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INFLUENCE OF THE TYPE OF CALCIUM SULFATE ON THE STRENGTH AND HYDRATION OF PORTLAND CEMENT UNDER AN INITIAL STEAM-CURING CONDITION

Hong Zhang[1], Zhongsou Lin[2] and Damao Tong[2]
[1]Dept. of Coal Utilization, China University of Mining and Technology,
Jiangsu 221008, P.R. China
[2]Dept. of Materials Engineering, Wuhan University of Technology ,
Hubei 430070, P.R.China

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ABSTRACT

The influence of gypsum (G) and anhydrite (A) on the strength and hydration of ordinary Portland cement (OPC) has been investigated. Under an initial steam-curing condition (65°C × 4 h), optimum SO_3 contents of both samples were found rising to 4-5% SO_3 and a higher optimum strength was gained with anhydrite as the retarder. Tests show that compared with Sample G, Sample A has higher non-evaporable water content, higher $Ca(OH)_2$ content, less pore volume and lower average pore diameter. Pore solution analyses show that it's the higher $[SO_4^{2-}]$ and lower $[OH^-]$ concentrations in Sample A that result in the above differences. *Copyright © 1996 Elsevier Science Ltd*

Introduction

There are two naturally occurring calcium sulfates. They are gypsum ($CaSO_4.2H_20$) and anhydrite ($CaSO_4$). Gypsum is widely used as cement retarders. But in areas rich in anhydrite deposits, anhydrite is often used instead.

Previous investigations have demonstrated that different kinds of $CaSO_4$ have different solubility (1) (2), which results in different strength in sulphoaluminate cement (3), fluoaluminate cement (2) and OPC (4) (5). Most research has been conducted at room temperature (20°C). Under standard curing conditions, optimum SO_3 content in OPC is 1.5-2.5%. To avoid excessive expansion, most countries restrict the maximum SO_3 content in OPC below 3.5%. Optimum SO_3 contents at high temperature may exceed maximum SO_3 content at room temperature (7).

The present work studies the influence of gypsum and anhydrite on the strength and hydration of OPC under steam curing conditions.

Since Longuet et al. (8) first introduced the pore solution extraction method, it has been used as a practical and effective method to study hydration. In this work, the pore solution extraction technique, together with XRD, TG-DTA, SEM and pore size analysis technique, was used.

Experimental

Materials. An ordinary Portland cement cliker (OPCC), with oxide and mineralogical compositions given in Table 1, was used in this investigation. The Blaine surface area was found to be 280 m^2/kg.

Gypsum was from Yincheng Gypsum Mines, Hubei, P.R. China and anhydrite from Nanjing Anhydrite Mines, Jiangsu, P.R. China. Their chemical compositions are given in Table 1. The Blaine surfaces of G and A powders were 530,540 m^2/kg respectively.

A commercial superplasticizer, named NF, was used. Its main composition is naphthalene.

Strength Test. Cements with varying contents of SO_3 for each type of $CaSO_4$ were weighed, mixed, and moulded (40 × 40 × 160 mm). The mixing proportions (in weight) of the beam mortar were as follows. Cement : Standard Sand = 1 : 2 , Water : Cement = 0.3 and NF addition = 0.7%.

The specimens were subjected to a 6 h - 20°C - 90% r.h. initial cure, then the temperature was increased to 65°C at a rate of 15°C/h. After steam-cured for 4 h at 65°C, the beams were cooled in air to room temperature, then demoulded and put in water at 20°C. Strength tests were carried out on the 3rd and 28th day.

Determination of Hydration Rate. The contents of non-evaporable water and $Ca(OH)_2$, as well as heat evolution rate, were determined to evaluate the rate of hydration. $Ca(OH)_2$ was studied with TG-DTA and XRD.

Pore Size Analysis. The specimens prepared for porosity measurement were first put in acetone solution to stop the hydration reaction at selected hydration times, then dried at 105°C for 24 h. Pore size distributions were determined using a mercury intrusion porosimeter.

An SEM was used to supplement information of the morphology of the hydration products.

Pore Fluid Extraction. The pore solution extraction device used was similar to that described by Longuet et al. (8) and Xue Jungan et al. (9).

Cement paste specimens were prepared at a constant water/cement ratio of 0.5. They were mixed and cast in plastic bags, sealed and cured under the same conditions as for the strength tests.

[OH^-] concentration in the pore solution was determined by direct titration against nitric acid using phenolphthalein indictor. Concentrations of other ions were determined with emission spectrochemical analysis.

