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SHALE ASH CONCRETE

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ABSTRACT

This paper describes the use of an industrial waste product oil shale ash as a pozzolana and as a carrier for superplasticizer to form carrier fluidifying agent. For a series of concrete mixes with a wide range of w/c ratios, test results indicated that the partial replacement of cement by an equal weight of shale ash could effect an increase in the compressive strength. For 10% replacement, the compressive strength of the concrete could be increased by 5 to 10% at 28 days and 10 to 15% at 56 days. When shale ash was used to act as the carrier for a superplasticizer, the resulting carrier fluidifying agent could control the loss of slump of concrete mixes. For a 1.5% dosage of the carrier fluidifying agent, the slump of concrete was maintained for 90 minutes. © *1997 Elsevier Science Ltd*

Introduction

Large quantity of oil shale are quarried in Maoming, Guangdong Province, China. The oil content of the quarried ore is about 20% and the ore is used to generate electricity with an ebullition furnace to combust the oil shale. The oil shale ash discharged from one furnace is estimated to be more than six hundred thousand tons each year. Two ore combusting furnaces are going to be installed in Maoming and the total annual discharge of oil shale ash is expected to top one million and two hundred thousand tons. It will be of great practical significance for the building materials production industry and for the protection of environment if the industrial waste residue can be utilized in the construction works.

This paper describes the development of a pozzolana (1) and the development of a carrier fluidifying agent (2) to control the loss of slump for high strength concrete with this type of industrial waste product (3). It was found in experiments performed on concretes with a wide range of water to total cementitious materials ratios (W/C + M) from 0.30 to 0.50, that 10% replacement of cement in concrete by equal weight of shale ash could effect 5-10% increase of compressive strength at 28 days and 10-15% increase at 56 days in comparison with the corresponding control concrete without the shale ash.

When using the oil shale ash as the carrier for superplasticizer (4), the resulting carrier fluidifying agent can effectively control the loss of slump of high strength concrete (5). With the addition of 1.5% of shale ash carrier fluidifying agent, the slump of concrete can be retained for 90 minutes without significant change.

In this paper, the strengthening mechanism of shale ash in concrete is studied by combining the use of x-ray diffraction, (XRD), thermal gravimetry (TG), scanning electron microscope (SEM), energy dispersive analysis of x-ray (EDAX), and mercury intrusion porosimetry (MIP). Emphasis was placed on the mechanism of enhancement of the inner structure, pore structure in hardened cement paste (hcp) and the improvement of interface structure by the shale ash strengthening agent.

Materials Used in Experiments

Shale Ash

a. Chemical composition. The chemical compositions of shale ash are given in Table 1.

b. XRD profile and scanning electron micrographs. From the XRD profile, it can be shown that the main components of shale ash are α-SiO_2, and $CaMgSiO_4$. Some kinds of clay mineral can also be found.

c. Chemical reactivity of shale ash. The shale ash, in its nature, is a type of pozzolanic material, the soluble SiO_2 and Al_2O_3 can react with the calcium hydroxide precipitated during the hydration of cement to produce C-S-H gel, which contributes to the strength of concrete. The soluble SiO_2 and Al_2O_3 contents was determined as follows,

1. Shale ash was boiled in saturated $Ca(OH)_2$ solution for 3 hours.
2. The solution was neutralized by hydrochloric acid and then filtered.
3. The filtrate was used to determined the soluble SiO_2 and Al_2O_3 contents.
4. The soluble SiO_2 content was determined by volumetric analysis using potassium fluosilicate (K_2SiF_6) solution.
5. The soluble Al_2O_3 content was determined by Differential Thermal Analysis.

The chemical reactivity can be assessed in terms of content of soluble SiO_2 content:

$$\frac{\text{Soluble } SiO_2}{\text{Total } SiO_2} = 4.2\%$$

and soluble Al_2O_3:

$$\frac{\text{Soluble } Al_2O_3}{\text{Total } Al_2O_3} = 42.3\%$$

It can be seen that fairly high content of soluble Al_2O_3 are contained in the shale ash.

TABLE 1

Chemical Analysis of Shale Ash (% weight)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Soluble SiO_2	Soluble Al_2O_3	L.O.I.
56.25	30.24	9.22	2.58	1.53	2.34	12.78	1.26

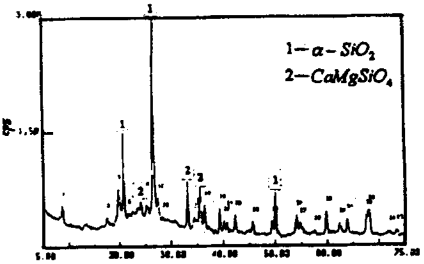


FIG. 1.
XRD profile of shale ash.

