



# Co-utilisation of alkaline solid waste and compressed-or-supercritical CO<sub>2</sub> to produce calcite and calcite/Se<sup>0</sup> red nanocomposite

G. Montes-Hernandez<sup>a,\*</sup>, F. Renard<sup>a,b</sup>

<sup>a</sup> CNRS and University Joseph Fourier, LGCA/ISTerre, OSUG/INSU, BP 53, 38041 Grenoble Cedex 9, France

<sup>b</sup> Physics of Geological Processes, University of Oslo, Norway

## ARTICLE INFO

### Article history:

Received 27 July 2010

Received in revised form 4 November 2010

Accepted 9 November 2010

### Keywords:

CO<sub>2</sub> mineralization

Calcite

Nanocomposites

Alkaline solid waste

Elemental selenium

Seleno-L-cystine

## ABSTRACT

The coal combustion fly-ash and alkaline paper mill waste were previously used to sequester CO<sub>2</sub> via waste-water–CO<sub>2</sub> interactions. For this case, a solid mixture (calcite and un-reacted waste) was obtained after carbonation process. In the present study, we propose a solid–water separation of free lime (CaO) or free portlandite (Ca(OH)<sub>2</sub>) contained in waste prior to carbonation experiments in order to produce pure calcite or calcite/Se<sup>0</sup> red composite. The calcite and carbonate composite syntheses have been also independently studied, but for both cases, a commercial powdered portlandite was used as calcium source.

For this study, the extracted alkaline-solution (pH = 12.2–12.4 and Ca concentration = 810–870 mg/L) from alkaline solid waste was placed in contact with compressed or supercritical CO<sub>2</sub> at moderate or high temperature, leading a preferential nucleation-growth of submicrometric particles of calcite (<1 μm) with rhombohedral morphology at 90 °C and 90 bar (9 MPa), whereas a preferential nucleation-growth of nanometric particles of calcite (<0.2 μm) with scalenohedral morphology at 30 °C and 20 bar (2 MPa) were observed. When, the extracted alkaline-solution was placed in contact with supercritical CO<sub>2</sub> (90 bar) at high temperature (90 °C) and in presence of unstable seleno-L-cystine compound, the nucleation-growth of calcite/Se<sup>0</sup> red nano-composite taken place. The composite consisted predominantly of spherical, amorphous nanometric-to-submicrometric of elemental red selenium (<500 nm) deposited on the calcite matrix. Here, the calcite was constituted by nano- to microrhombohedral crystals (<2 μm) and micro-metric agglomerates and/or aggregates (<5 μm). These results on the particle size and morphology of crystal faces are very similar to calcite produced using commercial powdered portlandite as alkaline reactant and calcium source. This study is a nice example of feasibility to obtain possible ecological and economical benefits from waste co-utilisation.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

### 1.1. General comments

In this study, we demonstrated that the co-utilisation of alkaline solid waste (containing free lime (CaO) and/or free portlandite (Ca(OH)<sub>2</sub>)) and carbon dioxide allows the production of pure calcite or calcite/Se<sup>0</sup> red composite. The lime and portlandite powdered minerals are extremely reactive in contact with water; in fact, the lime is chemically stable only under dry conditions (relative humidity ≈ 0). In aqueous systems, the lime and portlandite are instantaneously dissolved until their solubility limit (e.g. 1.5 g/L at 25 °C for portlandite). The lime excess in the solid/water system is

completely transformed to portlandite [1]. On the other hand, as mentioned in the literature, the calcite and selenium powdered-materials are widely used as ingredient in antacid tablets, mineral filler powders, pigments, dietary supplement, etc. ([2–4] and references therein). Note that selenium is a key trace element required in small quantities in humans and animals, in particular for a number of selenium-dependent enzymes, such as glutathione peroxidase (GPX) and thioredoxin reductase. However this element can also be toxic in larger doses and the range between deficiency and toxicity is narrow for this element (approximately 30–300 μg/day for adults, respectively). Both the beneficial and toxic effects of selenium are based on the ingested concentration and on its chemical form and speciation. Selenium occurs in four different oxidation states in aqueous and subsurface systems and in living organisms, namely –2, 0, +4 and +6 (see for example [4] and references therein). Recently, original synthesis methods (triphasic gas–liquid–solid systems under isobaric or anisobaric conditions) had been proposed to produce submicrometric particles of calcite

\* Corresponding author. Tel.: +33 4 76 64 02 77.

E-mail address: [german.montes-hernandez@obs.ujf-grenoble.fr](mailto:german.montes-hernandez@obs.ujf-grenoble.fr) (G. Montes-Hernandez).

and calcite/Se<sup>0</sup> red nanocomposite using synthetic portlandite particles as calcium source [2–4]. On the other hand, the ex situ mineral sequestration of CO<sub>2</sub> via aqueous carbonation of coal combustion fly-ash and alkaline paper mill waste, containing free lime and free portlandite, respectively, had been also studied. For this case, a solid mixture (calcite and un-reacted waste) was obtained after carbonation process [1,5]. In the present study, we propose a solid–water separation of free lime (CaO) or free portlandite (Ca(OH)<sub>2</sub>) contained in waste prior to carbonation experiments in order to synthesize sub-micrometric particles of calcite or calcite/Se<sup>0</sup> red nanocomposite (refer to Section 2). For calcite/Se<sup>0</sup> composite synthesis, the use of seleno-L-cystine (SeCys) compound is based on the fact that Se (–2) contained into SeCys is quickly oxidized to elemental selenium (Se<sup>0</sup>), selenite (SeO<sub>3</sub><sup>–2</sup>) and selenate (SeO<sub>4</sub><sup>–2</sup>) depending on the oxygen concentration into interacting solution (see [4]). Infrared spectroscopy (FTIR) and electron microscopy (FEG-SEM and TEM/EDS) were used to characterize the powdered products.

