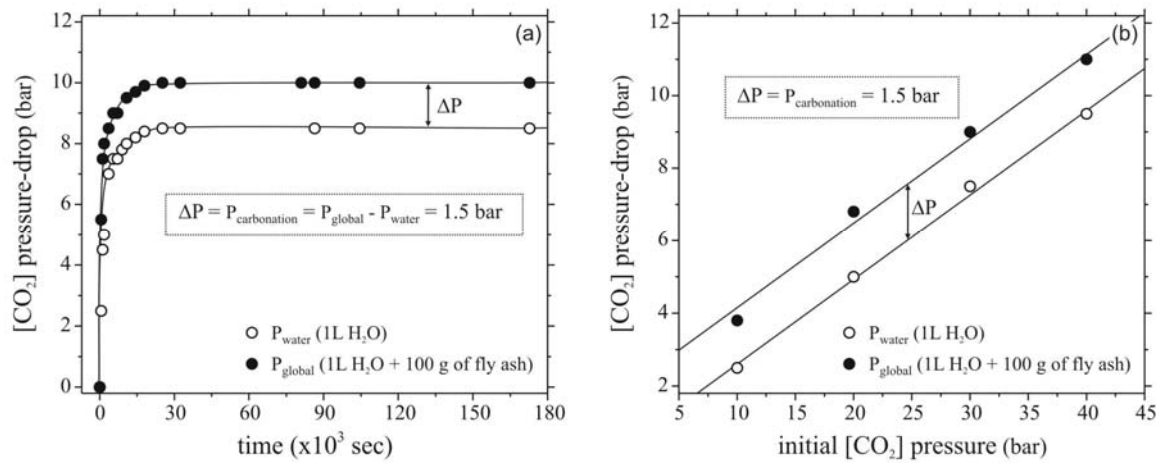
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Figure 2. (a-b) SEM images of fly-ash before reaction. (c-d) Calcite particles precipitated during CO₂ sequestration experiments.



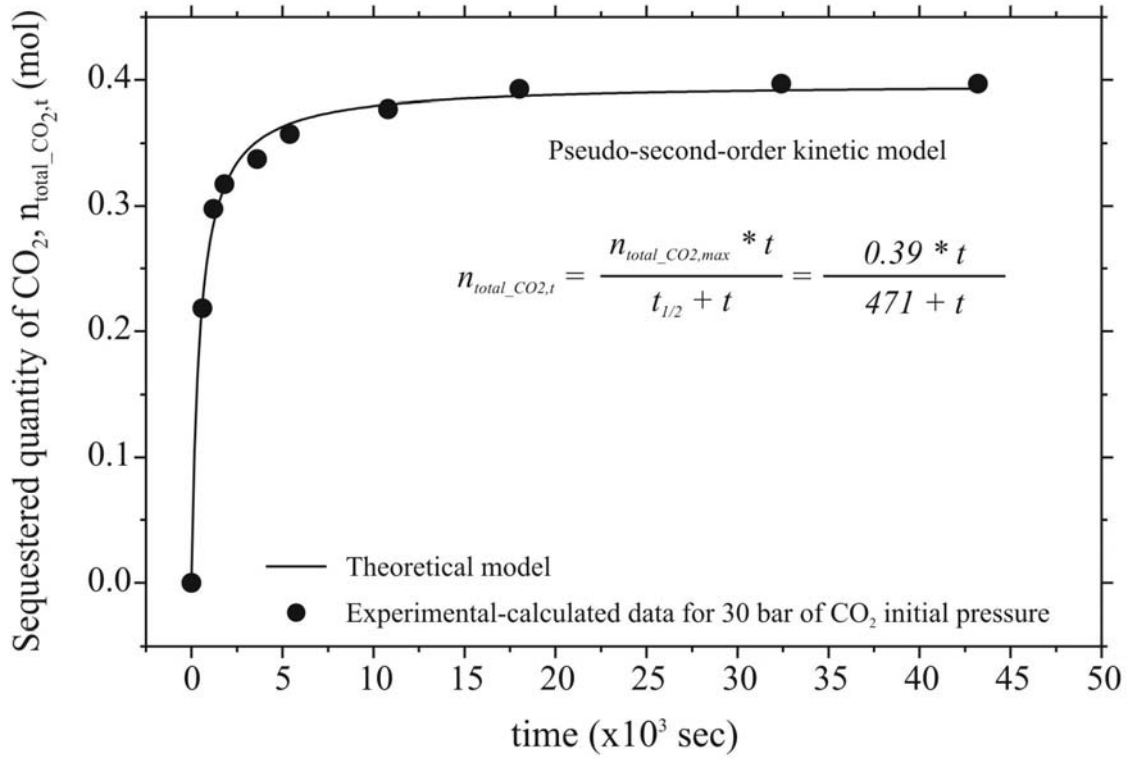
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Figure 3. XRD spectra of starting fly-ash and solid products after carbonation during 2 h. C: Calcite, M: Mullite, Q: Quartz, L: Lime. These spectra demonstrate the total consumption of lime and the production of calcite.



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Figure 4. (a) Kinetic behaviour of pressure decrease in the reactor at 30°C and for 30 bar initial pressure of CO₂. (b) Linear correlation between the pressure decrease at equilibrium and the initial pressure of CO₂.



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7 Figure 5. Kinetic modeling of sequestered CO₂ in a fly-ash-water suspension for 30 bar initial

8 pressure of CO₂.

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