Adsorption Of CO_2 To The Hardened Cement Paste

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Abstract: The isothermal adsorption of carbon dioxide to different hardened cement pastes were studied in this paper. The Symmetrical Gravimetric Analyzer (SGA-100 from VTI Corporation) was used for gas adsorption/desorption experiments. Raman spectrum test was done on the cement pastes with Spex-1403 Raman spectroscopy from USA. The results showed that addition of fly ash has great effect on the microstructure of hydrated cement gels and the ability of CO_2 adsorption. CO_2 adsorption to cement pastes can be divided into high increment adsorption step and steady adsorption step. A special reaction was likely happened between CO_2 molecules and cement gel during adsorption, resulting in a transitional carbonization state of cement gel. CO_2 adsorption provides a new method for studying carbonization mechanism of cement pastes.

Key words: isothermal adsorption; carbonation; carbonization mechanism

1. Introduction

Cement-based material is a kind of multiphase porous composite containing solid, liquid and gas. Pore size distribution of cement-based materials ranges from several nm to mm, and the broad pore distribution determines the special adsorption characteristics of the materials. Many processes of cement-based materials, such as water transport, bulk expansion and shrinkage, ion exchange and chemical action, are associated with their adsorption characteristics, so the adsorption is an important characteristic of cement-based materials.

The adsorption of cement-based materials is closely related to their microstructures. Nitrogen and water vapor were two widely used adsorbates for measuring surface area, pore size distribution et al.

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Feldam[1] investigated the surface area and pore size distribution of cement pastes by nitrogen adsorption; Powers[2,3] initially measured the surface area of cement pastes by water vapor, and studied the effects on adsorption caused by water to cement ratio, curing methods and curing time et al. Many scholars have successively used this method to do relative research on the structure and physical properties of cement pastes. The model of cement hydration [5,6], ion transport [7], carbonization [8], shrinkage[9] were also discussed according to those data.

Fly ash concrete is a world wide method used for quality and economical requirements: Fly ash can not only improve the workability, pore structure and aperture distribution, but also reduce the possibility of alkali-aggregate reaction et al. However, fly ash concrete has been thought to be easily carbonized, and the carbonization mechanism is not well comprehended up to now.

Traditional mechanism of carbonization was given as equation (1) based on a series of experiments:

$$CO_2 + Ca(OH)_2 \xrightarrow{H_2O} CaCO_3 + H_2O \qquad \text{(Eq.1)}$$

In this case, enough water content (or RH) is necessary, and the diffusion of CO_2 and water transport is very crucial, but these cannot explain why fly ash concrete is prone to carbonization because of the advantages of fly ash given above. To get insight into the carbonization mechanism, CO_2 adsorption experiment was performed in this investigation.

To simulate the real carbonization of cement-based materials, the experiments of CO_2 adsorption were also done at room temperature. The interaction between CO_2 and cement pastes was studied by comparing with the results of water isothermal adsorption. There is also a further discussion on the mechanism of carbonization.

2. Experiments
2.1 Raw materials and sample preparation
The Chinese Huaxin ordinary cement (Grade 42.5) was cast into 4cm×4cm×16cm cement pastes (the proportion in Table 1), which were then immediately put into isolated chamber to prevent water loss and

surface carbonization. At the designated age, the samples were oven dried at 105 for 24 hours in N_2 protected atmosphere, then the central part of each sample was cut and polished into a 2mm thick slice (see Fig.1). After cleaned by ethanol the slice was placed in the sample chamber of SGA-100, further dried at 105 for 3 hours with the relative humidity less than 1% before adsorption/desorption tests.

Table 1 Proportions of cement pastes

	water to cement ratio	fly ash (%)
SA	0.45	0
SB	0.45	15

SA and SB respectively stand for sample A and B, SA3, SA7 and SB3 appeared in this paper respectively stand for sample A and B at the age of 30th day and 70th day.