TABLE 1

Composition of OPCC, Gypsum and Anhydrite

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	LOI	C_3S	C_2S	C_3A	C_4AF	f-CaO
OPCC	65.48	20.64	5.64	4.85	1.34	0.30	1.70	60.08	13.85	6.74	14.74	1.00
Gypsum	31.28	3.42	0.90	0.33	0.38	42.72	20.39	-	-	-	-	-
Anhydrite	39.09	1.34	0.41	0.07	2.29	50.62	4.86	-	-	-	-	-

Results

Strength Test. Strength data of cements with varying content of SO_3 of both G and A are presented in Fig.1.

Fig.1 shows that the optimum SO_3 content under an initial steam curing condition (65°C x 4 h) is raised to 4-5%, which is about 2-3 % higher than that under standard curing conditions (20°C).Similar results were observed by Khahil and Ward (6).

As to $CaSO_4$ type, an interesting trend can be found. With the increase of SO_3 content, the strength of Sample G gradually decreased until it was lower than Sample A.

Hydration Rate

Non-evaporable water. Fig.2 shows the change of non-evaporable water content in sample G and A (SO_3 5%) with curing time.

As non-evaporable water content represents the amount of whole hydration products. It can be concluded that Sample A hydrates faster than Sample G over the whole period. Furthermore, the gap between the two samples widens with hydration time.

$Ca(OH)_2$. TG-DTA and XRD are frequently used for analyzing $Ca(OH)_2$ content in cement paste. Results with the two methods are presented in Table 2.

The results of TG-DTA indicate that $Ca(OH)_2$ content in Sample A is higher than that in Sample G, while XRD shows the opposite. This seemingly controversial result can be reconciled by the following knowledge.

TG-DTA gives a $Ca(OH)_2$ content by dictating the weight loss over 430-520°C, When $Ca(OH)_2$ decomposes. These results do not change whether $Ca(OH)_2$ is crystal or amorphous. But XRD can only detect $Ca(OH)_2$ in the crystalline state. It can be concluded that by the 3rd day, there is more $Ca(OH)_2$ in Sample A but most of it exists in the amorphous state.

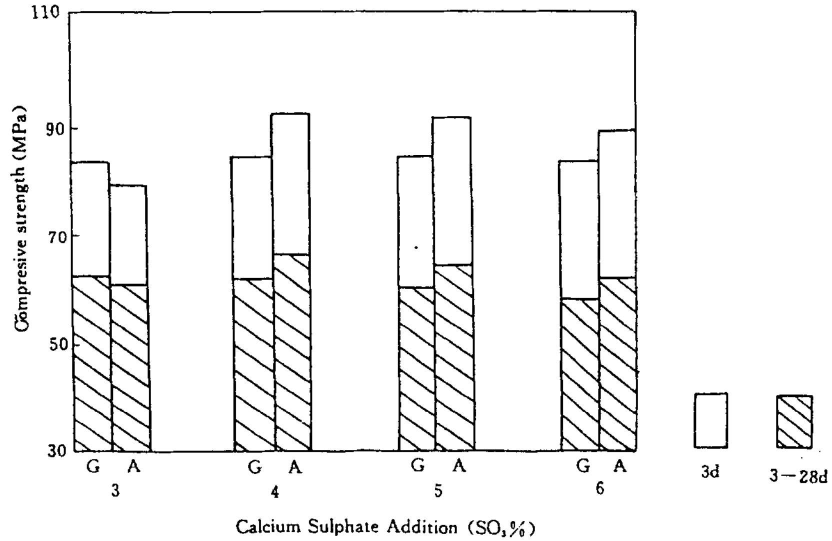

FIG. 1.
Variation of strength with SO_3 content and type of $CaSO_4$.

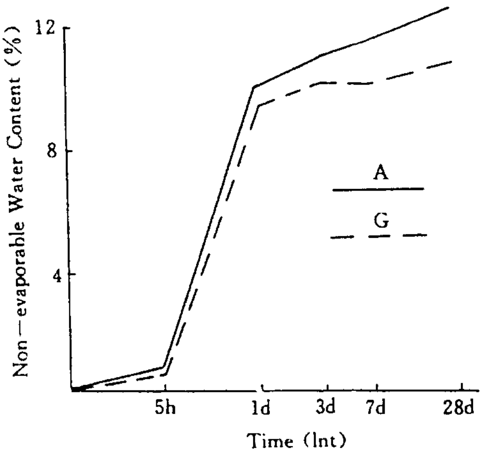

FIG. 2.
Variation of non-evaporable water content with curing time and type of $CaSO_4$.

