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Direct mineral carbonation of new materials for CO_2 sequestration

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Abstract

This work presents results about the enstatite ($MgSiO_3$) carbonation reaction; which synthesized by starting from the calcination the rough clay coming from a tertiary formation located at the East of the average Atlas (Morocco) at 1000°C. The carbonate of the magnesium ($MgCO_3$) formed after the tender of the sample to a flow of pure CO_2 during 15 min in the normal conditions of temperature and pressure. The appearance of magnesite ($MgCO_3$) in diffraction of x-rays is justified by the dissolution of the enstatite was caused by the current of carbonic gas; this indicates that the mineral was reacted to form carbonate of magnesium (magnesite), The analysis of the Raman one was used to supplement the results of XRD, A peak can be observed in the curves (TGA and DTA) between 530 °C and 600 °C which is in connection with the decomposition of carbonate; the actual loss of the weight is roughly 18%.

1. Introduction

The increasing factious carbon dioxide emission, mainly was caused by fossil fuel combustion, has led to concerns about global warming. Reduction of carbon dioxide by mineral carbonation has been proposed as one of the most promising options. There are many effective starting materials and reaction routes for mineral carbonation. Recently, many studies have focused on the aqueous reaction of carbon dioxide with the alkaline earth minerals such as serpentine, olivine and wollastonite [5].

The rapid increase in the carbon dioxide (CO_2) emissions from industrial sources is considered as one of the main causes for the Earth's changing climate (IPCC, 2007). The reduction of CO_2 emissions can be realized by improving energy efficiency, implementing renewable carbon-free energy sources, and developing carbon capture, utilization and storage (CCUS) technologies. The use of world energy will continue to increase (IEA, 2010), and thus, CCUS could provide an immediate solution to carbon [1].

Comparing with other options of storage of CO_2, one proposed the mineral carbonation like promising technology. Mineral sequestration is a chemical route of sequestration to produce the stable ore thermodynamically. Consequently, the mineral carbonation can be imprisoned in a permanent way without need for monitoring after storage once CO_2 was fixed [2]. Moreover, this process imitates the normal disintegration of the rocks above geological time. The state of energy of a mineral carbonation is 60 to 180 kJ/mol lower than CO_2 (400 kJ/mol). Consequently, this process is the exothermic reaction which can make the consumption of energy and the costs of sequestration carbon reduced. However the mineral carbonation has a serious disadvantage which requires the great numbers of ores of Ca/Mg to sequester a great number of emitted CO_2 of the fossile fuel combustion, although sufficient the suitable ores is available on a total scale [3].

The basic concept of the mineral carbonation is to imitate the normal processes of disintegration in which the Calcium or the magnesium containing of the ores is converted into magnesium or calcium carbonates:

$$(Ca, Mg)SiO_3 \ + \ CO_2 \quad \rightarrow M_gCO_3 + SiO_2 \qquad \text{Eq.I}$$

It should be noted that this diagrammatic type of assessment can be written with any mineral pole containing of the cations (Mg^{2+}, Fe^{2+}, Ca^{2+}, Na^+ etc….). In contexts of high temperature (metamorphism), these processes can be considered by direct interaction of the fluid rich in CO_2 with the solids. But in general, and systematically at low temperature, the mechanism implies an aqueous phase according to two stages. The first stage acts of the production of ions in water (Eq.II), and the second relates to the precipitation of the carbonates (Eq.III):

$$MS_iO_3 + 2CO_2 + H_2O \leftrightarrow M^{2+} + \mathrm{H}CO_3^- + S_iO_2 \qquad \text{Eq.II}$$

$$M^{2+} + 2\mathrm{H}CO_3^- + H_2O \leftrightarrow \mathrm{M}CO_3 + CO_2 + H_2O \qquad \text{Eq.III}$$

The sum of the assessments of the reaction (II) and (III) led to the equation (I). It should be noted that the precipitation of carbonates is unfavourable with respect to the CO_2 trapping as it is schematized in the reaction (III). On the other hand it would be dangerous, with respect to qualities of stability and durability required in the mineral trapping, to consider the reaction (II), like the only interesting option. In this case CO_2 is well, in this case ,stored in the form of ions HCO_3^- but a re-equilibration of the aqueous fluid with the atmosphere is done on scales of times generally much faster than in the mineral trapping (lower than 100000 years) [4].

