



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

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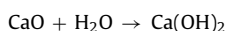
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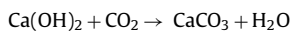
Calcite

ABSTRACT

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



second, the spontaneous carbonation of calcium hydroxide suspension.



A significant CaO–CaCO₃ chemical transformation (approximately 82% of carbonation efficiency) was estimated by pressure–mass balance after 2 h of reaction at 30 °C. In addition, the qualitative comparison of X-ray diffraction spectra for reactants and products revealed a complete CaO–CaCO₃ conversion. The carbonation efficiency of CaO was independent on the initial pressure of CO₂ (10, 20, 30 and 40 bar) and it was not significantly affected by reaction temperature (room temperature “20–25”, 30 and 60 °C) and by fly-ash dose (50, 100, 150 g). The kinetic data demonstrated that the initial rate of CO₂ transfer was enhanced by carbonation process for our experiments.

The precipitate calcium carbonate was characterized by isolated micrometric particles and micrometric agglomerates of calcite (SEM observations). Finally, the geochemical modelling using PHREEQC software indicated that the final solutions (i.e. after reaction) are supersaturated with respect to calcium carbonate (0.7 ≤ saturation index ≤ 1.1).

This experimental study demonstrates that 1 ton of fly-ash could sequester up to 26 kg of CO₂, i.e. 38.18 ton of fly-ash per ton of CO₂ sequestered. This confirms the possibility to use this alkaline residue for CO₂ mitigation.

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1. Introduction

1.1. General concepts

Motivated by concerns about climate change, technical solutions are searched to minimize these harmful consequences. The main actions include: (I) the increase of the efficiency of energy conversion, (II) the reduction of energy demand and (III) the use of carbon

free energy sources (nuclear, solar, wind, geothermal and biomass energy) [1–3]. However, fossil fuels account for 85% of world energy needs in the current energy system, and hence, rapid variations of the demand or the prices in the market may seriously harm the global economy. Likewise, the use of fossil fuels will likely continue at the next decades owing to both its low cost and high availability.

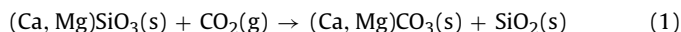
An alternative to reduce the CO₂ emission without modifying the energy production system is the retention or sequestration of carbon dioxide in stable geological reservoirs [4–7]. Such a strategy, so-called geological carbon sequestration, consists of capturing gaseous CO₂ from emissions sources and injecting it as a supercritical fluid in terrestrial reservoirs, such as saline aquifers, depleted oil and gas fields or deep coal seams. In geological reservoirs, the super-

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critical CO₂ could be retained by stratigraphic or structural trapping (physical isolation), solubility trapping (dissolved in the aqueous phase) and/or hydrodynamic trapping (associated to long residence time of dissolved CO₂-bearing fluids in aquifers). However, the main concerns about the application of the geological carbon sequestration strategies in the high pressure and temperature variations caused by the large CO₂ accumulation on the reservoirs. These thermodynamic variations could exert forces that diminish the reservoir confinement due to the formation of cracks and faults either in reservoir itself or in the cap rocks. Moreover, the CO₂ dissolution into the pore water and the consequent carbonic acid formation can result in the dissolution of several minerals (mainly carbonate, oxides and hydroxide minerals) affecting the long-term confinement properties of the reservoirs [8].

In terrestrial reservoirs, the CO₂ pressure can decrease in the long term as a consequence of another retention mechanism: mineral trapping or mineralogical carbon sequestration. The stored CO₂ may transform to stable carbonate minerals by reactions with aqueous ions (mainly calcium, magnesium and iron) resulting from silicate weathering [9–12]. Although this mechanism favours the permanent CO₂ sequestration, it is expected to be slow in geological formation (hundreds of years) due to the slow kinetics of silicate mineral dissolution and carbonate mineral precipitation. However, mineralogical carbon sequestration could contribute significantly to CO₂ sequestration in the proximity of the emission source, without the need of storing the gas into a geological reservoir. This technology is called ex-situ mineral sequestration of CO₂, as originally proposed by Seifritz [13] and first studied in detail by Lackner et al. [14]. At the present time, several theoretical and/or experimental studies on CO₂ sequestration have been reported in the literature (see for example [4–12]). The basic concept behind mineral CO₂ sequestration is to mimic natural weathering processes in which calcium or magnesium silicates are transformed into carbonates:



Various publications (see for example [15–17]) have proposed the mineral sequestration of CO₂ in controlled reactors as a viable approach to reduce CO₂ emissions into the atmosphere using liquid or solid alkaline residues such as municipal-waste combustion fly-ash, bottom ash, brine alkaline solutions, waste concrete and cements, steel slag, coal combustion fly-ash, alkaline paper mill waste, asbestos, etc. Obviously, the capacity to sequester CO₂ for these alkaline residues depends directly on the proportion of binary oxides (CaO and MgO) and/or hydroxides (Ca(OH)₂ and Mg(OH)₂) contained in the waste matrix. This present study was focused on the mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash. Herein, a simplified method was proposed in order to estimate the waste capacity to sequester CO₂ and the initial rate of CO₂ transfer during carbonation process from the water-fly ash dispersion.

1.2. General description of coal combustion fly-ash

Coal combustion in power plants provides approximately 40% of world electricity generation. At present, the coal reserves are estimated around 900 billion tons [18]. Considering that coal consumption reached 5 billion tons in 2003, coal-energy production will continue, and even increase, in the next centuries due to the energy demand for industrial and domestic uses [19]. Therefore, the continuous building of power plants is envisaged to sustain this energy production system. This may cause serious disruption to the global climate since each 500 MW coal power plant emits about 3 million tons of CO₂ per year. Likewise, the worldwide production of fly-ash, estimated currently at 600 million tons per year, will also

increase exponentially in the near future. The main producers of fly-ashes are China, Russia and the United States of America.