2.2 Instruments
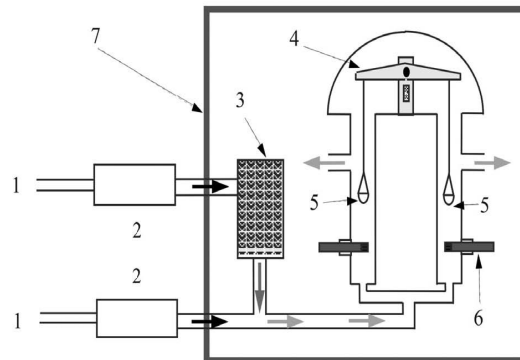

Fig. 1 Sample for adsorption/desorption

Fig.2 The sketch of SGA-100. 1–admission of dry gas; 2–dosing device; 3 – RH/RP controller; 4–microbalance; 5–sample/reference sample; 6–temperature probe; 7–thermostatic chamber

Both water and CO_2 adsorption measurements are done in SGA-100 Symmetrical Gravimetric Analyzer, the working principle sketch was shown in Fig. 2 and similar detailed description in reference [11]. Constant relative humidity or relative pressure (RH or RP) is established by mixed gas, which passes through the sample. In this way the RH or RP can be varied from 0% to 95%. The core of the instrument is an isothermal aluminum block

including the sample chamber, which can exactly control the temperature and RH. The temperature in the block is kept stable by a constant temperature bath and the deviation is less than 0.01°C. Isotherms were plotted automatically by the SGA-100 software [12].

The Raman spectrum test on samples after CO_2 adsorption/desorption cycles was employed to detect the formation of $CaCO_3$.

2.3 Surface area calculation

According to the isotherms, surface area can be derived from the two-parameter equation of Brunauer, Emmett and Teller (BET):

$$\frac{P/P_0}{W \times (1 - P/P_0)} = \frac{1}{W_m \times C} + \frac{(C-1) \times P/P_0}{W_m \times C} \qquad \text{(Eq.2)}$$

P/P_0 is the relative pressure of gas, W is the mass of gas adsorbed by the sample per gram, W_m is the amount of gas required to be a monolayer of coverage and C is a BET constant related to the heat of adsorption. The surface area S of the sample, can then be calculated from W_m by the following relation:

$$S = W_m * N * \sigma \qquad \text{(Eq.3)}$$

N is the Avogadro constant; σ is the cross-section area of the adsorbed molecule.

When the adsorbate is water, the relative humidity (RH) can instead of P/P_0, and $\dfrac{RH}{100} = \dfrac{P}{P_0}$, after substituting the RH for P/P_0, equation (2) can be simplified to equation (4):

$$\frac{RH}{W \times (100 - RH)} = \frac{1}{W_m \times C} + \frac{(C-1) \times RH}{100 \times W_m \times C} \qquad \text{Eq.4}$$

The SGA-100 software will automatically plot a straight line by equation (4). C and Wm can be obtained from the intercept and slope, $W_m = 1 \Big/ (\text{int } ercept + slope)$ and $C = slope \Big/ \text{int } ercept + 1$, combined with equation (2) can get the surface area.

