



## CO<sub>2</sub> sequestration on new materials

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### Abstract

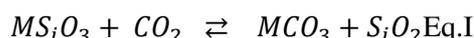
This work presents results about the enstatite (MgSiO<sub>3</sub>) carbonation reaction, the later is synthesized starting from the calcination with 1000 °C of the rough clay which comes from a tertiary formation located at the East of the average Atlas (Morocco). The carbonate of the magnesium (MgCO<sub>3</sub>) formed after the tender of the sample to a flow of pure CO<sub>2</sub> during 15 min in the normal conditions of temperature and pressure. It was evaluated by electronic scan microscopy, diffraction of x-rays, analysis of both thermogravimetric and thermal differential. These three techniques of analyse chemical-physics confirm the CO<sub>2</sub> collection efficiency of our material.

**Keywords:** carbonation; enstatite; calcinations; material.

### 1. Introduction

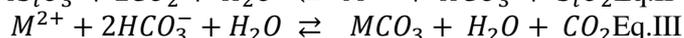
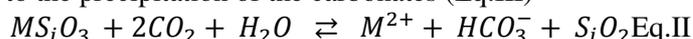
Currently, the many techniques of capture and storage of CO<sub>2</sub> studied aims to limit the gas emissions to greenhouse effect. These techniques still require significant developments to prove their effectiveness. Contrary to the technological solutions most mature, the mineral carbonation is still at a stage of upstream of its development. This solution to limit the anthropogenic emissions of CO<sub>2</sub> has the advantage of offering a mode of capture and perennial storage of CO<sub>2</sub>. It also makes it possible to quickly convert silicates natural or anthropogenic into carbonates under environmental conditions of temperature and pressure. The mineral reactions of carbonation are exothermic and the formed carbonates are thermodynamically stable.

The mineral CO<sub>2</sub> trapping is an essential natural geodynamic process in the establishment of the thermal and chemical conditions of the surface envelopes of the earth. The essence of oxidized carbon is in the form of solid carbonates, which explains the relatively low CO<sub>2</sub> content in the atmosphere and the pH is close to neutrality for the ocean. The total solid carbon mass on the surface of the earth is equal to 5, 4.10<sup>19</sup> kg including 80% in the form of carbonates and 20% in the form of organic matter [1]. Thus, the exchange between CO<sub>2</sub> and the carbonates solid, primarily via the deterioration of the rocks and the carbonate precipitation by the living organisms in the ocean, are an essential mechanism of regulation of the CO<sub>2</sub> rate in the atmosphere [2]. The total CO<sub>2</sub> flow consumed by the deterioration of the rocks can which that be estimated at 0.25 carbon Gt per annum (0,92 CO<sub>2</sub> Gt), 40% of this flow being related to the deterioration of silicates rich in Na, K, Ca, Mg [3]. actually, the planet having appreciably the same total quantity of carbon, for lack of mineral trapping, its quasi integrality is in the form of CO<sub>2</sub> atmospheric from where a very important greenhouse effect. Schematically, the implied reaction can be written:



M represents a divalent action.

It should be noted that this diagrammatic type of assessment can be written with any mineral pole containing of the cations (Mg<sup>2+</sup>, Fe<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup> etc....). In contexts of high temperature, these processes can be considered by direct interaction of the fluid rich in CO<sub>2</sub> 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). The second relates to the precipitation of the carbonates (Eq.III)



The sum of the assessments of the equations (II) and (III) leads to the equation (I). It should be noted that the precipitation of carbonates is unfavourable with respect to the CO<sub>2</sub> 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<sub>2</sub> is well stored in the form of ions HCO<sub>3</sub><sup>-</sup> 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) [3]. In this respect, the storage of the CO<sub>2</sub> 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 [3]. 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 [4-3-5].

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 is the answer to high CO<sub>2</sub> flows of anthropic origin. The mineral trapping can also be under consideration by CO<sub>2</sub> reaction with industrial sources of materials but in this work, we will be restricted with the mineral trapping in contexts of geological storage, by focusing on the particular case of the silicate magnesium compounds.