## 1.2. Basic concepts on the CO<sub>2</sub> mineralization

The biotic and abiotic (i.e. chemical) formation of carbonates plays a crucial role in the global carbon cycle, and in addition, carbonate minerals often sequester various trace elements (actinides and lanthanides), metalloids, and heavy metals, and thus control in part their global cycling. Moreover, calcium carbonates are the privileged minerals for the fabrication of structural bio-minerals in invertebrates. At the present time, the non-regulated CO<sub>2</sub> emissions into the Earth's atmosphere, mainly caused by fossil fuel combustion, has led to concerns about the global warming. The long term geological storage is a realistic and available technology to reduce the CO<sub>2</sub> emissions because high volumes can be stored in various geological deep formations. In the last decades, it has been demonstrated that the ex situ mineralization of CO<sub>2</sub> (using controlled industrial reactors) could also contribute to reducing CO<sub>2</sub> emissions, mainly from point industrial sources (e.g. [6–8]).

Carbonate minerals can be formed in natural or artificial environments by three different mechanism pathways and/or conditions: (1) aqueous nucleation-growth in homogeneous or heterogeneous systems (aqueous conditions), e.g. the chemical or biogenic formation of carbonates in lakes, oceans, CO<sub>2</sub> storage sites, natural caves, etc. [9–12]; (2) solid–gas carbonation of alkaline minerals in presence of adsorbed water (water humidity conditions, 0 < water activity < 1), e.g. the carbonates formation in unsaturated soils, in terrestrial or extraterrestrial aerosols, etc. [13,14]; (3) dry solid–gas carbonation of granular/porous ultrabasic materials (dry conditions, water activity ≈ 0), e.g. the industrial mineralization, recovery or capture of CO<sub>2</sub> under high temperature using binary oxides or metastable alkaline silicates (nanoparticles) [15–19].

The natural weathering processes of calcium or magnesium silicates, commonplace at the Earth surface, produce solid particles and ions that are transported via rivers to lakes and oceans. For example, the weathering reaction of a calcium pyroxene can be release calcium, which will be later incorporated into carbonates minerals via chemical or biogenic pathways. Thus, the natural weathering of mafic/ultramafic rocks, followed by carbonate formation, consumes carbon dioxide and represents a simple example of a natural CO<sub>2</sub> mineralization process. This fundamental process lends credence to the geological sequestration of anthropogenic CO<sub>2</sub> (i.e. in situ mineral sequestration of CO<sub>2</sub>) in order to reduce carbon dioxide emissions into the atmosphere [20–22]. As mentioned above, the ex situ mineralization of CO<sub>2</sub> (using controlled industrial reactors) has been also proposed to contribute on the reduction of CO<sub>2</sub> emissions into atmosphere. For this case the natural alkaline minerals or alkaline solid–liquid waste (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.) can be used to mineralize the CO<sub>2</sub> [1,5,23–25]. Obviously, the capacity to sequester CO<sub>2</sub> using alkaline residues depends directly on the proportion of free binary oxides (CaO and MgO) and/or free hydroxides (Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>) contained in the waste matrix. Conversely, when the natural alkaline minerals are used as reacting particles, the mineralization of CO<sub>2</sub> is mainly controlled by the dissolution process of these reacting particles. Note that, the in situ or ex situ sequestration of CO<sub>2</sub> can involve multiphasic gas–liquid–solid systems under hydrothermal or solvothermal conditions. In the same context, our study combines this previous knowledge and we propose a simplified method to produce pure calcite particles or calcite/Se<sup>0</sup> red nanocomposite via co-utilisation of alkaline solid waste and carbon dioxide. This method required a solid–water extraction of free portlandite (Ca(OH)<sub>2</sub>) or free lime (CaO) contained in waste matrix prior to carbonation experiments.

## 2. Materials and methods

### 2.1. Synthesis of alkaline mother solutions

50 g of coal combustion fly-ash containing about 4% of free lime (CaO) or 5 g of alkaline paper mill waste containing about 55% of free portlandite (Ca(OH)<sub>2</sub>) were dispersed in 1 L of Millipore MQ water (18.2 MΩ) at atmospheric conditions for 10 min. The produced alkaline solutions were separated from un-reacted solid by centrifugation (30 min at 12,000 rpm). Then, the solutions were filtered through a 0.2 μm Teflon filter. 10 mL of filtered solutions were immediately acidified for measurement of [Ca], [Ni], [Zn], [Cu], [Fe] and [Sr] by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The pH was also measured using MA235 pH/ion analyser in filtered solutions. The average ion concentration and pH (three independent measurements) of produced alkaline-solutions are shown in Table 1.

### 2.2. Synthesis of submicrometric calcite particles

One litre of alkaline mother solution (Ca concentration = 810–870 mg/L and pH = 12.2–12.4) was placed in a titanium reactor (autoclave with internal volume of 2 L). The alkaline solution was immediately heated to 30 or 90 °C with a specific furnace adapted to the reactor under mechanical agitation (400 rpm). When the solution temperature was reached (after about 1 h for high temperature), 6 g of CO<sub>2</sub> (provided by Linde Gas S.A.) were injected in the reactor and the total pressure in the system was immediately adjusted to 20, 55 or 90 bar (or 2, 5.5 or 9 MPa, respectively) by argon injection. Under these T and P conditions, the vapour phase consists mainly of an Ar + CO<sub>2</sub> mixture with the CO<sub>2</sub> in gaseous or supercritical state. Based on previous studies [1–5], 1 h was considered as reaction duration for all carbonation experiments.

At the end of the experiment, the autoclave was removed from heating system and immersed in cold water, particularly for carbonation experiments performed at 90 °C. The reaction cell was

**Table 1**

Average ion concentration and pH of produced alkaline-solutions by dispersion of fly ash and alkaline paper mill waste in Millipore MQ water (18.2 MΩ) at atmospheric conditions for 10 min.

Source	pH	Ion concentration (mg/L)					
		[Ca]	[Sr]	[Zn]	[Cu]	[Ni]	[Fe]
Fly ash	12.2	810	8	nd	nd	nd	nm
APMW	12.4	870	1	nd	nd	nd	nd

APMW: alkaline paper mill waste, nd: not detected (<6 μg/L), nm: not measured.

depressurized during the water cooling period. After water cooling at 35 °C (about 15 min) the autoclave was disassembled, and the solid product was carefully recovered and 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 60 °C, manually recovered and stored at atmospheric conditions.