Fly-ash material is used as cement raw material and as a partial replacement for cement in concrete. However, the global production of fly-ash exceeds their potential uses [20], and hence, it is considered a residual by-product. Only around a 30% of the total production is used as a construction material. At present, numerous investigations are focused on the search of new applications for this residue. Three main research lines use fly-ash: (i) to synthesize zeolites used as filter material in water decontamination and gas retention [21,22], (ii) as an effective technique in metal retention processes in contaminated soils [23,24] and, (iii) for the treatment of acid mine drainage [25,26]. Recently, Soong et al. [15] propose the use of coal combustion fly-ash and brine solutions (waste from oil and gas production) to sequester CO₂ via aqueous mineral carbonation. For this study, CaO-rich fly-ashes were added to increase the pH level of the reactant brine (also containing Ca) in order to maximize the reaction efficiency of the carbonation process. This process was found to generate a high purity CaCO₃ product. We think that the use of CaO-rich fly-ashes as reactant to sequester CO₂ via aqueous mineral sequestration could be an attractive possibility for CO₂ mitigation in punctual sources at industrial scale. For this case, a recyclable CaCO₃-rich fly-ash material will be produced in the process.

A previous investigation showed that the carbonation of calcium hydroxide suspension under high pressure of CO₂ (initial $P_{\text{CO}_2} = 55$ bar) and moderate and high temperature (30 and 90 °C) is a potential method to synthesize fine particles of calcite [27]. In addition, the reported results have important ecological implications for the ex-situ mineral sequestration of CO₂ by alkaline solid waste containing CaO (lime) and/or Ca(OH)₂ (portlandite).

The objective of integrated waste management is the search for sustainable development, i.e. to balance the fulfilment of human needs with the protection of the natural environment in the present and indefinite future. With this in mind, the main aim of this work is precisely to quantify the CO₂ amount that may be sequestered by calcite precipitation using fly-ash–water dispersion. This study is in our opinion especially attractive since the residual solid by-products from power plants could be used to mitigate the residual gaseous wastes produced by the same plants.

2. Materials and methods

2.1. Fly-ash material

The fly-ash used in the present study is a waste residue generated from coal combustion at Los Barrios power station, Cádiz, south Spain. It is a powder composed mainly of spherical microparticles collected from electrostatic precipitators located at the outlet of the chimney where combustion gases are liberated to the atmosphere. Size distribution analysis indicates that the particles have a median diameter of 40 μm. The specific surface area is $0.63 \pm 0.022 \text{ m}^2 \text{ g}^{-1}$ determined by BET gas adsorption method (MICROMERITICS ASAP 2000 instrument). Mineral abundances are similar to those reported by Querol et al. [28], and show that fly-ash is composed of mullite (20.8 wt.%), quartz (4.5%), lime (4.1%), anhydrite (1.3%), K-feldspar (2.5%), magnetite (0.5%) and a chalc-aluminosilicate glass phase (66.4%). The chemical composition measured by X-ray fluorescence (XRF, BRUKER PIONEER instrument) shows that Los Barrios fly-ash is a residue rich in Si (41.3 wt.% SiO₂), Al (27.5 wt.% Al₂O₃), C (16 wt.% CO₂), Ca (5 wt.% CaO), and Fe (3.3 wt.% Fe₂O₃) with minor elements (wt.%): Sr (0.3%), Cl (0.02%), Cr (0.01%), Ni (0.02%), Zn (0.01%), V (0.01%), Cu (0.01%), Co (0.01%) and Sc (0.003%). The presence of lime (CaO, 4.1 wt%) in fly-ash

accounts for the high potential of both alkalinity and dioxide carbon sequestration as discussed below.

2.2. CO₂ sequestration experiments in a stirred reactor

In the present study, the effects of fly-ash dose, the CO₂ pressure, the reaction temperature and the reaction time were investigated as follows.

One litre of high-purity water with electrical resistivity of 18.2 MΩ cm and 50, 100 or 150 g of fly-ash were placed in a titanium reactor (autoclave Parr with internal volume of two litres). The fly-ash particles were immediately dispersed by mechanical stirring (450 rpm). The dispersion (solution + solid particles) was then heated to 30 °C or 60 °C using an oven specifically adapted to the reactor. The experiments were also carried out at room temperature (20–25 °C). When the dispersion temperature was reached, 10, 20, 30 or 40 bar of CO₂ (provided by Linde Gas S.A.) was injected in the reactor (see Fig. 1). This was the initial pressure of CO₂ which was equal to the total initial pressure in the system. After CO₂ injection, the pressure drop was monitored as a function of time until CO₂ equilibrium pressure in the system (anisobaric system) in order to estimate separately the rate of CO₂ transfer in pure water and during carbonation process from the dispersion.

Obviously, both the sorption–dissociation of CO₂ in the solution and aqueous carbonation process produce a global pressure drop in the system, $P_{\text{global.pressure-drop}}$. In order to estimate the pressure drop produced only by the process of CaO carbonation (noted $P_{\text{carbonation.pressure-drop}}$), two complementary systems were proposed for each experiment. First, the pressure drop $P_{\text{water.pressure-drop}}$ related to the sorption–dissociation of CO₂ into pure water only was measured. Secondly, the pressure drop $P_{\text{Ca-rich.pressure-drop}}$ related to the sorption–dissociation of CO₂ in a Ca-rich solution was measured independently. In this second experiment, a concentration of 1 g/L of calcium was chosen, that represented the average concentration after fly-ash dispersion in water. These two experiments demonstrated that the Ca-concentration (0–1 g/L) has no measurable effect on the sorption–dissociation of CO₂ because the monitored pressure drop in pure water $P_{\text{water.pressure-drop}}$ was equivalent to the monitored pressure drop in presence of Ca $P_{\text{Ca-rich.pressure-drop}}$. Consequently,

the pressure drop produced by the carbonation process of CaO was calculated by a simple pressure balance:

$$P_{\text{carbonation.pressure-drop}} = P_{\text{global.pressure-drop}} - P_{\text{water.pressure-drop}} \quad (2)$$

Under isothermal conditions, $P_{\text{global.pressure-drop}}$ and $P_{\text{water.pressure-drop}}$ are proportional to the initial CO₂ pressure.