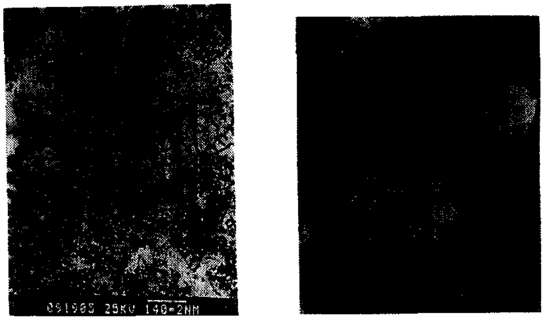


FIG. 2.
Scanning electron micrograph of shale ash. (A) Shale ash before grinding (B) Ground shale ash.

d. Specific surface area: 6000 ~ 8000 cm²/g

e. Specific gravity: 2.53

Cement

Two types of cement were used:

a) Xiangxiang brand ordinary Portland cement complies with Chinese National Standard GB175-92, the compressive strength determined at 28 days = 51.5MPa;

b) Peal River brand cement, the compressive strength determined at 28 days = 56.5MPa;

c) Fineness of both types of cement: percentage retained on 0.08mm sieve: 2.4%

Aggregates

a) Coarse aggregate: diameter of gravel 5 ~ 20mm, bulk density 1340kg/m^3, specific gravity 2.60, dust content 0.6%, content of irregular and flaky particles 19.7%

b) Fine aggregate: middle - coarse sand, fineness modulus = 3.0, bulk density = 1540 kg/m^3, specific gravity = 2.65, moisture content = 0.5%.

Superplasticizer. The superplasticizer used was naphthalene type, named NF, which was developed at Tsinghua University and complied with Chinese National Standard specified by GB8077-87.

TABLE 2

Composition of Mineral Admixture and Denotations

Denotation of Admixture	Composition
Y	100% Shale Ash
YG1	70% Shale Ash + 30% Natural Zeolite
YG2	70% Shale Ash + 30% Powder of Limestone
YG3	90% Shale Ash + 10% Gypsum

Carrier Fluidifying Agent. It is a patented product by Tsinghua University, made of shale ash which carries a specific amount of superplasticizer and other minor admixtures (6).

Constituents of Carrier Fluidifying Agent:

1) Shale Ash
2) Superplasticizer
3) Plasticizer
4) Lime

Mineral Admixtures. The mineral admixtures incorporated into the concretes were oil shale ash, powder of zeolite, limestone and gypsum.

Experimental Details

In the research, the shale ash was used to make the mineral admixtures for concrete, and the carrier for superplasticizer to form carrier fluidifying agent.

Denotation and Composition of The Mineral Admixtures. The composition of admixtures and their denotations are given in Table 2.

Strengthening Effect of Different Types of Admixtures. In the experiments, concrete mixes with water to total cementitious materials ratios (W/C + M) ranging from 0.30 to 0.5 were prepared with 10% of cement in the concrete mixes was replaced by the mineral admixture Y, YG1, YG2, or YG3 respectively. The mix proportion of concretes is presented in Table 3. The strength of concretes with different types of mineral admixture was determined at 3,7,28 and 56 days and was compared with that of corresponding control concrete without any mineral admixture.

Retention of Slump of Concrete by Shale Ash Carrier Fluidifying Agent. The rapid loss of slump of concrete containing superplasticizer imposes difficulties in construction. Especially for the ready mixed concrete, due to its loss of slump during the transportation, the superplasticizer is usually redosed on site, consequently entailing more equipment and labour and causing the inconvenience of management and poor quality control. The shale ash carrier fluidifying agent can be added at the ready mixed concrete batching plant, and the slump of

TABLE 3

Mix Proportion of Concretes with and without Mineral Admixture

Mix No.			1	2	3	4	5	6
W/(C + M)			0.30	0.34	0.38	0.42	0.46	0.50
Materials (kg/m^3)	Cementitious Materials	Cement in Control Concrete	600	500	450	400	400	400
		Cement in Concrete with Mineral Admixture *	540	450	405	360	360	360
		Mineral Admixture *	60	50	45	0	40	40
	Water		180	170	171	168	184	200
	Sand		600	620	620	640	650	660
	Gravel		1200	1210	1200	1220	1210	1210
	Superplasticizer NF		7.2	6.0	5.0	3.6	3.2	2.4

* Strengthening agents Y, YG1, YG2 and YG3 were respectively used to replace 10% of cement in concrete.