### 2.3. Synthesis of calcite/Se<sup>0</sup> red nanocomposite

One litre of alkaline mother solution (Ca concentration = 810–870 mg/L and pH = 12.2–12.4) and 200 mg of seleno-L-cystine  $\text{CO}_2\text{HCH}(\text{NH}_2)\text{CH}_2(\text{Se})_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$  (provided by Sigma–Aldrich) with chemical purity ( $\geq 98.0\%$ ) were placed in a titanium reactor (autoclave with internal volume of 2 L). The alkaline solution and selenocystine particles were immediately

stirred with mechanical agitation (400 rpm). At room temperature the gas argon with 99.999% chemical purity (provided by Linde Gas S.A.) was injected into the reaction cell in order to control the pressure at 90 bar (9 MPa) during 30 min. After this time period, the suspension was heated to 90 °C with a furnace adapted to the reactor. Obviously, during heating stage the pressure increased into the system, but it was kept constant at about 90 bar (9 MPa) using successive manual purge until the temperature was stabilized (about 60–90 min). Then, a flash purge was carried out until atmospheric pressure was reached. Theoretically, the heating of aqueous dispersion under argon pressure and gas purge, allowed a partial removal of dissolved oxygen. We note that the reactor configuration did not permit the measurement of the oxygen concentration inside the reactor. When the atmospheric pressure was reached in the reactor, 6 g of  $\text{CO}_2$  with 99.995% chemical purity (provided by Linde Gas S.A.) were injected in the reactor

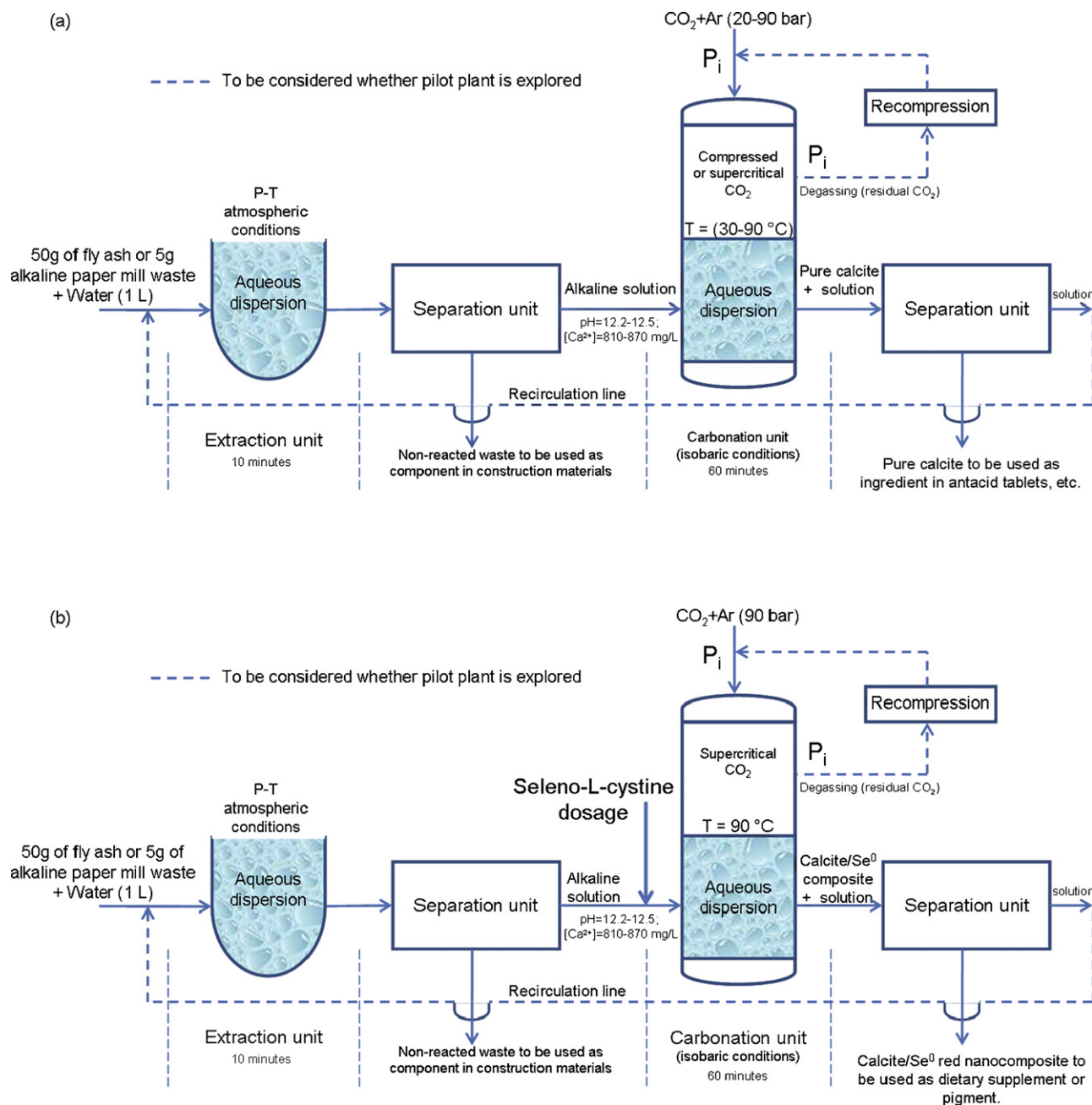


Fig. 1. Flow diagrams for co-utilisation of alkaline solid waste and carbon dioxide to produce (a) pure calcite and (b) calcite/Se<sup>0</sup> red composite.



and the total pressure in the system was immediately adjusted to 90 bar (9 MPa) by argon injection. Under these T and P conditions, the vapour phase consists mainly of an Ar + CO<sub>2</sub> mixture with the CO<sub>2</sub> in a supercritical state. 1 h was also considered as reaction duration for this experiment. Finally, the recovery of calcite/Se<sup>0</sup> red composite was performed by following the same procedure than for pure calcite.

The syntheses of submicrometric calcite particles and calcite/Se<sup>0</sup> red nanocomposite, including the synthesis of alkaline mother solution from waste are schematically represented in Fig. 1.