At the end of the experiment, the reactor was removed from the heating system and was immersed into cold water. The reaction cell was depressurized for 15 min during the water cooling period. Upon cooling to 30 °C the reactor was disassembled, and the solid product was separated by centrifugation (30 min at 12,000 rpm), decanting the supernatant solutions. Finally, the solid product was dried directly in the centrifugation flasks for 48 h at 65 °C. The supernatant solutions were filtered through a 0.2 μm Teflon filter. Adsorption on the filter and filter holder was considered negligible. The filtered solutions were immediately acidified for measurement of [Ca], [Ni], [Zn], [Cu] and [Sr] by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The pH was also measured by using MA235 pH/ion analyser in filtered solutions without acidification.

2.3. Characterization of the solid phase

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

2.4. Calculation of saturation indexes

Solution saturation indexes with respect to solid phases ($SI = \log(IAP/K_s)$, where SI is the saturation index, IAP is the ion activity product and K_s is the solid solubility product, and aqueous speciation of the leachates were calculated using the equilibrium geochemical speciation/mass transfer model PHREEQC [29] and database of the speciation model MINTEQ. Zero, negative or positive SI values indicate that the solutions are saturated, undersaturated and supersaturated, respectively, with respect to a solid phase.

3. Results and discussion

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. The effects of fly-ash dose, the CO₂ pressure, the reaction temperature and reaction time are also commented in the following sub-sections.

3.1. Chemical reactions of CO₂ sequestration by fly-ash

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

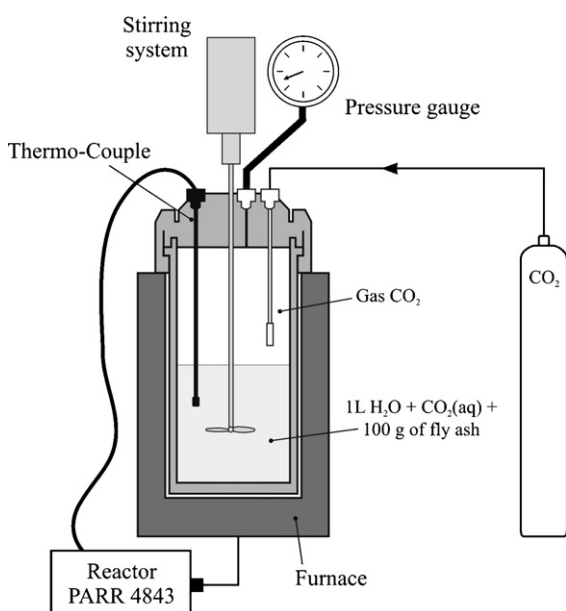


Fig. 1. Schematic experimental system for mineral sequestration of CO₂ by aqueous carbonation of fly-ash in a stirred reactor.

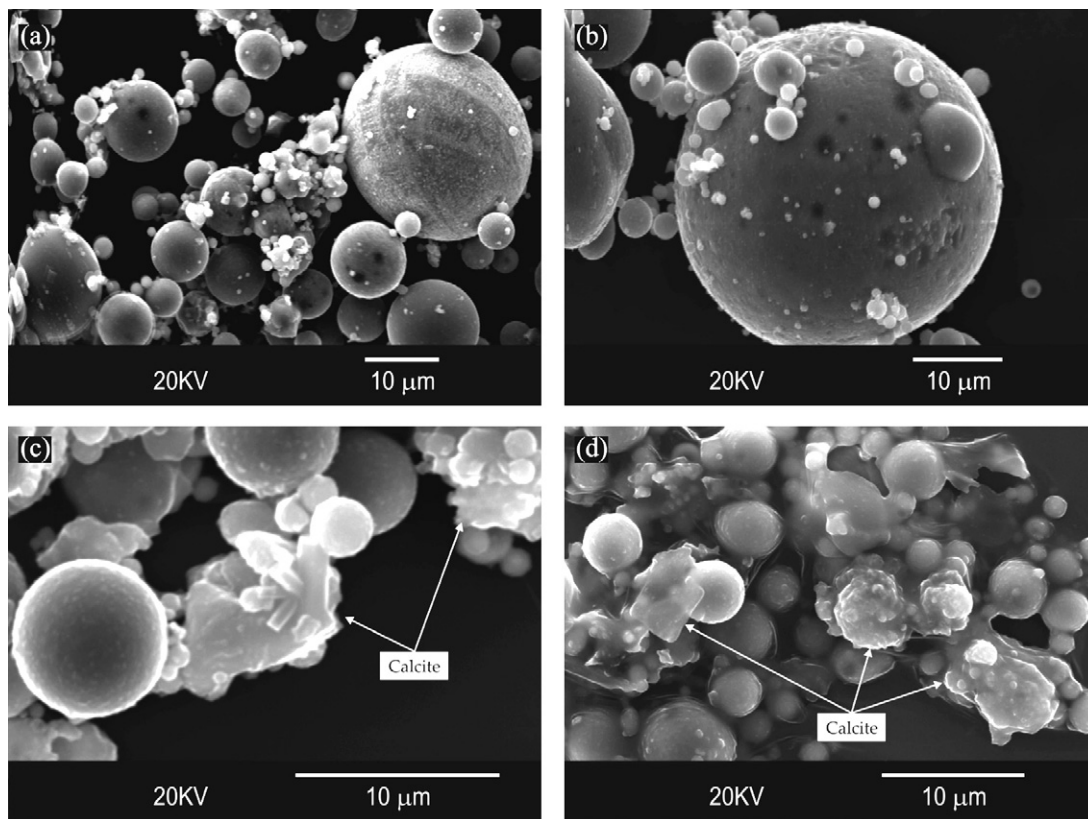


Fig. 2. (a and b) SEM images of fly-ash before reaction. (c and d) Calcite particles precipitated during CO₂ sequestration experiments.