In this respect, the storage of the CO_2 excess by mineral trapping according to the assessment (I) seems a “natural” way. Moreover, this mineral trapping would present the maximum guarantees in terms of safety of storage and durability on the long run. The typical time of residence of a carbonate on the surface of the ground was estimated at 30 million years [4].

An important problem is that of the scales of time, one is accustomed to consider these natural processes of mineral trappings over durations about several tens of thousands even of million years [4, 5, 6,].

A major scientific stake, considering the current problem, is the comprehension of these geological processes on scales of time much shorter, the control of the possible factors of their acceleration, in particular in answer to high CO_2 flows of anthropic origin.

The mineral trapping can also be under consideration by CO_2 reaction with industrial sources of materials but in this work, we will be restricted to the mineral trapping in contexts of geological storage, by focusing us on the particular case of the silicated magnesium compounds (enstatite).

Several methods, using various processes and carried out in situ or in industrial environment, were suggested to carry out the carbonation [5, 6].

There exist two big families of processes of mineral sequestration of CO_2, the direct and indirect processes. Upstream of the stages of carbonation of the studies are realized on the pretreatment of the carbonatable materials with the aim of increasing the output of the reaction of carbonation [7, 8].

In order to improve the output of the process of carbonation, the carbonatable materials can undergo a pretreatment. The purpose of the pretreatments developed in the literature are principal to increase the specific surface of these compounds, this improves the contact between the carbonatable compound and CO_2. The developed pretreatments are crushing and thermal pretreatment.

2. Experimental details

We have chosen to study the direct carbonation of magnesian silicate more abundant and available than the calcic silicates. The material which one will name “enstatite” in this work is mainly made up of MgSiO3. This material is resulting from a natural material “clay” which comes from a tertiary formation located at the East of the average Atlas. The loam pit is in the province of Missour constitutes in a natural state of 32.46% from MgO and 57.94% of SiO_2.

The starting material “clay” was crushed and filtered to obtain a fraction of 90 μm, there after our material was calcines with 1000°C and activated by MgO with molar fractions $XMgSiO_3=0.66$ and $XMog = 0.34$ the mixture was agitated using a magnetic stirrer until the stabilization of the pH with 11. After filtration, clay is dried during 24 hours with 60 °C. The diffractometry of x-rays (DRX) and electronic scan microscopy (MEB) were carried out to identify the phase MgSiO3 [9]. The experiments of CO_2 fixing in this work proceed in an engine (tri-cone balloon) under agitation. It comprises a container allowing the insulation of the external atmosphere, equipped with a pH-meter allowing the control of the pH lasting the reaction, and contains two bored being used the entry and the exit as CO_2.

2.1 Techniques of instrumental analyses

2.1.1 Diffraction of x-rays

The diffractometer of x-rays used is X' PERT PRO PANALATYCAl equipped with a detector with scintillation X' CeleratorUltrarapide with Beam of radiation Kα (λ = 0,154060 Nm), functioning with the tension 40 Kv and current 30 mA with a copper target. The data was collected between 10° and 80° in 2θ on powder samples.

2.1.2 Electronic scan microscopy

The samples were analyzed by an electron microscope with sweeping (FEI QUANTA 200) equipped with EDX for microanalysis of surface.
A sample of 1 g crushed is dispersed in 40 ml of distilled water, and then injected by successive amounts of the carbonic gas (CO_2) until the stabilization of pH, under atmospheric pressure and room temperature. At the end of experiment, the sample is let rest during 24h then dried and analyzed.