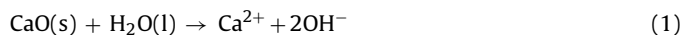
#### 2.4. Characterization of solid products

Field emission gun scanning electron microscopy (FEG-SEM), using a Zeiss Ultra 55 microscope with a resolution around 1 nm at 15 kV was used to characterize the particle size and morphology of crystal faces. The samples (powders) were previously dispersed by ultrasound in absolute ethanol during 5 min. Then, one or two drops of suspension were deposited directly on the metallic supports for SEM observations. Isolated fine particles (oriented on carbon Ni grids) of the selected samples were also studied using a JEOL 3010 Transmission Electron Microscope (TEM) equipped with an energy dispersive X-ray analyzer (EDS) to characterize the morphology of crystal faces and particles size. Chemical maps were determined by energy dispersive X-rays using K lines for Ca, O and Se. Finally, solid products were also characterized using infrared spectrometry, with a BRUKER HYPERION 3000 infrared microscope in transmission mode, with a MCT mono-detector at 4 cm<sup>-1</sup> resolution. The typical size of the infrared spot onto the sample was ~50 × 50 μm<sup>2</sup>. For these measurements, some aggregates of solid products were manually compressed between two KBr windows in order to deposit a thin film of sample on a KBr window.

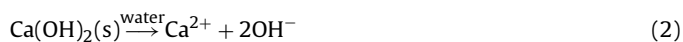
### 3. Results and discussion

Three previous experimental studies have demonstrated that alkaline solid waste can be used to sequester carbon dioxide and/or toxic ions (e.g. selenium and arsenic) via aqueous nucleation-growth process of calcite [1,5,26]. In the present experimental study, the same alkaline solid waste (alkaline paper mill waste and coal combustion fly-ash) were used to produce submicrometric cal-

cite particles and calcite/Se<sup>0</sup> red nanocomposite. These syntheses are schematically shown in Fig. 1. Note that both syntheses required a solid–water extraction of free portlandite (Ca(OH)<sub>2</sub>) or free lime (CaO) contained in waste matrix prior to carbonation step. The involved dissolution reactions to recovery the free lime or free portlandite from waste, i.e. by producing an alkaline solution (termed here “alkaline mother solution”) can be expressed as:

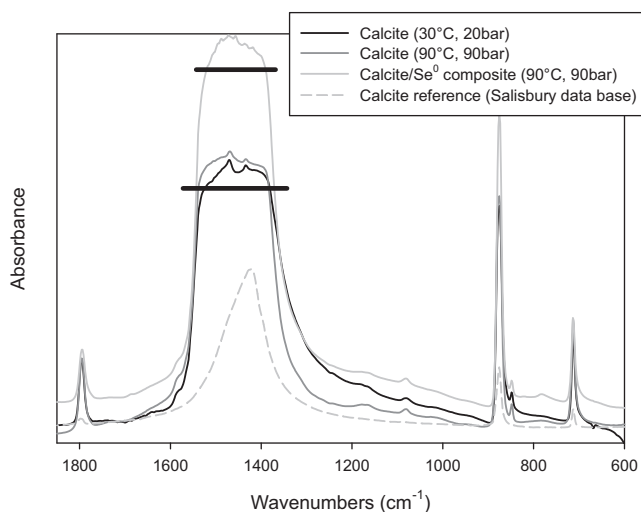


for free lime contained on coal combustion fly-ash,

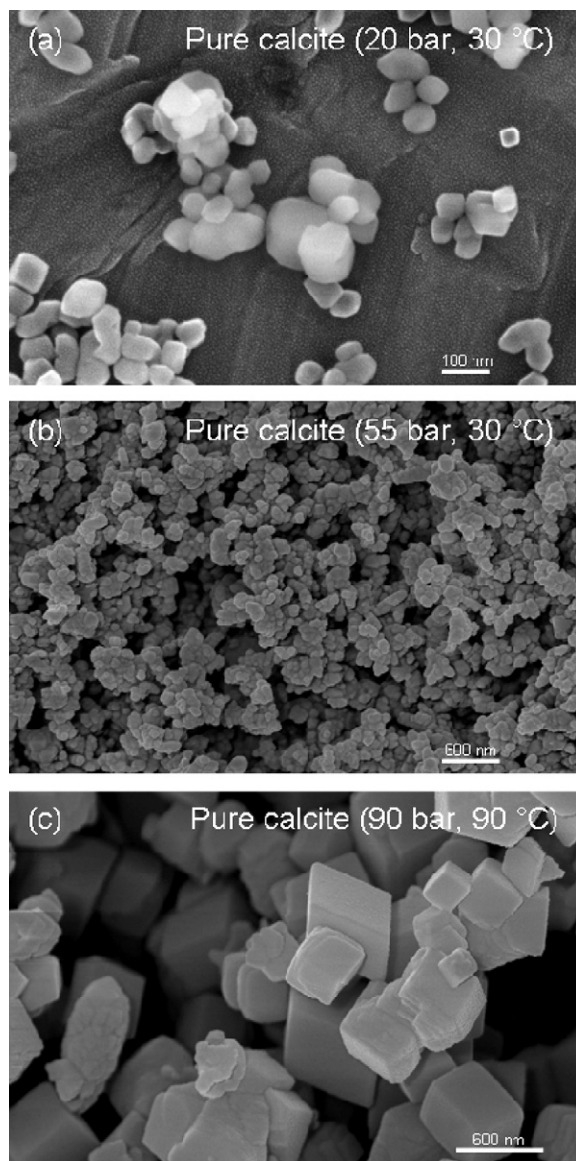


for free portlandite contained on paper mill waste.

The free lime or free portlandite contained in waste matrix are instantaneously dissolved in water at atmospheric conditions, producing alkaline solutions (pH = 12.2–12.4) concentrated in calcium (from 810 to 870 mg/L) (Table 1). These solutions were separated from un-reacted solid waste and then used for carbonation experiments. The particle size of calcite or calcite composite and



**Fig. 2.** Infrared spectra for calcite and calcite/Se<sup>0</sup> composite compared with calcite reference (source: Salisbury database). Note the strong ν<sub>3</sub> band of CaCO<sub>3</sub> is saturated (thick horizontal line).

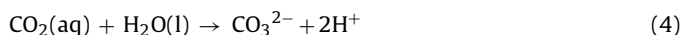


**Fig. 3.** Sub-micrometric particles of calcite precipitated from alkaline mother solution in contact with compressed or supercritical CO<sub>2</sub> under isobaric conditions. (a–c) FEG-SEM micrographs obtained via secondary electrons.

morphology of crystal faces are described and discussed in the following paragraphs.