second, the spontaneous carbonation of calcium hydroxide suspension:

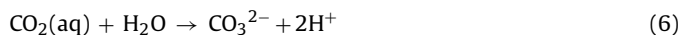


It was assumed that this global reaction takes place at high pH because the dispersion of the fly-ash in pure water at atmospheric conditions for liquid to solid ratios (10 or 20) increases rapidly the solution pH up to about 12.5 units. The aqueous carbonation of Ca(OH)₂ described by the global reaction (4) is an exothermic

process that concerns simultaneously the dissolution of Ca(OH)₂,



and the dissociation of aqueous CO₂,



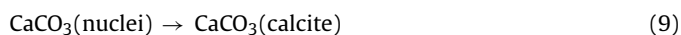
these processes produce a fast supersaturation (S_1) of solution with respect to calcite,

$$S_1 = \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_{sp}} > 1 \quad (7)$$

where (Ca^{2+}) and (CO_3^{2-}) are the activities of calcium and carbonate ions in the solution, respectively, and K_{sp} is the thermodynamic solubility product of calcite. Then, the nucleation stage (formation of nuclei or critical cluster) takes place in the system,



Finally, the crystal growth occurs spontaneously until the equilibrium calcite and the solution is reached,



The metastable crystalline phases of CaCO₃, such as vaterite and aragonite, were not identified in the X-ray diffraction spectra during the Ca(OH)₂ carbonation process in our experiments.

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

The chemical-element concentrations for Ca, Ni, Zn, Cu and Sr in the solution after two or eighteen hours of fly-ash-pure

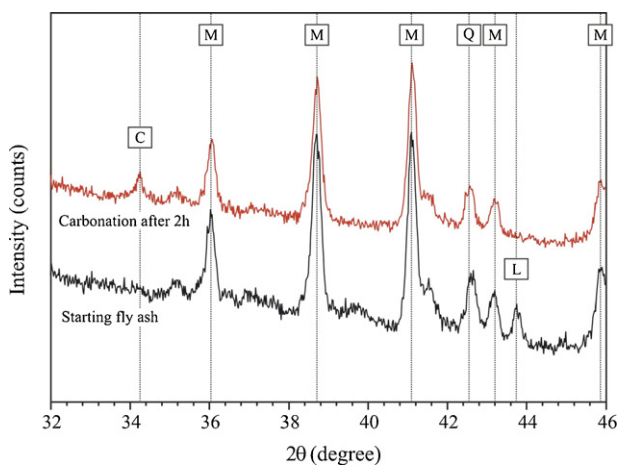


Fig. 3. XRD spectra of starting fly-ash and solid products after carbonation during 2 h. C: calcite, M: mullite, Q: quartz, L: lime. These spectra demonstrate the total consumption of lime and the production of calcite.

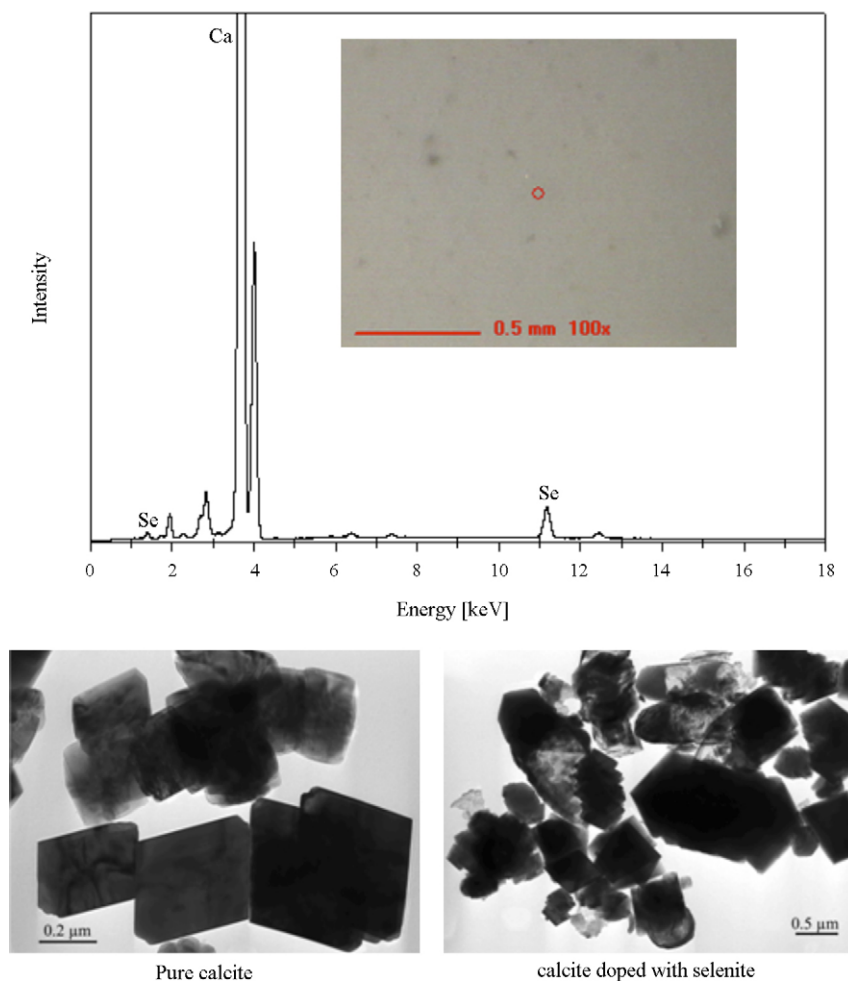


Fig. 4. Removal of selenite (SeO_3^{2-}) by aqueous carbonation of $\text{Ca}(\text{OH})_2$. Energy dispersive X-ray microanalysis (EDAX) and TEM micrographs.