3. Results and analysis

CO_2 adsorption/desorption isotherms of SA3, SA7 and SB3 are shown in Fig.3. All the curves are Type adsorption isotherms; each has a protuberant inflection point (approximately at RP=5%) close to the first adsorption point, which is the BET monolayer capacity. When the RP varied from 10% to 90%, the amount of adsorption almost increased linearly with RP. It demonstrates that the initial amount adsorbed was bigger; the later adsorption on the monolayer adsorbate is relatively steady. These two remarkable steps were respectively called high increment adsorption and steady adsorption step. The desorption curves are hysteresis during the whole range of relative pressure. Similar results of hysteresis were also reported elsewhere from water adsorption experiments [7,10]. The hysteresis is related to the high polarity of CO_2 molecule and high quadrupole of CO_2. H_2O and CO_2 are very sensitive to the polar groups or ions on the surface of the solid, which can easily form strong action between the adsorbed molecules and the solid, and this causes the hysteresis.
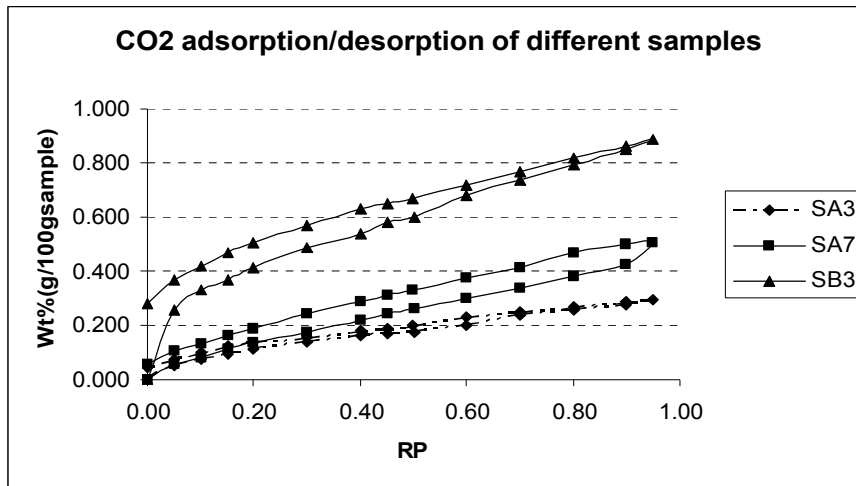

Fig.3 Isotherms of CO_2 sorption on different cement pastes

In fig.3, SA3 and SA7 adsorption isotherms show the CO_2 adsorption characteristics of cement pastes in different ages. Under the same relative pressure, per unit sample adsorbs more CO_2 with the age increasing for pure cement pastes. But the hysteresis of adsorption-desorption curves becomes more obvious. Table 2 shows that the CO_2 adsorption constant Wm (SA3) < Wm (SA7), which means the 70th day sample had more CO_2 adsorption locations than that of the 30th day sample. Because with the age increasing, the contents of $Ca(OH)_2$ and others in hydrate products increased, all of them can provide more adsorption locations for CO_2

adsorption. The increase of surface area from water adsorption indicates the increase of the hydrated cement gel production, because the surface area of cement pastes is mainly formed by cement gel.

The surface area S and the BET constant C are listed in Table 2. In this paper, the cross-section molecule areas of CO_2 and H_2O were respectively $22.2×10^{20}m^2/g$ and $12.5×10^{20}m^2/g$.

Table 2 surface area and BET adsorption constant

	Wm(mols/g) (CO$_2$ adsorption)	C1 (CO$_2$ adsorption)	S1 (m^2/g) (CO2 adsorption)	Wm(mols/g) (water adsorption)	C2 (water adsorption)	S2 (m^2/g) (water adsorption)
SA3	$2.67×10^{-5}$	12.4	3.55	$1.12×10^{-3}$	45.4	84.6
SA7	$3.64×10^{-5}$	7.6	4.85	$1.34×10^{-3}$	42.3	101.0
SB3 (the first cycle)	$8.17×10^{-5}$	41	10.88	$1.04×10^{-3}$	66.4	78.3
SB3 (the second cycle)	$7.82×10^{-5}$	20.2	10.41			

Fig.3 shows that the CO_2 adsorption ability of cement paste with fly ash (SB3) is much higher than those of SA3 and SA7. But in Table 2, the value of surface area of SB3 from water adsorption was not higher than that of SA3, even much less than SA7. This indicates that the surface area of cement pastes did not change obviously at the same age when fly ash was added. However the surface area of the paste from CO_2 adsorption became much larger, in addition, the adsorption constant C of SB3 is so much higher than those of SA3 and SA7 for CO_2 adsorption. It is known that the constant C is related to the heat of adsorption, the higher C is, the more energy are released during the process of adsorption. So for the higher constant C, more locations per unit samples are required for their interaction with adsorbates to result in higher surface area. Therefore the difference between constant C and surface area of samples gives information of adsorption location, and the number of CO_2 adsorption locations provided by fly ash cement pastes sharply raised. The same conclusion was also

made by Rudolph [9] in his doctor thesis, which illuminated that the addition of fly ash not only improved the connectivity between pores, but also broke the long chain of hydrated products into shorter ones. Thus there were more adsorption locations for per unit cement hydration products, which were shown in Fig.4.