### 3.1. Nucleation-growth of pure calcite (submicrometric particles)

Some studies have reported the co-utilisation of alkaline solid waste and carbon dioxide to produce pure calcite (e.g. [27,28] and references therein). In general, the carbon dioxide was bubbled through alkaline solution, leading the nucleation-growth of micrometric particles of calcite ( $>5\ \mu\text{m}$ ). Note that the textural properties such particle size, specific surface area, morphology of crystal faces, etc. in powdered materials are essential parameters to define their industrial or medical applications. In previous carbonation studies using synthetic portlandite particles as calcium source, we demonstrated that the use of compressed or supercritical carbon dioxide allowed the synthesis of sub-micrometric particles of calcite [2,3]. Based on this previous knowledge, we demonstrated that physicochemical interactions between the alkaline mother solutions and compressed or supercritical  $\text{CO}_2$  (gas pressure = 20–90 bar) at moderate and high temperature (30 or  $90^\circ\text{C}$ ) produce fast nucleation-growth of calcite until an equilibrium state in this discontinuous reactor. This carbonation process can be explained by the following reactions:



At high pH ( $>10$ ) was assumed that the aqueous carbon dioxide is completely dissociated to carbonate ion (reaction (4)). However, the carbonate ions can accept protons ( $\text{H}^+$ ), forming  $\text{HCO}_3^-$  or  $\text{H}_2\text{CO}_3^0$  soluble species because the pH decreases progressively during carbonation process until equilibrium state. The formation of carbonate ions (Eq. (4)) in the interacting alkaline solution (concentrated with calcium ions) produces a fast supersaturation of interacting solution with respect to calcite and then a spontaneous homogeneous-nucleation of calcite (formation of nuclei or critical

cluster),

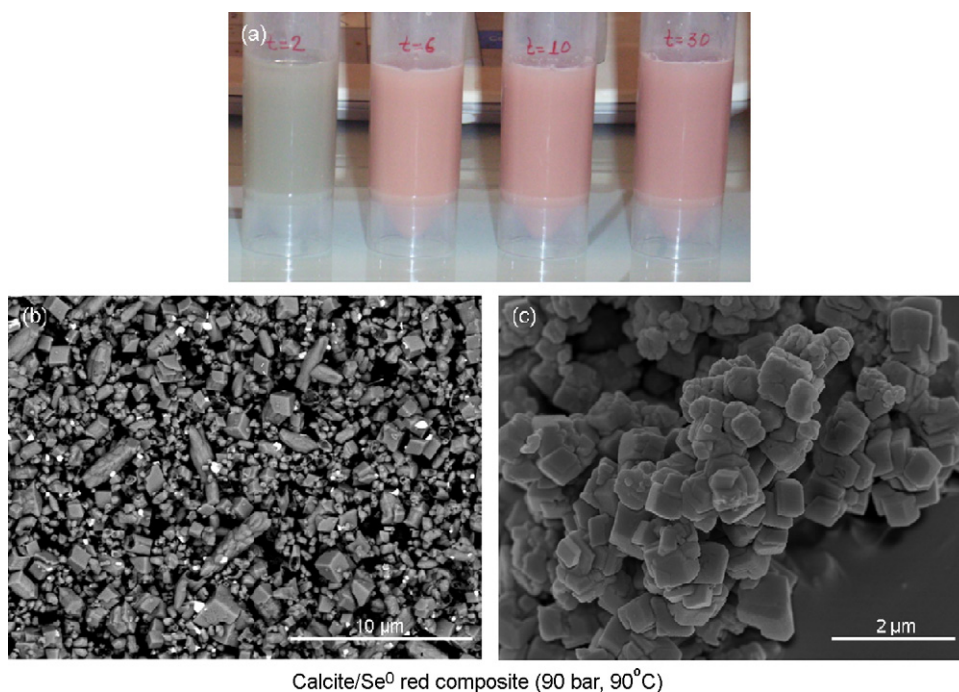


Finally, crystal growth occurs spontaneously until a thermodynamic equilibrium between calcite and the solution is reached in this closed system,



Infrared (shown in Fig. 2) and X-ray diffraction (not shown) measurements confirm the calcite nature for solid products. For example, on the infrared spectra, the  $\text{CO}_3$  stretching vibration band ( $\nu_3$ ) at  $1410\text{--}1490\ \text{cm}^{-1}$  and the  $\text{CO}_3$ -bending vibration band ( $\nu_2$ ) at  $877\ \text{cm}^{-1}$  are typical fundamental bands for calcite. Metastable calcium carbonates such as aragonite and vaterite were not identified in the solid products. These results were clearly supported by microscopic (SEM or TEM) observations. In fact, microscopic observations suggest a preferential nucleation-growth of submicrometric particles of calcite ( $<1\ \mu\text{m}$ ) with rhombohedral morphology at  $90^\circ\text{C}$  and 90 bar, whereas a preferential nucleation-growth of nanometric particles of calcite ( $<0.2\ \mu\text{m}$ ) with scalenohedral morphology at  $30^\circ\text{C}$  and 20 bar were observed (Fig. 3). The same order of particle size and the similar morphology of crystal faces for calcite were observed in previous carbonation experiments using synthetic portlandite particles as calcium source (see for example [3]).

In technological applications, we think that this powdered calcite could be used as active ingredient in antacid tablets and as mineral filler in printing inks and papermaking industry. These uses for calcite have been proposed in several studies (e.g. [2,29–31]). The un-reacted solid separated prior carbonation process (as shown in Fig. 1) could be used as component in construction materials, aerogels fabrication, etc. (e.g. [32,33]). At the pilot plant or industrial scale the aqueous solutions and residual  $\text{CO}_2$  should be re-circulated in the system. For this case, the argon gas (used in laboratory experiments) could be replaced by compressed air (this suggestion was not tested in the laboratory).



Calcite/ $\text{Se}^0$  red composite (90 bar,  $90^\circ\text{C}$ )

**Fig. 4.** Calcite/ $\text{Se}^0$  red composite precipitated from alkaline mother solution in contact with supercritical  $\text{CO}_2$  and seleno-L-cystine compound. (a) Photographs, (b) FEG-SEM micrograph obtained via backscattering electrons showing elemental selenium particles (white areas) and (c) FEG-SEM micrograph obtained via secondary electrons.