water-carbon dioxide interactions suggest a preferential and rapid dissolution of lime phase and possibly a slight dissolution of the glass phase ($[\text{Ca}] \approx 800 \text{ mg/L}$) [26]. Concerning, of the trace elements contained in the fly-ash only the strontium was detected in the solution by ICP-AES ($[\text{Sr}] \approx 8 \text{ mg/L}$). Consequently, the concentrations of Ni, Zn and Cu were considered to be smaller than 6 ppb (detection limit). This demonstrates that the fly-ash dispersion into pure water did not favour the liberation of toxic metallic ions after two or eighteen hours of solid-fluid interaction at moderate temperature. In fact, preliminary experiments show that the selenite oxyanion (SeO_3^{2-}) can be successfully sequestered during calcite precipitation from aqueous solutions (Fig. 4). This economical and ecological method could allow the removal of toxic cations and/or oxyanions as well as the mineral sequestration of CO_2 [30].

Finally, the thermodynamic calculations by using PHREEQC code indicate that after reaction the solutions are slightly supersaturated with respect to calcium carbonate. Saturation indexes of calcite are in the range 0.7–1.1. The pH measured after carbonation process varies from 6.5 to 6.7 units. Note that the pH measurement was carried out at 25°C after filtration, cooling and degasification of the solutions. Obviously, this measurement is not representative of in situ pH behaviour, but, it can give a reasonable quantification of the solution saturation index with respect to the solid phases at standard conditions (25°C and 1 atm).

3.2. The sequestered quantity of CO_2 by calcite precipitation

A simplified method was developed to estimate the sequestered quantity of CO_2 by carbonate precipitation. This method was partially described in the Section 2.2. Herein, the pressure drop produced by the carbonation process of CaO (Eqs. (3) and (4)) in the system was calculated by a simple pressure balance described by Eq. (2). The carbonation pressure drop, $P_{\text{carbonation, pressure-drop}}$ was close to 1.5 bar and it was independent on the initial pressure of CO_2 (10, 20, 30, 40 bar) after 18 h of solid-liquid interaction (Fig. 5a). For these experiments, water to fly-ash ratio equal to 10 (w/w) and 30°C of reaction temperature were used. Systematically, the pressure drop was monitored with the time. These kinetic data showed that the CO_2 equilibrium pressure was reached after about 2 h of fly-ash-fluid interaction. In contrast, the CO_2 equilibrium pressure in pure water was reached after about 3 h (Fig. 5b). This means that the carbonation process enhances the rate of CO_2 transfer in the system. For more details, see the following sub-section.

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

$$n_{\text{CO}_2} = \frac{P_{\text{carbonation, pressure-drop}} V}{RT} \quad (10)$$

where, the V is the reactor volume occupied with gas (1L), T is the temperature of reaction ($\approx 303^\circ\text{K}$) and R is the gas constant ($0.08314472 \text{ L bar}/^\circ\text{K mol}$). Using the calculated value

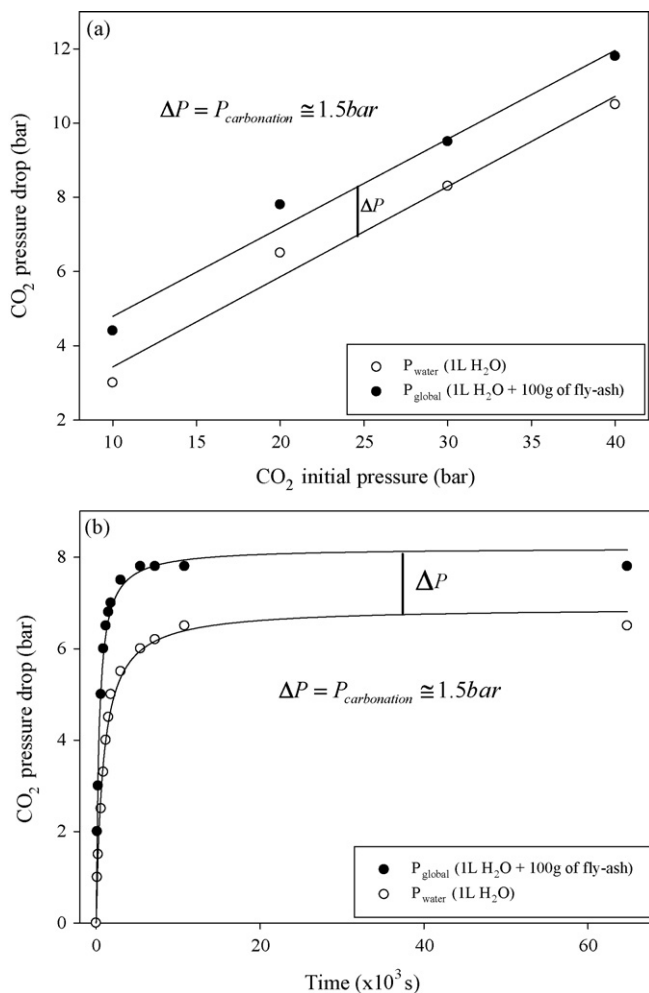


Fig. 5. (a) Linear correlation between the pressure decrease at equilibrium and the initial pressure of CO₂ (from 10 to 40 bar). (b) Kinetic behaviour of pressure decrease in the reactor at 30 °C and for 20 bar initial pressure of CO₂.