Several methods, using various processes and carried out in situ or in industrial environment, was suggested to carry out the carbonation [5-6]. There exist two big families of processes of mineral sequestration of CO<sub>2</sub> via the direct and indirect processes. Upstream of the stages of carbonation they of the studies are realized on the pretreatment of carbonate materials with an aim of increasing the yield of the reaction of carbonation [7-8].

In order to improve the yield of carbonation, carbonate materials can undergo a pretreatment. The purposes of the pre-treatment developed in the literature are principal to increase the specific surface of these compounds. This improves the contact between carbonate materials and CO<sub>2</sub>. The developed pretreatments are crushing and thermal pretreatment. The thermal pretreatment of material with 1000 °C makes it possible to eliminate the water contained in materials, the organic matter and to increase specific surfaces of materials. Table 1 shows the influence of the heat treatment on the yield of the reaction. This last is not improved in a notable way when the temperature reaches 400 °C, but starting from this temperature it increases progressively up to 82% to 800 °C.

**Table.1** Influence thermal pretreatment on the yield of the reaction of carbonation of serpentine under the operating conditions of the aqueous direct processes basic [9].

| Thermal pretreatment, temperature of heating T (°C), 2h | 200 | 400 | 640 | 900 |
|---|-----|-----|-----|-----|
| Yield (%)   | 20  | 20  | 79  | 82  |

## 2. Material and methods

We chose to study the direct carbonation of magnesium silicates more abundant and available than the calcic silicates. The material which is named enstatite in this work is mainly MgSiO<sub>3</sub>. This material is resulting from natural material clay which comes from a tertiary formation located in the East of the average Atlas of Morocco. The loam pit is in the province of Missouri constitutes in a natural state of 32.46% from MgO and 57.94% of SiO<sub>2</sub>.

The starting material “clay” was crushed and sifted to obtain a fraction of 125 µm and thereafter our material was activated by a NaOH solution (1M) with a liquid solid ratio of 1/5 for 30 min. the suspension was agitated using a magnetic stirrer until the stabilization of the pH at 12.97. After filtration, clay is dried during 24h at 60 °C then calcined at 1000°C during 3h for the decomposition of the organic matter and the improvement of the crystal structure of the enstatite (MgSiO<sub>3</sub>) which is active in the reaction of CO<sub>2</sub> carbonation. The X-rays diffractometry (XRD) and scanning electronic microscopy (SEM) were carried to identify the phase MgSiO<sub>3</sub> [10]. The experiments of CO<sub>2</sub> fixing in this work proceed in an engine (tri-cone balloon) under agitation. It comprises a container that allows the insulation of the external atmosphere equipped with a pH-meter allowing the control of the pH during the reaction, and contains two boredone for the entry and the other for exit of CO<sub>2</sub>.

### 2.1 Techniques of instrumental analyses

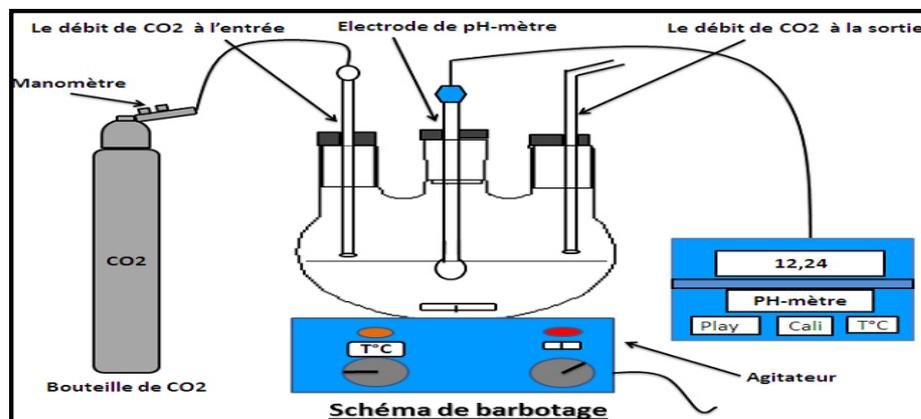
#### 2.1.1 Diffraction of x-rays

The diffractometer of x-rays used is X' PERT PRO PANALATYCAI equipped with a detector with scintillation X' Celerator Ultrarapide 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 were 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<sub>2</sub>) 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.