### 3.2. Nucleation-growth of calcite/Se<sup>0</sup> red nano-composite

Particularly, the alkaline mother solution in contact with supercritical CO<sub>2</sub> (gas pressure = 90 bar) at high temperature (90 °C) and in presence of unstable seleno-L-cystine compound, produce fast nucleation-growth of calcite/Se<sup>0</sup> red nano-composite (Fig. 4a). Infrared measurements confirm only calcite nature on the composite (Fig. 2). The Se–Se bond was not identified by infrared measurements, but the elemental selenium nanoparticles were clearly identified in FEG-SEM micrograph obtained via backscattering electrons (Fig. 4b) and in elemental 2D mapping obtained via energy dispersive X-ray (EDX) in TEM images (Fig. 5a).

The carbonation mechanism was assumed similar to carbonation mechanism for pure calcite (reactions (3)–(6)). However, the nucleation-growth of calcite was perturbed by unstable seleno-L-cystine. Herein, axial elongation and an atypical aggrega-

tion/agglomeration of calcite particles, leading to star and shell-like forms were observed (Fig. 6). The selenium (oxidation state = –2) contained in the seleno-L-cystine compound was oxidised to form elemental selenium (Se<sup>0</sup>) nanoparticles during carbonation process. These results are in agreement to a previous study, where the synthetic portlandite particles were used as calcium source [4]. Globally, the red composite consisted predominantly of spherical, amorphous nanoparticles of elemental selenium (<500 nm) deposited on the calcite matrix. Here, the calcite was constituted by nano- to microrhomboidal crystals (<2 μm) and micrometric agglomerates and/or aggregates (<5 μm). Most sophisticated analytic techniques such as orbitrap mass spectrometry, X-ray absorption spectroscopy (XAS) and high resolution transmission electron microscopy will be required to elucidate two unsolved questions (1) what is the nanometric organization and crystallinity on/in atypical aggregates/agglomerates? and (2) what is the oxida-

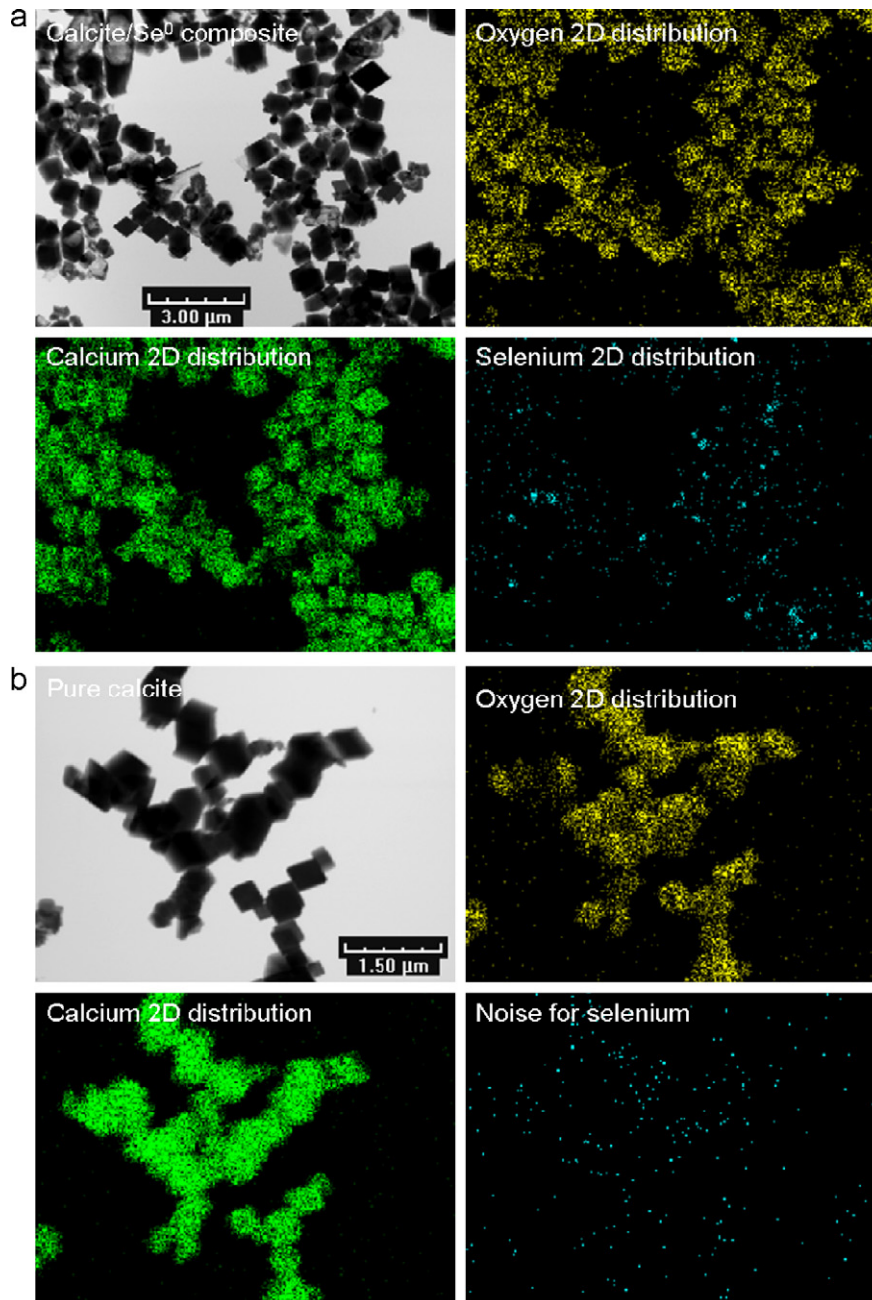
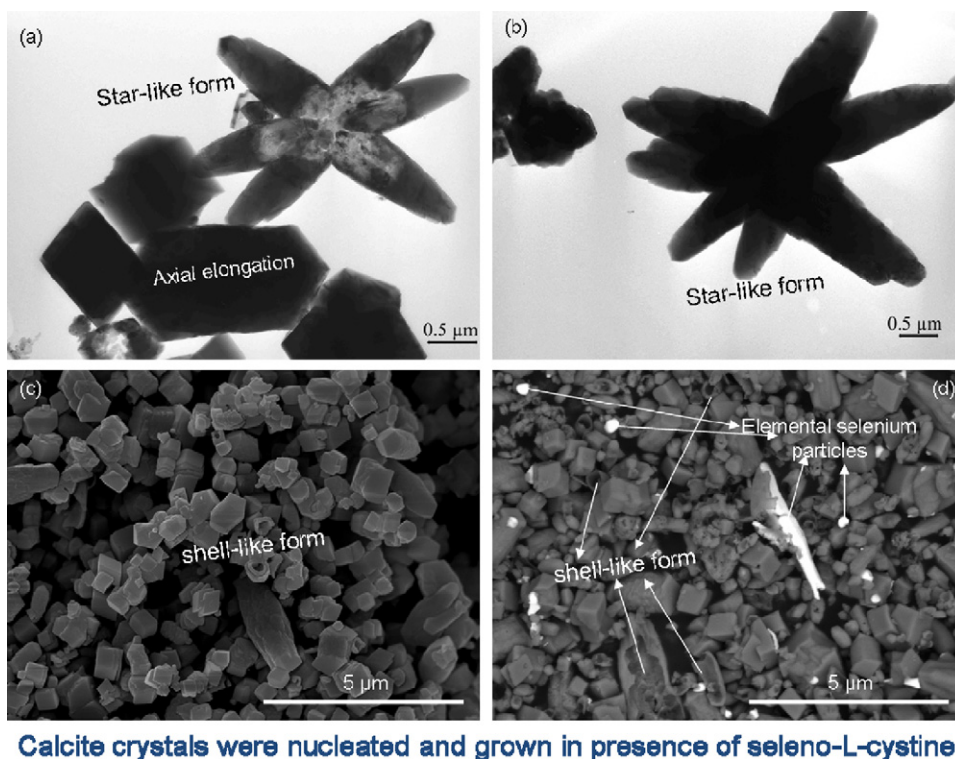