$P_{\text{carbonation, pressure-drop}} = 1.5 \text{ bar}$, we calculated that 0.05954 mol of CO₂ were consumed by the carbonation process. Taking into account reactions (3) and (4) and the fact that the fly-ash contains 4.1 wt.% of lime (CaO), the carbonation efficiency CE can be calculated by the following expression:

$$CE = \frac{n_{\text{CO}_2} M_{\text{CO}_2}}{(w_{\text{CaO}}/M_{\text{CaO}}) M_{\text{CO}_2}} \times 100 \quad (11)$$

where n_{CO_2} is the mol number of consumed CO₂, calculated by Eq. (10) (0.05954 mol), M_{CO_2} is the molar mass of CO₂ (44.01 g/mol), w_{CaO} is the starting mass of CaO in the reactor (4.1 g) and M_{CaO} is the molar mass of CaO (56.077 g/mol). The carbonation efficiency was then calculated to 82% after 18 h of solid–fluid interactions at 30 °C. In contrast, the qualitative comparison of X-ray diffraction spectra for reactants and products revealed a complete CaO–CaCO₂ conversion. Two hypotheses could explain this incoherence, (1) significant error on the lime content estimation, (2) solution acidification by CO₂ excess in the system.

The carbonation efficiency is not significantly affected by reaction temperature (room temperature “20–25”, 30 and 60 °C) and by fly-ash dose (50, 100, 150 g).

Theoretically 1 ton of fly-ash containing 4.1% of lime could sequester 32.17 kg of CO₂. With our experimental protocol, 26.19 kg of CO₂ per ton of fly-ash could be successfully sequestered into stable calcite, i.e. 38.18 ton of fly-ash per ton of CO₂ sequestered.

Indeed, this is an attractive result concerning the ex-situ mineral sequestration of CO₂, preferentially, if the lime content in the solid waste is >10% wt.

3.3. Kinetic modelling of CO₂ transfer in pure water and in a fly-ash–water suspension

The monitoring of the pressure drop for any controlled system under ideal gas conditions allows the kinetic modelling of CO₂ transfer after gas injection in an aqueous solution or in a solid–liquid system (fly-ash–water dispersion for this study). This can be done using a simple correlation function, $n_{\text{total,CO}_2} = f(t)$, where $n_{\text{total,CO}_2}$ is the total mol quantity of CO₂ to be sequestered in pure water or in the fly-ash–water dispersion and t is the time after gas injection.

Several kinetic models including first-order, pseudo-first-order, second-order, pseudo-second-order, parabolic diffusion and power function kinetic expressions are reported in the literature for fitting the kinetic experimental or calculated data of the solid–fluid interaction processes. For this study, the kinetic modelling concern the total sequestered quantity of CO₂ in pure water or in a fly-ash–water dispersion, i.e. the CO₂ sorption–dissociation in water, possibly the CO₂ adsorption on the fly-ash and, sequestered CO₂ by carbonation process. For this case, the best fit (attested by a correlation factor close to 1) of the experimental–calculated data was achieved when using a pseudo-second-order kinetic model according to the following expression:

$$\frac{dn_{\text{total,CO}_2,t}}{dt} = k_s(n_{\text{total,CO}_2,\text{max}} - n_{\text{total,CO}_2,t})^2 \quad (12)$$

where k_s is the rate constant of sequestered CO₂ (1/mol s) for a given initial pressure of CO₂ in the system, $n_{\text{total,CO}_2,\text{max}}$ is the maximum sequestered quantity of carbon dioxide at equilibrium [mol], $n_{\text{total,CO}_2,t}$ is the sequestered quantity of carbon dioxide at any time, t (mol).

The integrated form of Eq. (12) for the boundary conditions $t=0$ to $t=t$ and $n_{\text{total,CO}_2,t=0} = 0$ to $n_{\text{total,CO}_2,t} = n_{\text{total,CO}_2,t}$ is represented by a hyperbolic equation:

$$n_{\text{total,CO}_2,t} = \frac{n_{\text{total,CO}_2,\text{max}} t}{(1/k_s n_{\text{total,CO}_2,\text{max}}) + t} \quad (13)$$

In order to simplify the fitting of experimental–calculated data, we have defined the constant $t_{1/2} = k_s n_{\text{total,CO}_2,\text{max}}$. Physically, $t_{1/2}$ represents the time after which half of the maximum sequestered quantity of carbon dioxide was reached and is called “half-sequestered CO₂ time”. It can be used to calculate the initial rate of CO₂ transfer, $v_{0,s}$ (mol/s).

$$v_{0,s} = \frac{n_{\text{total,CO}_2,\text{max}}}{t_{1/2}} = k_s(n_{\text{total,CO}_2,\text{max}})^2 \quad (14)$$

The numerical fit of the experimental–calculated kinetic curves at 20 bar and 30 °C ($n_{\text{total,CO}_2,t}$ vs. t) using Eq. (13) are shown in Fig. 6. The parameters $t_{1/2}$ and $n_{\text{total,CO}_2,\text{max}}$ were estimated by applying a non-linear regression using the least-squares method. The initial rates of CO₂ transfer in pure water and in water–fly ash suspension were calculated using Eq. (14). These results demonstrated that the initial rate of CO₂ transfer was enhanced by carbonation process for our experiments. In addition, it’s well known that the CO₂ solubility in pure water increase with an increase of pressure. The present study showed that initial rate of CO₂ transfer in pure water also increases with pressure (from 10 to 40 bar) (Fig. 7). We think that this simplified kinetic method could be extended to estimate the effects of organic/inorganic impurities on the carbonation rate.