2.1.3 Analysis thermogravimetric and analysis thermal differential.

The simultaneous TG/DTG/DTA analyses were carried out using a Labsys Evo (1F) Setaram apparatus Instrument conditions:
-non-isothermal
-Nitrogen flow atmosphere of 30 ml.min^{-1}
- Alumina crucible.

2.1.2 Raman.

The name of the Ramam apparatus is SENTERRA of Brucker. (Laser of 785 Nm)

3. Resulats and Discussion

The diagrams of x-rays obtained for the sample of clay activated by MgO and calcines with 1000 °C before and after splashing east are presented in the figures 1-a and shows 1-b. The examination of Diffractograms (Figure1-a) watch that the enstatite ($MgSiO_3$), constitutes the Majoritaire phase of clay after activation by MgO and calcination with 1000 °C. The presence of magnesite ($MgCO_3$) in the figure 1-b is justified by the dissolution of the enstatite was caused by the current of carbonic gas; this indicates that the mineral was reacted to form carbonate of magnesium (magnesite).
The analysis of the Raman one was used to supplement the results of XRD, to observe amorphous phases, and to look more closely at the carbonation mechanisms. The magnesite shows the spectrum of Raman most distinctive with the peaks well defined in 209, 331, 738, 1097 and 1410 cm^{-1} (Figure 2-b).The spectrum Raman of the nesquehonite watch of the peaks with 187, 228, 703, 1099, 1419 and 1509 cm^{-1} (Figure 2-b). The formation of magnesite is indicated by the presence of the moderately strong peaks to 209, and 1095 cm^{-1}. The mode of bending of in-plane v4 of the carbonate ion (CO_3^{2-}) is in activity of Raman with 725 cm^{-1} and its asymmetrical peaks extending v3 mode appear with 1430 cm^{-1}.The dominant peak in the Magnesium-carbonate spectra is the symmetrical end right of the group of CO_3^{2-} which varies from 1095 to 1125 cm^{-1} according to the environment of coordination of carbonate. According to the compositions out of carbonate (magnesite, hydromagnesite and nesquehonite), the bands of v1 symmetrical mode extending from CO_3^{2-} were distinctly plac in this margin [1]. The process of drying was followed in an inert atmosphere of nitrogen inside the experimental device. The curves obtained (Figure 3-b) are presented a first great weight loss to approximately 100°C due to the process of dehydration. The second weight loss with approximately 400°C is associated with Mg hydroxylation $(OH)_2$ [11-12-15].