**Fig1:** experimental device of the tests of CO<sub>2</sub> carbonation.

### 2.1.3 Analysis thermogravimetric and analysis thermal differential.

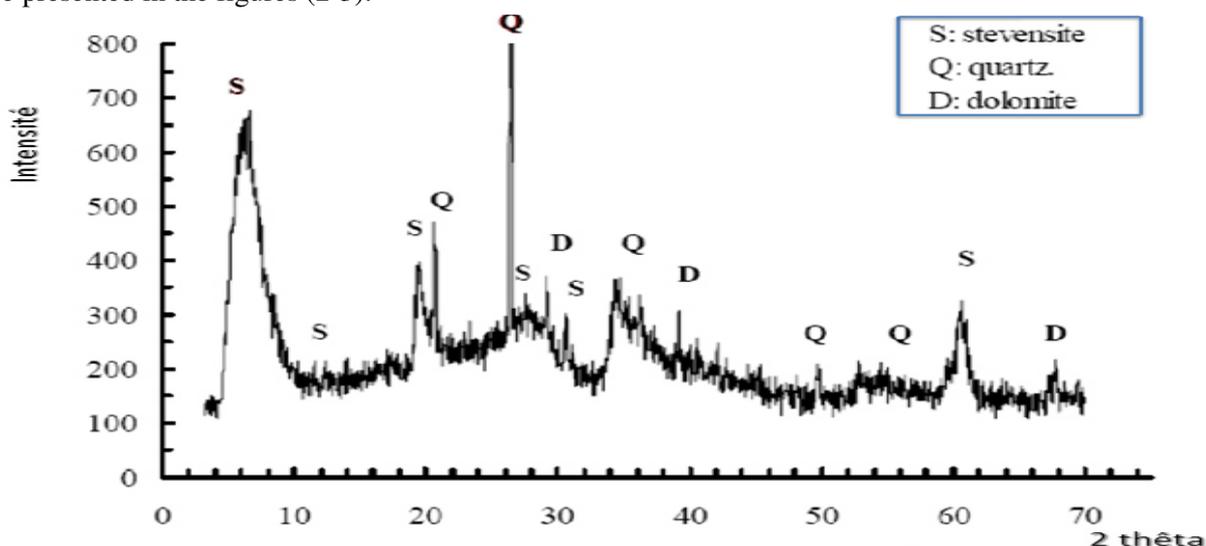
The simultaneous TG/DTG/DTA analyses were carried out using a Labsys Evo (1F) Setaram apparatus. Instrument conditions:

- non-isothermal mode
- Nitrogen flow atmosphere of 30 ml.min<sup>-1</sup>
- Alumina crucible.

## 3. Results and discussions

### 3-1-Characterization of materials before splashing

The diagrams of x-rays obtained from the samples of natural clay and clay activated by NaOH calcined at 1000 °C are presented in the figures (2-3).