Heat evolution rate. Heat evolution rates were recorded for pastes having W/C= 10 at 30°C, Heat evolution at early stage of hydration of both samples is shown in Table 3.

The results show that heat evolution at early stage in Sample A is lower than that in sample G. This may seem contrary to former results. But special attention should be paid to the hydration condition. The inconsistency results from the different conditions, as will be shown in the discussion.

Pore Analysis and SEM Observation. Fig. 3 shows changes of total pore volume and dv/dlgr with lgr at 3rd day.

The tests indicate that the specific pore volume of Sample A is 58.1 mm^3/g while that of Sample G 63.1 mm^3/g. Besides, the average pore diameter in sample A is 125Å while that in Sample G 150Å. SEM observations also show that the hydration products in Sample A have a finer structure.

Feldman and Beaudion (10) pointed out that specific pore volume is the principal factor affecting strength. Zaitsev (11) proved that at a given specific pore volume, the lower the average pore diameter, the higher the strength. These may well explain why Sample A has a higher strength than Sample G.

Pore Solution Analysis. Table 4 shows the pore fluid composition of Sample A and G at SO_3 5% with a water/cement ratio 0.5 at different curing times.

The results indicate that $[OH^-]$ concentration in Sample A is always lower than Sample G except for the lst hour. In addition, the gap widens with curing time. As to $[SO_4^{2-}]$, its concentration in sample A is higher than that in Sample G over the whole curing time.

TABLE 2

$Ca(OH)_2$ Content in Cement (SO_3 5%) Paste at 3rd Day

	Sample G	Sample A
TG-DTA	7.61%	8.84%
XRD	6.61%	5.45%

TABLE 3

Heat Evolution of Cement Paste (SO_3 5%) at Early Hours (cal/g)

Time	0.5 h	1.0 h	3.0 h	6.0 h
Sample G	0.89	1.41	3.44	8.74
Sample A	0.76	1.13	2.61	7.39

Discussion

Many authors (1)(2)(3) believe that absolute solubility of both types of $CaSO_4$ is similar, while the dissolution rate of gypsum is faster than that of anhydrite. However, in this investigation, it was found that Sample A has higher $[SO_4^{2-}]$ concentration.

There are other authors (12), Tai Liankui et al, who have given special attention to the influence of $CaSO_4$/water ratio on the dissolution rate of both types of $CaSO_4$. They found that the two types behave rather differently at varying $CaSO_4$/water ratios, as is shown in Fig. 4.

The dissolution rate of gypsum is relatively stable, while that of anhydrite grows with the increase of solid/water ratio. For example, at S/W 0.005, the $CaSO_4$ content in the solution of gypsum is 1.978g/l and that of anhydrite is 1.353g/l. But at S/W 0.05, gypsum is 2.031g/l while anhydrite 2.329 g/l. If Fig. 4 is compared with Fig. 1, the same trends can be found. It can be deduced that it is the higher dissolution rate of anhydrite that results in higher strength in Sample A.

In a system where solid $CaSO_4$ and solid $Ca(OH)_2$ coexist in the solution, the following equilibrium condition will be reached.

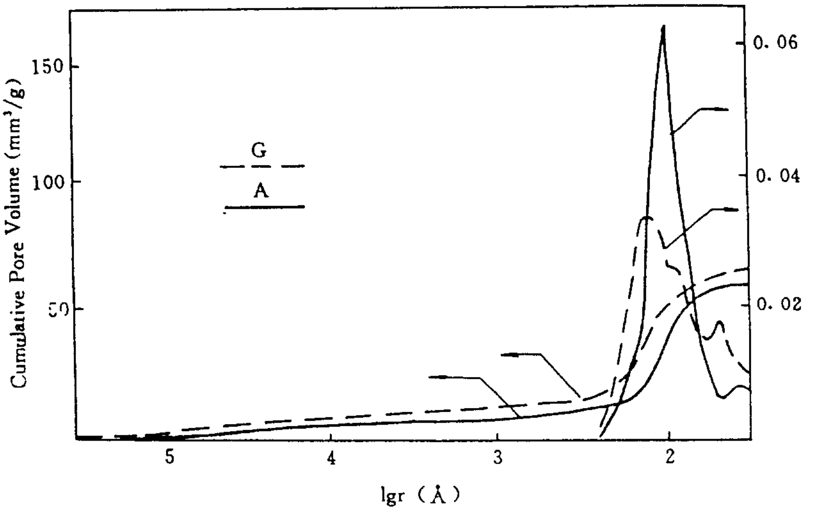

FIG. 3.
Change of total pore volume and dv/dlgr with lgr.