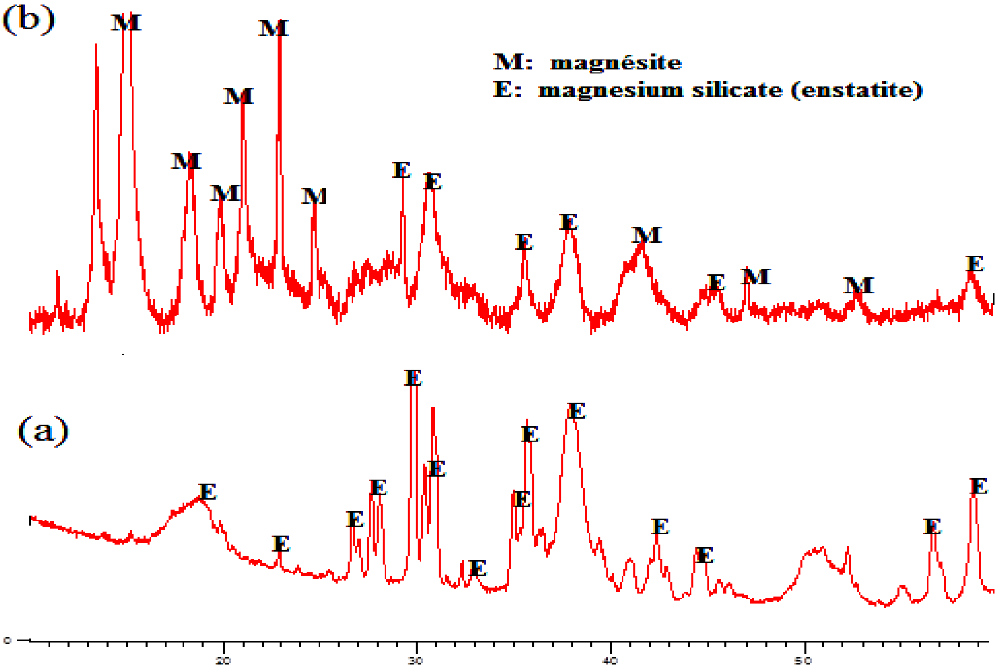

Figure1: Diffractograms of composes before the reaction of the barotage (a) and after the reaction of the carbonation during 15 the minute (b)

It is well-known that experimental conditions like the dimension and the morphology of the sample can affect considerably the rate of the thermal dehydroxylation [12], thus, this reduction in the temperature of dehydroxylation can be due obtained to the high reactive sector of the sample [10]. A peak can be observed in the curves (TGA and DTA) between 530 ºC and 600 ºC which is in connection with the decomposition of carbonate; the actual loss of the weight is roughly 18%. [4].

The study of electronic scan microscopy (Figure 4) makes it possible to check that the sample exposed to CO_2 contains carbonate crystals, the sample of Formed carbonates (magnesite) which appears in the form of crystals rhomboedric[13,14], is to a large extent similar to the results obtained by diffraction of x-rays.

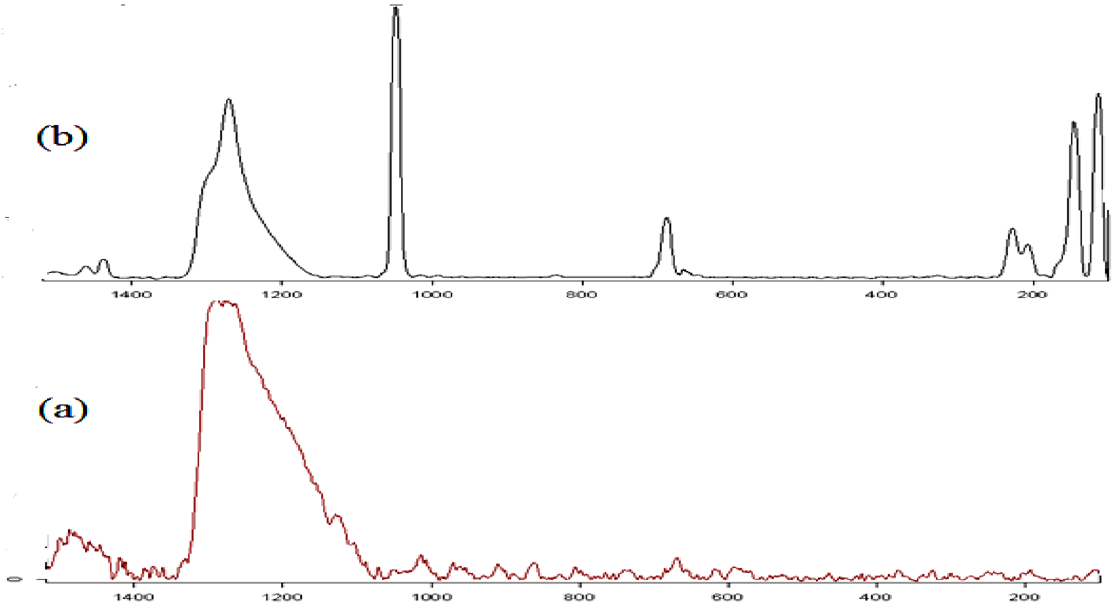

Figure 2: Spectra the Raman one of composes before reaction of splashing (a) and after Reaction of the carbonation during 15 min (b)