**Fig 2:** Diffractograms of clay Rough.

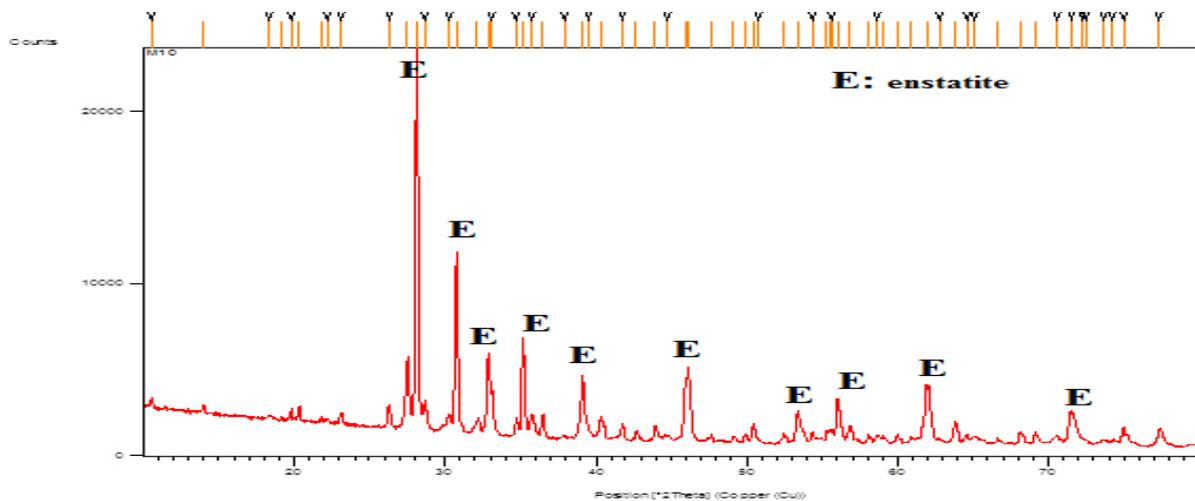
The examination of this diffractograms (Figure2) observed that the stevensite, constitutes the majority argillaceous phase of clay with the presence of free silica in the form of quartz and dolomite in small quantity. The examination of these diffractograms (Fig3) observed that the enstatite (MgSiO<sub>3</sub>) constitutes the majority phase of clay after the activation by basic solution and calcination at 1000 °C.

### 3.2 Result of Mineral Test of Carbonation

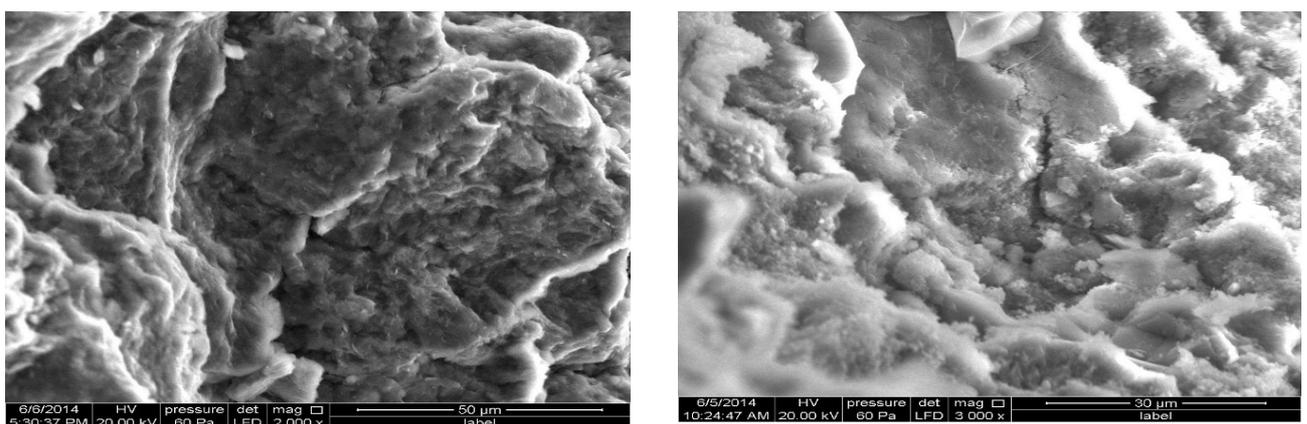
In order to examine the capacity of the CO<sub>2</sub> sequestration, the sample was characterized by analysing XRD to identify the peaks correspond to MgCO<sub>3</sub> (fig 5). The appearance of this last phase is justified by dissolution of the enstatite caused by the current of carbonic gas; which indicates that the mineral was reacted to form carbonate of magnesium (magnesite). For this reason the percentage of carbonate was calculated by analysis of the thermogravimetric TGA-DTA. figure 6 which the loss of the weight of the sample represents a peak observed in the curves (TGA and DTA) between 530 °C and 600 °C indicating the decomposition of carbonate. The real loss of the weight is approximately 10% [1].