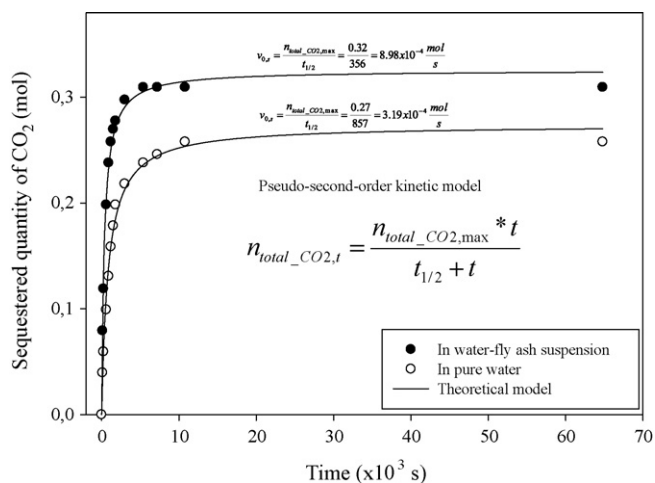


Fig. 6. Kinetic modeling of sequestered CO₂ in pure water and in a fly-ash–water suspension for 20 bar initial pressure of CO₂.

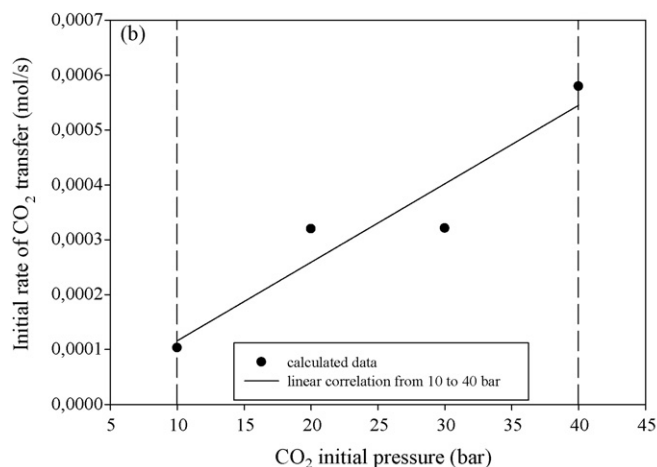
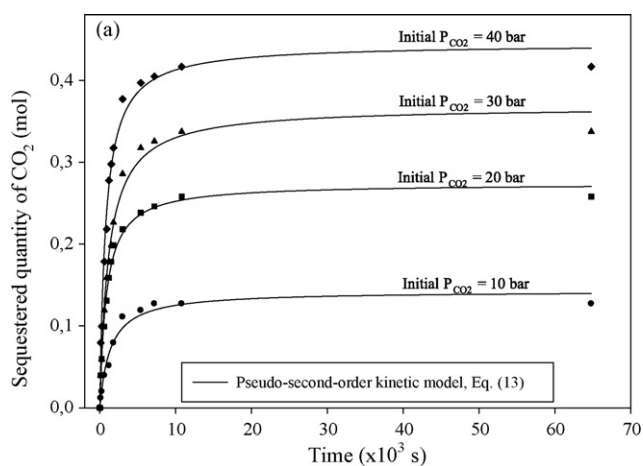


Fig. 7. (a) Kinetic modeling of sequestered CO₂ in pure water for 10, 20, 30 and 40 bar initial pressure of CO₂. (b) Linear increase of initial rate of CO₂ transfer with CO₂ initial pressure (from 10 to 40 bar).

4. Conclusion

The main purpose for this study was to demonstrate the feasibility to use coal combustion fly-ash to sequester CO₂ under mineral form via CaO carbonation. The results revealed a signifi-

cant CaO–CaCO₃ chemical transformation (approximately 82% of carbonation efficiency) by using a simplified pressure–mass balance method. The carbonation efficiency of CaO was independent on the initial pressure of CO₂ (10, 20, 30 and 40 bar) and it was not significantly affected by reaction temperature (room temperature “20–25”, 30 and 60 °C) and by fly-ash dose (50, 100, 150 g). In addition, the kinetic data demonstrated that the initial rate of CO₂ transfer was enhanced by carbonation process in our experiments.

In conclusion, the results presented of this study reveal that the ex-situ mineral sequestration of CO₂ by aqueous carbonation of fly-ash could be an attractive method to reduce the CO₂ emission in the atmosphere from power plants. This experimental investigation demonstrated that 1 ton of fly-ash, an industrial waste that contains about 4.1 wt.% of lime (CaO), could sequester up to 26 kg of CO₂, i.e. 38.18 ton of fly-ash per ton of CO₂ sequestered. This capacity to sequester CO₂ seems small compared with CO₂ sequestration capacity in production of steel slag. However, the annual average production of fly-ash in Los Barrios power station was approximately 1 million ton. This confirms the possibility to use this residue for CO₂ mitigation in punctual sources. Other advantages of the proposed method are (1) that the carbonation process takes place at low temperature (30 °C) and reduces the energy costs of the process at industrial scale and, (2) the use of moderate pressure in the system does not require expensive materials for reactor design.