TABLE 4

Mix Proportion of Concrete for Tests of Slump Retention

Mix No.	1	2
W/(C + M)	0.32	0.32
Water (kg)	176	176
Cement (kg)	550	500
Mineral Admixture YG3 (kg)	0	50
Sand (kg)	632	632
Gravel (kg)	1147	1147
Superplasticizer NF (kg)	4.95	4.95
Shale Ash Fluidifying Agent (kg)	8.25	8.25

the concrete can be maintained for 1.5 hours without significant change, hence the smooth progress of construction on site can be ensured.

The mix proportion of concrete for the tests of slump retention using the shale ash carrier fluidifying agent is given in Table 4. The addition of shale ash carrier fluidifying agent was 1.5% by weight of cement.

Test Results and Discussion

Effect of Different Mineral Admixtures on Concrete. Test results of slump of concrete with and without the mineral admixtures (Y, YG1, YG2, or YG3) are summarized in Table 5.

It is shown that for concrete with low W/(C + M) (≤ 0.34), the use of shale ash (Y, YG1, YG2 or YG3) to replace 10% of cement, could result in fairly large reduction of slump; but for the concrete with W/(C+M) ≥ 0.38, the replacement of 10% cement by mineral admixture (Y, YG1, YG2 or YG3) was beneficial to the increase of slump. As compared with the corresponding control concrete, the slump of most concretes was increased by the introduction of the shale ash admixtures.

From Figure 3, it can be shown that when W/(C + M) = 0.30, the compressive strength of concrete with shale ash replacing 10% of cement was almost equal to that of corresponding control concrete until the age of 28 days, but at the age of 56 days, the compressive strength of concrete containing 10% of the admixture YG3, was 12% higher than that of the corresponding control concrete. When W/C + M = 0.34, replacement of 10% cement by admix-

TABLE 5

Slump Values for Concrete with and without Mineral Admixtures

	Mix No.	1	2	3	4	5	6
	W/C + M	0.30	0.34	0.38	0.42	0.46	0.50
Slump (cm)	Control Concrete	13.0	12.0	10.5	10.5	13.0	11.5
	Concrete with YG1	2.5	7.0	17.0	14.5	13.0	11.5
	Concrete with YG2	1.0	7.0	16.5	13.5	11.5	12.0
	Concrete with YG3	1.0	6.0	18.0	14.5	13.0	14.0
	Concrete with Y	1.0	4.5	14.0	8.5	12.5	15.0