### 3.2 Mechanism of the reaction of carbonation

Kojima et al. [11] reported that the reaction did not occur between gas CO<sub>2</sub> and the material silicated (olivine) under atmospheric pressure at 515 K. On the other hand, Tanner and Al [12] found the carbonation of the rocks occurs in the presence of steam under 1-3 kbar at 500-850 °C, which explains why water is an essential component in the reaction of carbonation. The possible mechanism is proposed as follows: Firstly when water absorbs CO<sub>2</sub> above the aqueous phase, the aqueous phase becomes acid with the following species which exists simultaneously.

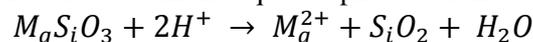


**Fig 3:** Diffractograms of clay activated by NaOH and calcined at 1000 °C

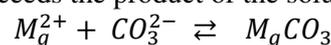


**Fig 4:** SEM images of natural clay

The magnesium contained in the enstatite dissolves in the aqueous phase as follows:



Finally, the ions of magnesium react with the ions of carbonate to form MgCO<sub>3</sub> precipitate when the ionic product of Mg<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> as follows exceeds the product of the solubility of MgCO<sub>3</sub>:



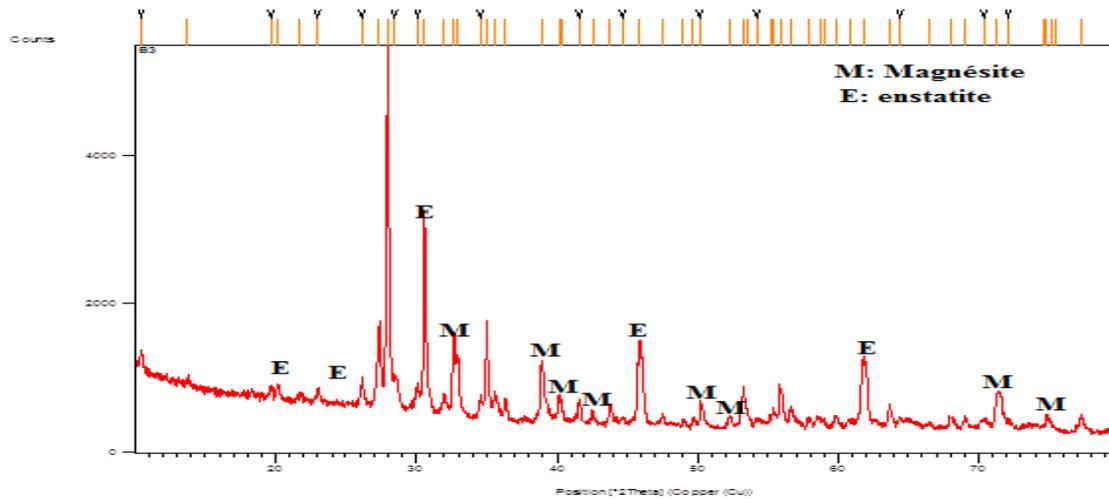


Fig5: Diffractograms of the enstatite after carbonation

The study of electronic scan microscopy makes it possible to check that the sample exposed to CO<sub>2</sub> contains carbonate crystals. The material formed of carbonates (magnésite) appears in the form of rhomboedral crystal structure, which is in a perfect agreement with the results obtained by diffraction of x-rays.

