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## Sequestration of carbon dioxide in commercial calcium oxide packings with inclusions of nano-sized calcium oxide near ambient temperatures

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### ABSTRACT

Calcium Oxide which has high sorption capacity for carbon dioxide and therefore has been used as a sorbent for carbon dioxide. In this study the effect of inclusion of nano calcium oxide in beds of micro-sized calcium oxide is studied. Nano calcium oxide of average pore size of 100nm is mixed with micro-sized calcium oxide (20  $\mu\text{m}$ ) and the mixture of calcium oxide was reacted with carbon dioxide at 30°C (near ambient temperature). It was observed that the rates of reaction decreased when particle size was reduced from micro to nano. It was also observed that the micro particles had a steep drop in the rate with concentration of Carbon dioxide which could be attributed to surface reactions in micro particles thus limiting approach of carbon dioxide to interior pores. The rates of absorption of 33.33% and 66.7% nano mixes were observed to be lower than 100% nano packings which could be attributed to filling up of micro pores of the micro-particle packings by nano particles requiring carbon dioxide to penetrate by diffusion through nano pores. These compositions were observed to represent approximately the voidage fraction (42%) of the micro-sized calcium carbonate indicating low effectiveness factors and involvement of Knudsen diffusional effects.

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### KEYWORDS

Absorption;  
Carbon dioxide;  
Calcium oxide;  
Rate of reaction.

### INTRODUCTION

Calcium oxides (CaO) is an appropriate carbon dioxide (CO<sub>2</sub>) sorbent since it fulfilled a number of properties like high sorption capacity (higher than 6 mol/kg of sorbent), long life-time, fast sorption/ desorption kinetics and good mechanical strength<sup>[1]</sup>.

Carbonation reaction of calcium oxide by carbon dioxide is a kind of non-catalytic gas solid reaction<sup>[2]</sup>. The kinetics of the CaO + CO<sub>2</sub> reaction are explained

by a gas-solid reaction model, in which the reaction rates are controlled by gas mass transfer through the porous CaO, the CO<sub>2</sub>-CaO surface interactions, and the diffusion of CO<sub>2</sub> through calcium carbonate (CaCO<sub>3</sub>). It can be represented by chemical reaction shown below:



However, in the presence of moisture the following reaction tend to occur.

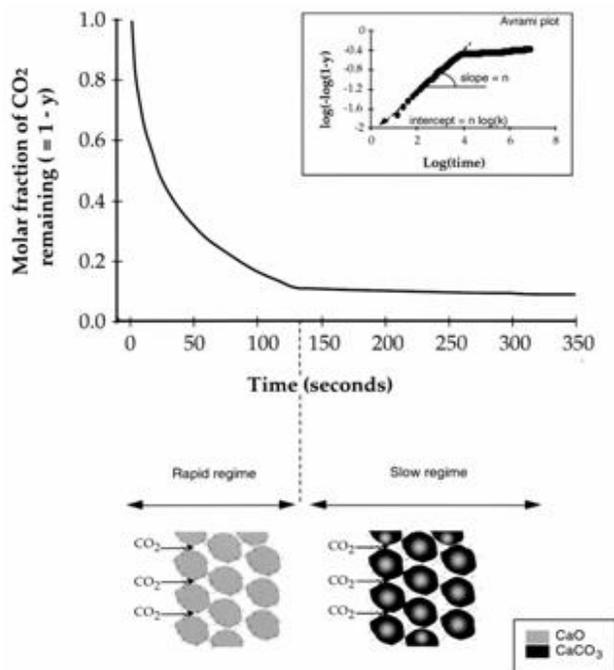


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Reaction (2) is usually followed by a spontaneous carbonation of calcium hydroxide suspension.



The succession of process  $\text{CO}_2 + \text{CaO}$  solid is illustrated in Figure 1.



**Figure 1 : Illustration of reaction and rate of reaction of  $\text{CO}_2$  with  $\text{CaO}$**

During the initial reaction phase surface of  $\text{CaO}$ , a very short kinetically-controlled carbonation occurs (first stage) followed by a mixed regime which is control by the kinetics and  $\text{CO}_2$  diffusion through the carbonate layer. When the carbonate layer reaches a critical thickness, the filling of the voids is finished. The carbonation is entering second stage. This new scale of diffusion is responsible for the drastic decrease of the rate of carbonation<sup>[4-6]</sup>.

### Fast surface chemical reaction stage

Initially, the  $\text{CO}_2$  reacts with the surface of the  $\text{CaO}$  solid to yield a thin film of  $\text{CaCO}_3$  coating the calcium oxide nano-crystallites. The initial fast regime of  $\text{CO}_2$  consumption could correspond to surface reaction and gas mass transfer. During the initial reaction stage, the  $\text{CaO}$  carbonation rate was very high owing to relatively low resistance of  $\text{CO}_2$  diffusion through various pores in porous  $\text{CaO}$  (easy accessibility of the  $\text{CaO}$  reaction surface for  $\text{CO}_2$ ) and sufficient reaction surfaces available

to the reacting gas  $\text{CO}_2$ . The fast stage of reaction is controlled by the  $\text{CO}_2$ - $\text{CaO}$  surface interaction and the diffusion of  $\text{CO}_2$  through the porous network of  $\text{CaO}$ <sup>[7]</sup>. During this stage, the reaction is concern only the filling of the small pores in the grains<sup>[2,3]</sup>. The transition from first stage to second stage occurs when the volume available in the small pores is filled by the  $\text{CaCO}_3$ .