Isotherms of repeated CO_2 adsorption on the same SB3 were given in Fig.5. The shapes of two curves are about the same, but the first cycle shows higher adsorptive ability than the second cycle. According to the values of surface area shown in table 2, the surface area became a little smaller after the first cycle's adsorption, and the constant C decreased sharply. This indicates that adsorption of CO_2 on cement pastes had caused some changes in their microstructures. Fig.5 implies that there was a lot of adsorbates remained, which explained that during the whole RP the changes of microstructures were caused by CO_2 adsorption. There existed an interaction between the CO_2 and cement pastes, which may be caused by a special bond or by chemical reactions. Bjorn Johannesson[8] got similar results in their studies of carbonization by water adsorption, there was 8% change of surface area before and after carbonization of cement pastes, it was very close to the results got in this paper by CO_2 adsorption.
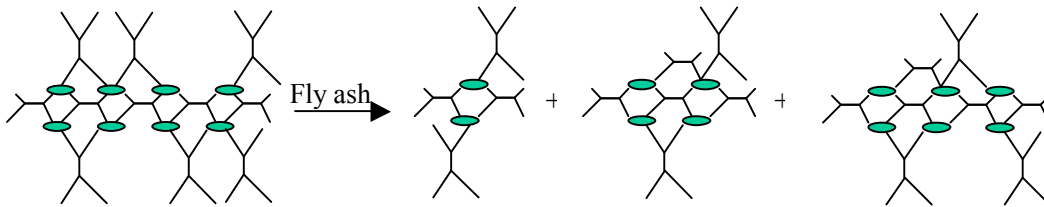

Fig 4 illumination of the effect of fly ash on polymerization degree of hydrated gel
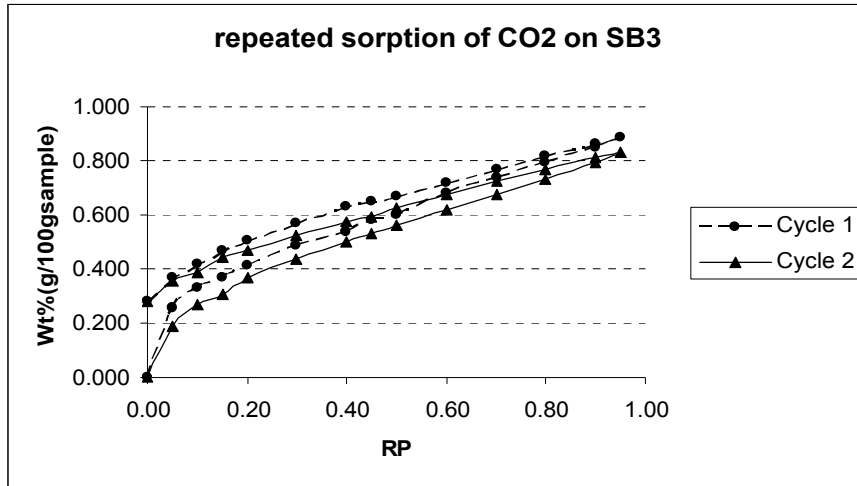
Fig.5 Repeated CO_2 sorption isotherms of SB3