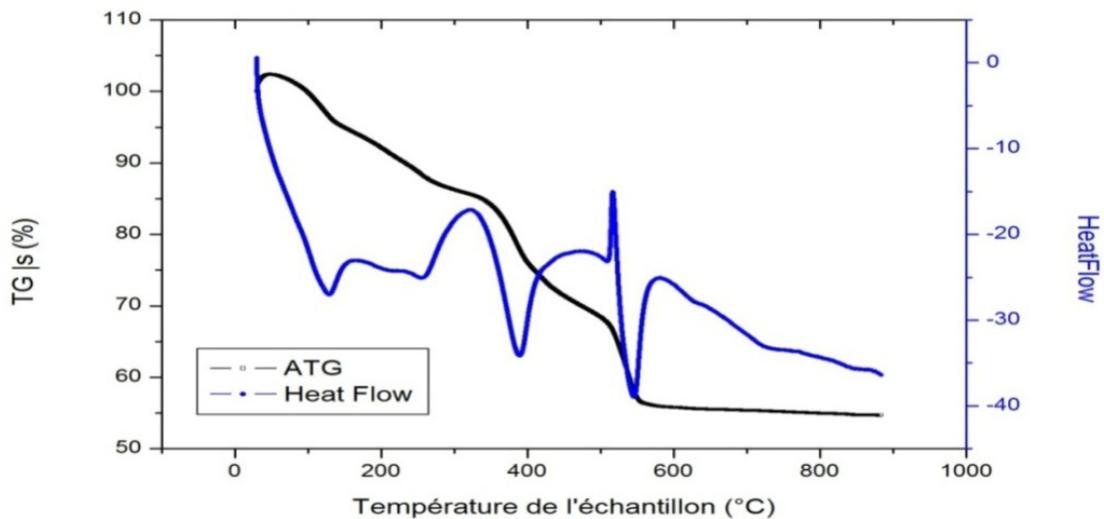


Fig 6: Curve TGA and DTA of composed after carbonation

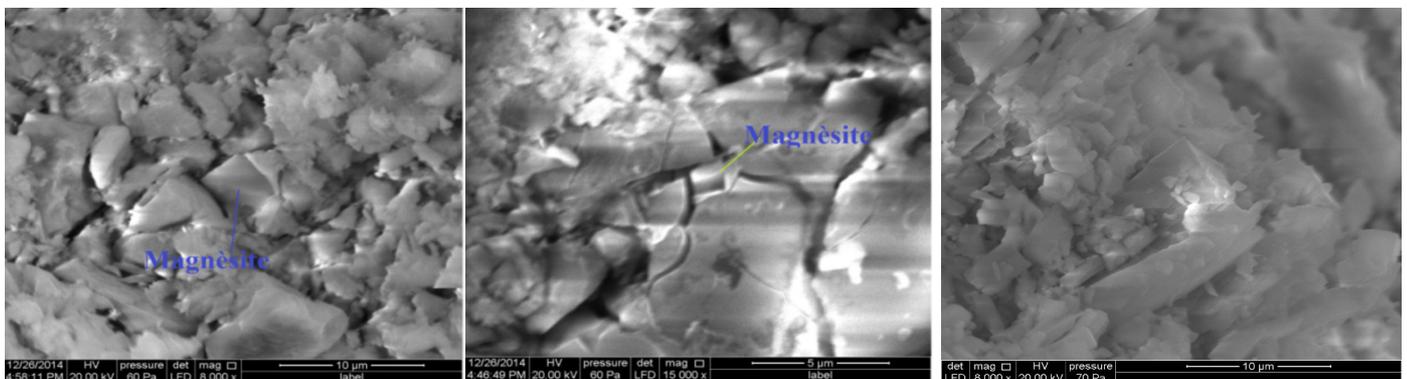


Fig 7: SEM image of the sample after reaction of the carbonation

## Conclusion

- 1 - The treatment allows the synthesis of the enstatite ( $\text{MgSiO}_3$ ), which has an important capacity of  $\text{CO}_2$  fixing higher than that of rough clay.
- 2 - The activation of the enstatite by a NaOH 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  $\text{CO}_2$ .

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