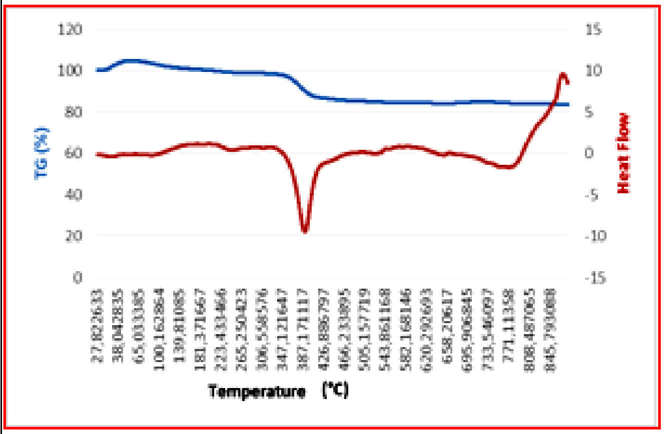	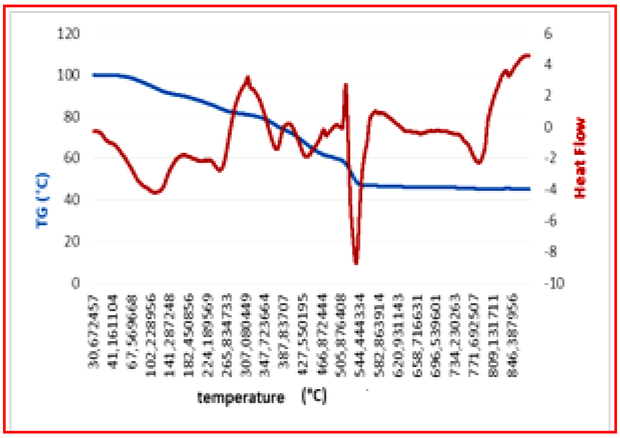
Figure 3-a : curves TGA and DTA of composes before reaction of the carbonation	**Figure 3-b :** curves TGA and DTA of composes after Reaction of the carbonation

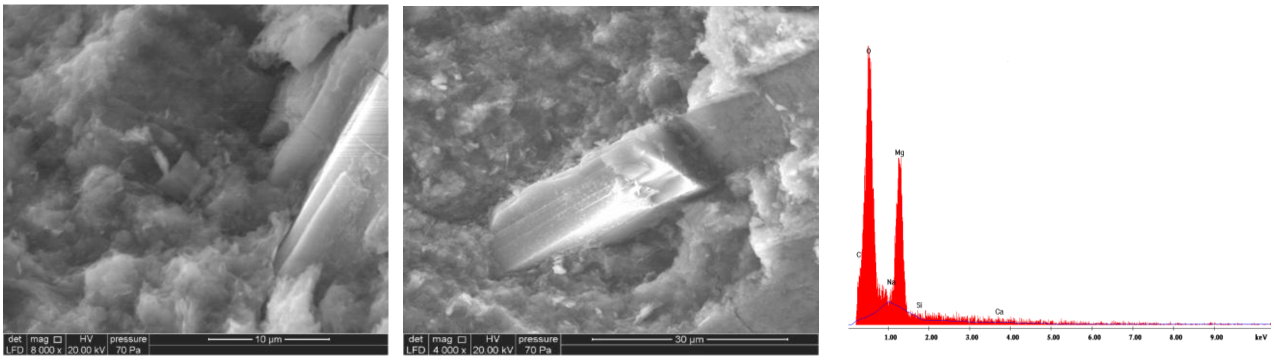

Figure 4: Photographs under the electron microscope with sweeping (MEB) of the sample after reaction of the carbonation during 15 min of reaction with CO2

Conclusions

1 - The treatment allows the synthesis of the enstatite ($MgSiO_3$), which has an important capacity of CO_2 fixing higher than that of rough clay.
2 - The activation of the enstatite by a MgO solution has made it possible to improve the formation of magnesite during the reaction of splashing.
3 - The reaction is effective in only 15min of flow of gas to the room temperature and under the atmospheric pressure.
4 - These characteristics are very effective for the fixing and the elimination of CO_2.

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