### Slow diffusion control stage

Following the initial stage, a compact layer of product  $\text{CaCO}_3$  is formed and developed on the outer region of a  $\text{CaO}$  particle. The gas has to diffuse though this  $\text{CaCO}_3$  coating to react the  $\text{CaO}$  in the crystallites interior. The rate of reaction will decrease due to the growth of a compact layer of  $\text{CaCO}_3$  as time progresses. During this stage, the reaction is controlled by  $\text{CO}_2$  diffuse through the product on the surface of  $\text{CaO}$ <sup>[5]</sup>. This diffusion control leads to decreasing reaction rates as time progresses. The reaction will stopped when most of the pores had been filled with a layer of product with a certain thickness or the outer surface of the grains had reacted and the internal pores had filled<sup>[3]</sup>. During this stage, the factors that determine the kinetics of  $\text{CaCO}_3$  formation are: (i)  $\text{CO}_2$  pressure; (ii) temperature of the  $\text{CaO}$ ; (iii) grain size of  $\text{CaO}$ ; (iv) thickness of the  $\text{CaCO}_3$ <sup>[5]</sup>.

## EXPERIMENTAL

### Materials

The chemical/raw materials used in this experiment include nano sized calcium oxide( $\text{CaO}$ ) in powder form which has an average particles size of 100nm of 99% purity (Aldrich). Micro-sized calcium oxide( $\text{CaO}$ ) powder with an average particle size of 20  $\mu\text{m}$  was prepared by calcining precipitated calcium carbonate of 99+% purity (Acros organics) until the weight loss achieved stoichiometric proportions. Calcination was carried out in a furnace at 600°C for 5 hours. The mixture of gas with 50% carbon dioxide and 50% nitrogen gas was used as reactant gas.

### Experiment

Nano size  $\text{CaO}$  and micro-sized size  $\text{CaO}$  were mixed according to the desired composition as indicated below. The composition of the powder mixture selected were 100%, 66.67%, 33.33% and 0% nano size  $\text{CaO}$

powder by weight. The mixture was well mixed and placed in a the reactor enclosed in a vertical furnace. The experiment was conducted at room temperature (30°C). Initially gas with 50% CO<sub>2</sub> and 50% N<sub>2</sub> was used for purging the reactor to replace the gas inside the reactor with CO<sub>2</sub> and N<sub>2</sub>. After purging out the gas impurities in the reactor, the pressure of reactor was increase to 1.8 bar by flowing in the gas with composition of 50% CO<sub>2</sub> and 50% N<sub>2</sub> and leak tests were carried out. The pressure drop was recorded every 5-10 minutes.

## RESULTS AND DISCUSSION

Figure 2 shows rates of absorption of carbon dioxide on the mixtures of calcium oxide. Nearly all the curves showed an increase of the rate with increase of concentration of carbon dioxide. The rates of absorption for 100% nano calcium oxide were observed to be higher than the 0% and 33.3% and 66.7% of nano CaO mixes for a given concentration of carbon dioxide. The drop of reaction rate with increase of nano content could be attributed to the effect of pore filling by nano particles in beds of micro material thereby needing increased control by diffusion due to void filling.. The void fraction of beds comprising of the 100% commercial (micro sized particles) and 100% nano sized bed were measured to be 40 to 42%. The beds with 33% to 67% compositions of nano particles lead to the void fractions of 0.15 to 0.2 indicating filling of voids of the micro sized bed thereby requiring pore diffusion attributing to the reduction of absorption rate. It could also be observed that the micro sized calcium oxide alone had a faster drop in reaction rate. SEM investigations of the surface of the micro par-

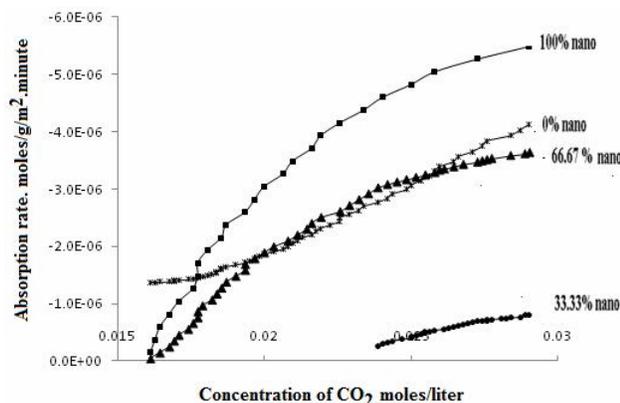


Figure 2 : Absorption rate of CO<sub>2</sub> from gas vs. concentration (30°C)

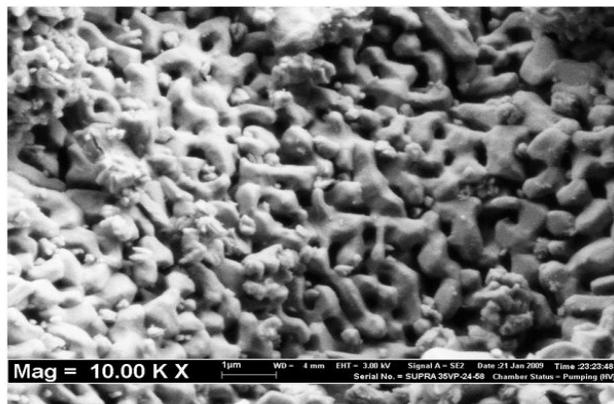


Figure 3 : Sem image of the surface of a micro-particle after reaction

ticles revealed a modification of the surface structure of the micro particles (Figure 3) indicating a possibility of surface coverage by CaCO<sub>3</sub> layers thereby retarding the reaction. The lower rates of absorption of 33.33 % nano calcium oxide filled micro particle bed could be due to the existence of Knudsen type of diffusion in nano pores of the nano packings.

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