Fig. 5. Elemental 2D mapping by energy dispersive X-ray in TEM images for (a) calcite/Se<sup>0</sup> red composite and (b) pure calcite.





**Fig. 6.** Calcite/Se<sup>0</sup> red composite produced in a triphasic gas–liquid–solid system under hydrothermal conditions (90 °C and 90 bar). (a and b) TEM micrographs showing the axial elongation and star-like forms for calcite [4]. (c) and (d) FEG-SEM micrographs showing shell-like morphology for calcite and elemental selenium particles (white areas on (d) image).

tive chemical fragmentation of seleno-L-cystine during carbonation process?

In the practice, we think that the synthesized carbonate–selenium composite could be used as pigment and as dietary supplement ([4,34,35] and references therein). As mentioned above, the non-reacted solid waste separated prior to synthesis of calcite–selenium composite could be used as component in construction materials, aerogels fabrication, etc. (e.g. [32,33]). The aqueous solutions and residual gases should be recirculated whether this synthesis is extrapolated at the pilot plant or industrial scale.

#### 4. Conclusion

In summary, we proposed a simplified method for co-utilisation of alkaline solid waste and carbon dioxide (CO<sub>2</sub>) to produce pure calcite and calcite/Se<sup>0</sup> red nanocomposite. This has relevant implications on the CO<sub>2</sub> mitigation and recycling of solid waste materials. The nano- to sub-micrometric size of calcite and calcite/Se<sup>0</sup> composite suggest a high potential for industrial and medical applications because the bioavailability of powdered materials is frequently related to particle size. However, a study has reported that there was no significant size effect of red elemental selenium (Nano-Se) from 5 to 200 nm in the induction of glutathione peroxidase (GPx), phospholipid hydroperoxide glutathione peroxidase (PHGPx) and thioredoxin reductase-1 (TrxR-1) in human hepatoma HepG2 cells and the livers of mice [35].

This study is a nice example of feasibility to obtain possible ecological and economical benefits from waste co-utilisation. But, several efforts are still necessary to optimize the synthesis, for example, only about 1.7 g of pure calcite or calcite/Se<sup>0</sup> composite are produced from 1 L of alkaline mother solution in each batch synthesis.

#### Acknowledgements

The authors are grateful to National Center for Scientific Research (CNRS) and University Joseph Fourier, Grenoble (UJF) for providing the financial support.

#### References

- [1] G. Montes-Hernandez, R. Perez-Lopez, F. Renard, J.M. Nieto, L. Charlet, Mineral sequestration of CO<sub>2</sub> by aqueous carbonation of coal combustion fly-ash, *Journal of Hazardous Materials* 161 (2009) 1347–1354.
- [2] G. Montes-Hernandez, F. Renard, N. Geffroy, L. Charlet, J. Pironon, Calcite precipitation from CO<sub>2</sub>–H<sub>2</sub>O–Ca(OH)<sub>2</sub> slurry under high pressure of CO<sub>2</sub>, *Journal of Crystal Growth* 308 (2007) 228–236.
- [3] G. Montes-Hernandez, A. Fernandez-Martinez, L. Charlet, D. Tisserand, F. Renard, Textural properties of synthetic calcite produced by hydrothermal carbonation of calcium hydroxide, *Journal of Crystal Growth* 310 (2008) 2946–2953.
- [4] G. Montes-Hernandez, A. Fernandez-Martinez, L. Charlet, F. Renard, A.C. Scheinost, M. Bueno, Synthesis of a Se<sup>0</sup>/calcite composite using hydrothermal carbonation of Ca(OH)<sub>2</sub> coupled to a complex selenocystine fragmentation, *Crystal Growth and Design* 8 (7) (2008) 2497–2504.
- [5] R. Perez-Lopez, G. Montes-Hernandez, J.M. Nieto, F. Renard, L. Charlet, Carbonation of alkaline paper mill waste to reduce CO<sub>2</sub> greenhouse gas emissions into atmosphere, *Applied Geochemistry* 23 (2008) 2292–2300.
- [6] K.J. Reddy, M. D. Argyle, A. Viswatej, 2008. Capture and mineralization of flue gas carbon dioxide. In: R. Baciocchi, G. Costa, A. Poletini, R. Pomi, (eds.) Conference proceedings of 2nd Accelerated Carbonation for Environmental and Materials Engineering, University of Rome, Rome, Italy, October 1–3, p. 221–228.
- [7] K.S. Lackner, A guide to CO<sub>2</sub> sequestration, *Science* 300 (2003) 1677–1678.
- [8] S.J. Gerdemann, W.K. O'Connor, D. Dahlin, L.R. Penner, H. Rush, Ex-situ aqueous mineral carbonation, *Environmental Science and Technology* 41 (2007) 2587–2593.
- [9] H.H. Teng, P.M. Dove, C.A. Orme, J.J. De Yoreo, Thermodynamics of calcite growth: baseline for understanding biomineral formation, *Science* 282 (1998) 724–727.
- [10] M. Temman, J. Paquette, H. Vali, Mn and Zn incorporation into calcite as a function of chloride aqueous concentration, *Geochimica et Cosmochimica Acta* 64 (2000) 2417–2430.
- [11] W. Stumm, J.J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed., John Wiley & Sons, 1995, 1024pp.