TABLE 4

Pore Fluid Composition of OPC (mM/L)

Type of Retarder	Curing Time (h)	Na^+	K^+	Ca^{2+}	SO_4^{2-}	OH^-
Anhydrite	1	25.70	68.08	29.03	34.69	80.82
	3	24.13	71.85	28.24	40.88	73.23
	5	26.48	72.54	28.80	42.00	73.95
	24	80.61	110.15	16.50	73.12	84.35
	3 x 24	85.30	125.15	1.88	47.16	129.70
	7 x 24	98.90	135.62	2.63	45.75	133.80
Gypsum	1	23.48	65.54	27.98	30.38	78.87
	3	24.65	67.46	27.38	32.53	76.54
	5	25.57	66.38	25.05	33.75	75.17
	24	78.26	98.69	15.50	61.22	92.31
	3 x 24	90.78	121.85	1.42	41.91	135.50
	7 x 24	96.65	132.31	0.38	29.53	178.30

$$CaSO_4(S) \leftrightarrow Ca^{2+} + SO_4^{2-} \qquad (1)$$

$$Ca(OH)_2(S) \leftrightarrow Ca^{2+} + 2OH^- \qquad (2)$$

In this case, $[OH^-]$ concentration will decrease with the increase of $[Ca^{2+}]$ concentration. If there is $CaSO_4$ and no $Ca(OH)_2$, only equilibrium (1) is reached. In this case, $[OH^-]$ will not change with $[Ca^{2+}]$.

Thus, the change of pore fluid composition in this investigation can be explained. At the time OPC is mixed with water, all its constituents hydrate. At a high $CaSO_4/H_2O$ ratio, anhydrite dissolves faster than gypsum and results in higher $[SO_4^{2-}]$ concentration, which accelerates C_3S hydration(13). This, in turn, results in higher $[OH^-]$ concentration. When

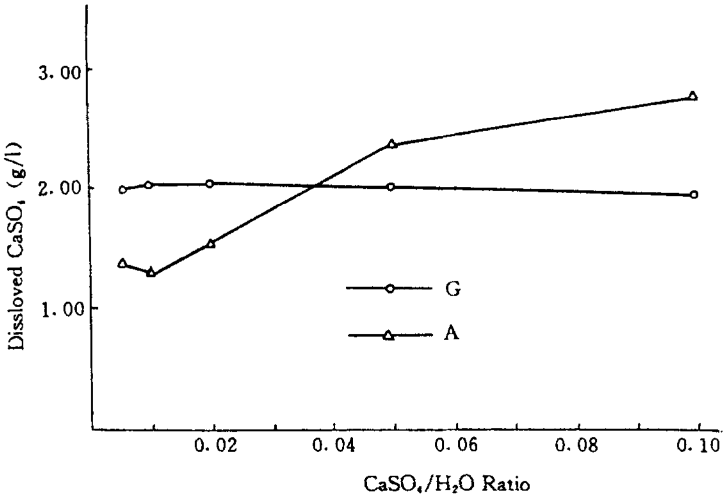

FIG. 4.
Change of dissolution rate of $CaSO_4$ with solid/water ratio.

$Ca(OH)_2$ crystallizes, solid $CaSO_4$ and $Ca(OH)_2$ exist. Equilibrium(1) and (2) are both reached. The higher solubility of anhydrite results in higher [Ca^{2+}] concentration, which drives [OH^-] concentration down. This time higher solubility of anhydrite results in lower [OH^-] concentration.

In a low [OH^-] solution, ettringite is created at a distance from the surface of the solid phase (14) (15), and the hydration of calcium silicates is accelerated. Thus, a more uniform and denser structure is formed.

Conclusions

1. The optimum SO_3 content of OPC under an initial steam-curing condition (65°C × 4h) is raised to 4-5%, whether gypsum or anhydrite is used as its retarder.
2. The sample with anhydrite as its retarder has higher strength, higher non-evaporable water content, higher $Ca(OH)_2$ content, less pore volume and lower average pore diameter than that with gypsum.
3. The concentration of [SO_4^{2-}] in the pore solution of Sample A is always higher than that of Sample G while [OH^-] concentration is always lower than in Sample G except for the first hour.
4. The higher dissolution rate of anhydrite at high $CaSO_4/H_2O$ ratios results in all the differences.

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