Fig. 6 shows the selected areas and corresponding Raman spectrums of fly ash cement paste after repeated CO_2 adsorption. Two major areas, white and black area, were selected for Raman spectrum test. The spectrums showed that the white area was the hydrated calcium silicate gel (CSH), and black area matched spectrum of $CaCO_3$. The existence of $CaCO_3$ proved the deduction of direct reaction by CO_2 and CSH.
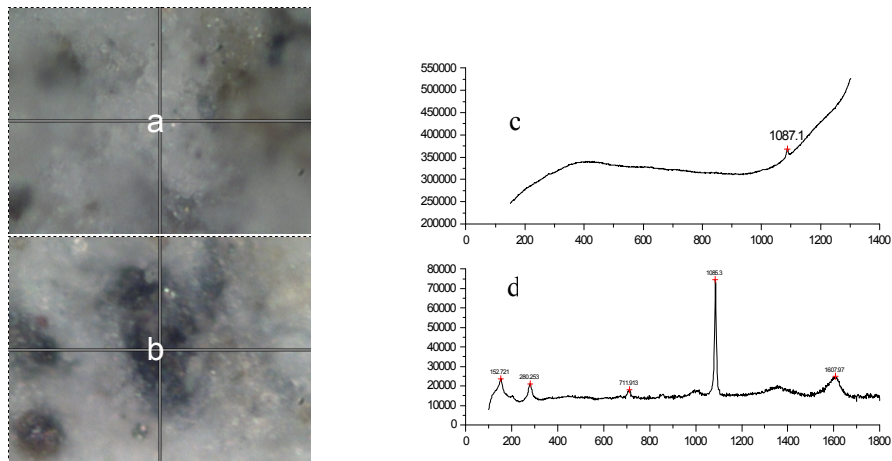

Fig.6 Raman spectrum after CO_2 adsorption; a) and b) two different selected area; c) and d) spectrum of a and b respectively

4. Discussions

BET adsorption was a traditional method used to get the microstructure

information of materials. It is usually combined with Kelvin-Laplace equation to get the microstructure of pores, so the adsorption experiments were done below the critical temperature of adsorbates. In this study, the CO_2 adsorption was not done below 195K (critical temperature of CO_2) but at room temperature, so the data from CO_2 adsorption isotherms could have certain differences from the data obtained below the critical temperature of the used adsorbates. But the main tendency was the same, and the adsorption constant Wm and C could also be used in this study to compare the effects made by the internal factors of materials in the same testing environment. So, this paper was intent to study microstructure under the same condition but not to investigate the differences of surface area by adsorption of different molecules.

Carbonization of cement pastes was normally considered as dissolution of CO_2 into pore water solution of cement-based material, then the reaction between carbonic acid and portlandite gets $CaCO_3$. It was also reported that the carbonization happened directly between carbonic acid and C-S-H gel. So the research on carbonization was always carried out under certain humidity. Carbonization research from direct CO_2 adsorption was seldom reported. In order to eliminate the free water or physically bonded water, sample preparation was strictly controlled, thus the dissolution of CO_2 was impossible. But the repeated adsorption results showed a certain reduction of surface area, which corresponded with the results got by Bjorn Johannesson[8]. The Raman spectrum test found $CaCO_3$, but without the dissolution of CO_2, there must be a strong bond between CO_2 and cement paste, also a chemical reaction between CO_2 and hydrated production was probably taken place, that is, the carbonization.

5. Conclusion
    This paper investigated the CO_2 adsorption characteristics of different cement pastes at different ages at room temperature and atmospheric pressure, which provided a new method for studying the mechanism of carbonization. The conclusions drawn from this study are as follows:
● There are two remarkable steps in CO_2 adsorption of cement pastes: high capacity adsorption and steady adsorption. The tremendous surface area of hydrated gels and the special properties of structure were the results of initially high capacity adsorption.
● Addition of fly ash changed the microstructure of hydrated cement gels, reduced the polymerization degree of hydrated gels and provided more

adsorption locations, thus greatly enhanced the CO_2 adsorption ability.

- A special action existed between CO_2 and hydrated calcium silicate gels, which caused strong bond or direct reaction between CO_2 molecules and cement pastes. Perhaps the CO_2 adsorption can lead cement gel to a transitional carbonization state.

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