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References

- [1] IPCC (Intergovernmental Panel on Climate Change), Climate Change 2007: The Physical Science Basis: Summary for Policymakers, 2007, http://www.ipcc-wg1.lucar.edu/wg1/Report/AR4WG1_Pub_SPM-v2.pdf.
- [2] IPCC (Intergovernmental Panel on Climate Change), Climate Change 2007: Climate Change Impacts, Adaptations, and Vulnerability, 2007, <http://www.ipcc-wg2.org/index.html>.
- [3] D.P. Schrag, Confronting the climate-energy challenge, *Elements* 3 (2007) 171–178.
- [4] S. Bachu, Sequestration of CO₂ in geological media: criteria and approach for site selection in response to climate change, *Energy Convers. Manage.* 41 (2000) 953–970.
- [5] S. Bachu, Sequestration of CO₂ in geological media in response to climate change: road map for site selection using the transform of the geological space into the CO₂ phase space, *Energy Convers. Manage.* 43 (2002) 87–102.
- [6] S. Bachu, J.J. Adams, Sequestration of CO₂ in geological media in response to climate change: capacity of deep saline aquifers to sequester CO₂ in solution, *Energy Convers. Manage.* 44 (2003) 3151–3175.
- [7] S.J. Friedmann, Geological carbon dioxide sequestration, *Elements* 3 (2007) 179–184.
- [8] Y.K. Kharaka, D.R. Cole, S.D. Hovorka, W.D. Gunter, K.G. Knauss, B.M. Friefeld, Gas–water–rock interactions in Frio Formation following CO₂ injection: implications for the storage of greenhouse gases in sedimentary basins, *Geology* 34 (2006) 577–580.
- [9] W.D. Gunter, E.H. Perkins, I. Hutcheon, Aquifer disposal of acid gases: modeling of water–rock reactions for trapping of acid wastes, *Appl. Geochem.* 15 (2000) 1085–1095.
- [10] J.P. Kaszuba, D.R. Janecky, M.G. Snow, Carbon dioxide reaction processes in a model brine aquifer at 200 °C and 200 bar: implications for geologic sequestration of carbon, *Appl. Geochem.* 18 (2003) 1065–1080.
- [11] J.P. Kaszuba, D.R. Janecky, M.G. Snow, Experimental evaluation of mixed fluid reactions between supercritical carbon dioxide and NaCl brine: relevance to the integrity of a geologic carbon repository, *Chem. Geol.* 217 (2005) 277–293.
- [12] D.E. Giammar, R.G. Bruant, C.A. Peters, Forsterite dissolution and magnesite precipitation at conditions relevant for deep saline aquifer storage and sequestration of carbon dioxide, *Chem. Geol.* 217 (2005) 257–276.

- [13] W. Seifritz, CO₂ disposal by means of silicates, *Nature* 345 (1990) 486.
- [14] K.S. Lackner, C.H. Wendt, D.P. Butt, E.L. Joyce, D.H. Sharp, Carbon dioxide disposal in carbonate minerals, *Energy* 20 (11) (1995) 1153–1170.
- [15] Y. Soong, D.L. Fauth, B.H. Howard, J.R. Jones, D.K. Harrison, A.L. Goodman, M.L. Gray, E.A. Frommell, CO₂ sequestration with brine solution and fly-ashes, *Energy Convers. Manage.* 47 (2006) 1676–1685.
- [16] W.J.J. Huijgen, G.-J. Witkamp, R.N.J. Comans, Mechanisms of aqueous wollastonite carbonation as a possible CO₂ sequestration process, *Chem. Eng. Sci.* 61 (2006) 4242–4251.
- [17] W.J.J. Huijgen, R.N.J. Comans, G.-J. Witkamp, Cost evaluation of CO₂ sequestration by aqueous mineral carbonation, *Energy Convers. Manage.* 48 (2007) 1923–1933.
- [18] BP (British Petroleum), Statistical Review of World Energy, 2006, <http://www.bp.com/productlanding.do?categoryId=6848&contentId=7033471>.
- [19] Energy Information Administration, International Energy Annual, Department of Energy, Washington, DC, 2006, <http://www.eia.doe.gov/iea>.
- [20] O.E. Manz, Worldwide production of coal ash and utilization in concrete and other products, *Fuel* 76 (1997) 691–696.
- [21] X. Querol, J.C. Umaña, F. Plana, A. Alastuey, A. Lopez-Soler, A. Medinaceli, A. Valero, M.J. Domingo, E. Garcia-Rojo, Synthesis of zeolites from fly ash at pilot plant scale. Examples of potential applications, *Fuel* 80 (2001) 857–865.
- [22] J. Cama, C. Ayora, X. Querol, J. Ganor, Dissolution kinetics of synthetic zeolite NaP1 and its implication to zeolite treatment of contaminated waters, *Environ. Sci. Technol.* 39 (2005) 4871–4877.
- [23] S.S. Brake, R.R. Jensen, J.M. Mattox, Effects of coal fly ash amended soils on trace element uptake in plants, *Environ. Geol.* 45 (2003) 680–689.
- [24] D. Dermatas, X. Meng, Utilization of fly ash for stabilization/solidification of heavy metal contaminated soils, *Eng. Geol.* 70 (2003) 377–394.
- [25] R. Pérez-López, J.M. Nieto, G.R. Almodóvar, Immobilization of toxic elements in mine residues derived from the mining activities in the Iberian Pyrite Belt (SW Spain): laboratory experiments, *Appl. Geochem.* 22 (2007) 1919–1935.
- [26] R. Pérez-López, J. Cama, J.M. Nieto, C. Ayora, The iron-coating role on the oxidation kinetics of a pyritic sludge doped with fly ash, *Geochim. Cosmochim. Acta* 71 (2007) 1921–1934.
- [27] G. Montes-Hernandez, F. Renard, N. Geoffroy, L. Charlet, J. Pironon, Calcite precipitation from CO₂-H₂O-Ca(OH)₂ slurry under high pressure of CO₂, *J. Cryst. Growth* 308 (2007) 228–236.
- [28] X. Querol, J.C. Umaña, A. Alastuey, C. Ayora, A. Lopez-Soler, F. Plana, Extraction of soluble major and trace elements from fly ash in open and closed leaching systems, *Fuel* 80 (2001) 801–813.
- [29] D.L. Parkhurs, C.A.J. Appelo, PHREEQC-2 version 2.12: a hydrochemical transport model. 2005, <http://www.brr.cr.usgs.gov>.
- [30] G. Montes-Hernandez, R. Perez-Lopez, F. Renard, L. Charlet, J.M. Nieto, Process for sequestration of CO₂ by reaction with alkaline solid waste European Patent application no. EP07123303.5 (2007).