- [12] J. Paquette, R.J. Reeder, Relationship between surface structure, growth mechanism, and trace element incorporation in calcite, *Geochimica et Cosmochimica Acta* 59 (1995) 735–749.
- [13] D.T. Beruto, R. Botter, Liquid-like H<sub>2</sub>O adsorption layers to catalyze the Ca(OH)<sub>2</sub>/CO<sub>2</sub> solid–gas reaction and to form a non-protective solid product layer at 20 °C, *Journal of the European Ceramic Society* 20 (2000) 479–503.
- [14] G. Montes-Hernandez, A. Pommerol, F. Renard, P. Beck, E. Quirico, O. Brissaud, In-situ kinetic measurements of gas–solid carbonation of Ca(OH)<sub>2</sub> by using an infrared microscope coupled to a reaction cell, *Chemical Engineering Journal* 161 (2010) 250–256.
- [15] C. Gauer, W. Heschel, Doped lithium orthosilicate for absorption of carbon dioxide, *Journal of Materials Science* 41 (2006) 2405–2409.
- [16] K. Essaki, M. Kato, H. Uemoto, Influence of temperature and CO<sub>2</sub> concentration on the CO<sub>2</sub> absorption properties of lithium silicates pellets, *Journal of Materials Science* 21 (2005) 5017–5019.
- [17] O.L. Shtepenko, C.D. Hills, N.J. Coleman, A. Brough, Characterization and preliminary assessment of a sorbent produced by accelerated mineral carbonation, *Environmental Science and Technology* 39 (2005) 345–354.
- [18] S. Stendardo, P.U. Foscolo, Carbon dioxide capture with dolomite: a model for gas–solid reaction within the grains of a particulate sorbent, *Chemical Engineering Science* 64 (2009) 2343–2352.
- [19] P. Sun, J.R. Grace, C.J. Lim, E.J. Anthony, A discrete-pore-size-distribution-based gas–solid model and its application to the CaO + CO<sub>2</sub> reaction, *Chemical Engineering Science* 63 (2008) 57–70.
- [20] W. Seifritz, CO<sub>2</sub> disposal by means of silicates, *Nature* 345 (1990) 486.
- [21] S. Bachu, Sequestration of CO<sub>2</sub> in geological media: criteria and approach for site selection in response to climate change, *Energy Conversion and Management* 41 (2000) 953–970.
- [22] S.J. Friedmann, Geological carbon dioxide sequestration, *Elements* 3 (2007) 179–184.
- [23] G. Costa, R. Baciocchi, A. Poletti, R. Pomi, C.D. Hills, P.J. Carey, Current status and perspectives of accelerated carbonation processes on municipal waste combustion residues, *Environmental Monitoring and Assessment* 135 (2007) 55–75.
- [24] E. Rendek, G. Ducom, P. Germain, Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash, *Journal of Hazardous Materials* B128 (2006) 73–79.
- [25] Y. Soong, D.L. Fauth, B.H. Howard, J.R. Jones, D.K. Harrinson, A.L. Goodman, M.L. Gray, E.A. Frommell, CO<sub>2</sub> sequestration with brine solution and fly ashes, *Energy Conversion and Management* 47 (2006) 1676–1685.
- [26] G. Montes-Hernandez, N. Concha-Lozano, F. Renard, E. Quirico, Removal of oxyanions from synthetic wastewater via carbonation process of calcium hydroxide: applied and fundamental aspects, *Journal of Hazardous Materials* 166 (2009) 788–795.
- [27] M. Lim, G.C. Han, J.W. Ahn, K.S. You, Environmental remediation and conversion of carbon dioxide (CO<sub>2</sub>) into useful green products by accelerated carbonation technology, *International Journal of Environmental Research and Public Health* 7 (2010) 203–228.
- [28] M. Uibu, O. Velts, R. Kuusik, Developments in CO<sub>2</sub> mineral carbonation of oil shale ash, *Journal of Hazardous Materials* 174 (2010) 209–214.
- [29] H.S. Lee, T.H. Ha, K. Kim, Fabrication of unusually stable amorphous calcium carbonate in an ethanol medium, *Materials Chemistry and Physics* 93 (2005) 376–382.
- [30] C. Domingo, J. Garcia-Carmona, E. Loste, A. Fanovich, J. Fraile, J. Gomez-Morales, Control of calcium carbonate morphology by precipitation in compressed and supercritical carbon dioxide media, *Journal of Crystal Growth* 271 (2004) 268–273.
- [31] A.M. Lopez-Periago, R. Pacciani, C. Garcia-Gonzalez, L.F. Vega, C. Domingo, A breakthrough technique for the preparation of high-yield precipitated calcium carbonate, *Journal of Supercritical Fluids* 52 (2010) 298–305.
- [32] O.E. Manz, Worldwide production of coal ash and utilization in concrete and other products, *Fuel* 76 (1997) 691–696.
- [33] 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 flay ash at pilot plant scale. Examples of potential applications, *Fuel* 80 (2001) 857–865.
- [34] G. Montes-Hernandez, L. Charlet, F. Renard, New selenium containing composites, their use and a process for preparing the same, Patent: WO 2009/112465 A1.
- [35] J. Zhang, H. Wang, Y. Bao, L. Zhang, Nano red elemental selenium has no size effect in the induction of seleno-enzymes in both cultured cells and mice, *Life Science* 75 (2004) 237–244.