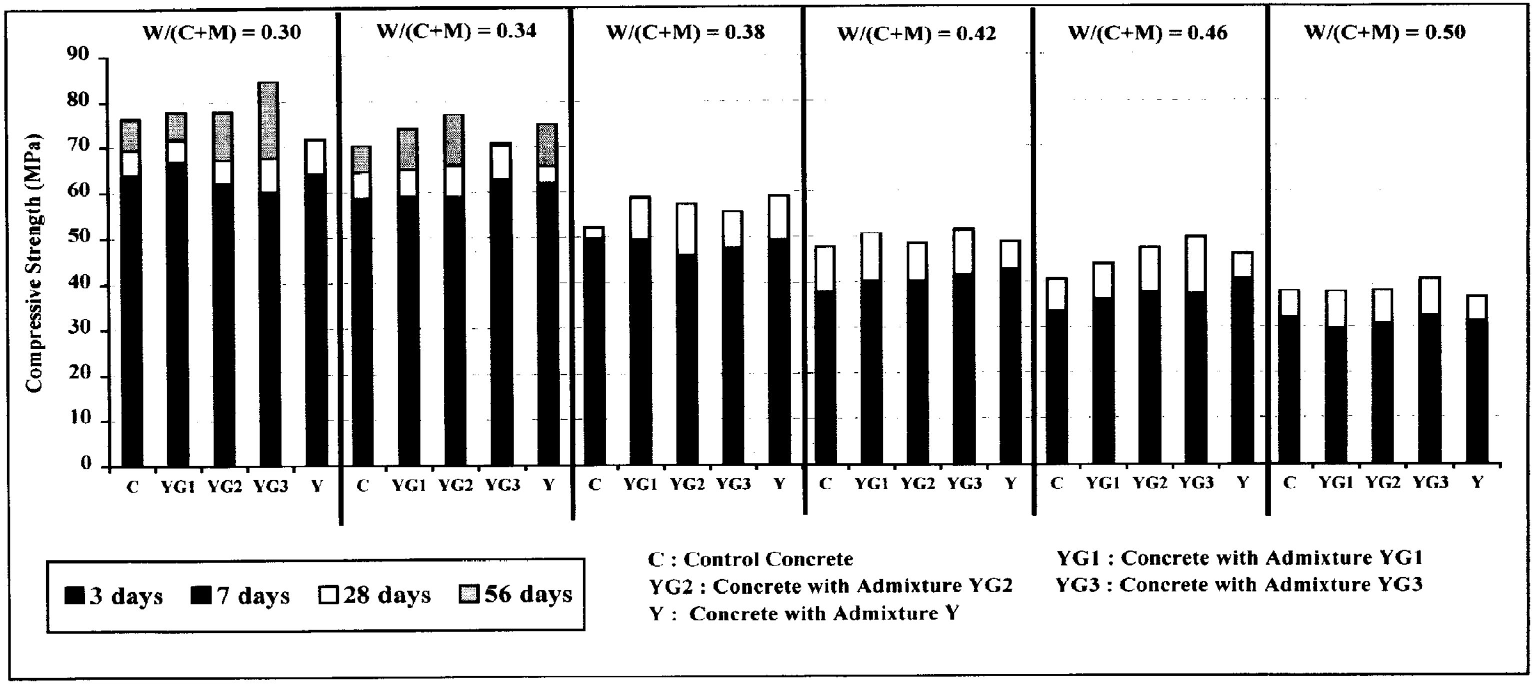


FIG. 3.

Relationship between compressive strength and water cementitious materials ratio.

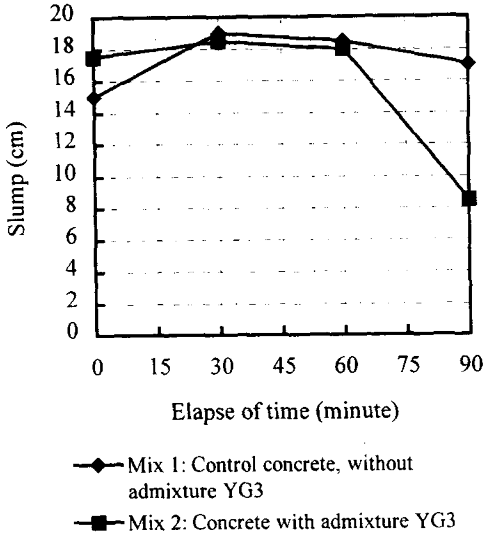


FIG. 4.

Slump behaviour of concretes adopted 1.5% shale ash carrier fluidifying agent.

ture YG3 could effect greater increase of strength than the other admixture, the increase of strength was 12% at 3 days, 6% at 7 days, 9% at 28 days, and 10% at 56 days as compared with the corresponding control concrete. When W/C + M = 0.38, the compressive strength of concrete with admixture YG3 at different ages was almost equal to that of control concrete. When W/C + M = 0.42 and 0.46, the strength of concrete containing YG3 at 7 days and 28 days was increased by 8-10% in comparison with the control concrete. For W/C + M = 0.50, the compressive strength of these two types of concrete was nearly equal to each other.

Among the four types of admixtures mainly composted of shale ash, the admixture YG3 was more effective in increasing the compressive strength of the concrete.

Retention of Slump of Concrete by Shale Ash Carrier Fluidifying Agent. Comparative tests were made to observe the effectiveness of shale ash carrier fluidifying agent in retaining the slump between the control concrete and concrete incorporated admixture YG3. The mix proportion are given in Table 4.

Mix 1 was control concrete but Mix 2 contained admixture YG3 to replace 10% of cement. After the initial slump was determined, the shale ash carrier fluidifying agent was added, and the concrete was reagitated. Slump test was carried out at every 30 minutes. The test results are plotted in Figure 2.

As manifested in Figure 4, the addition of 1.5% shale ash carrier fluidifying agent by weight of cement in high strength concrete mixture, Mix 1, can maintain the slump without any loss within a period of 90 minutes (7). However, in Mix 2, although 1.5% of carrier fluidifying agent was added, the loss of slump after 90 minutes was about 50% of the initial slump. The reason is probably that the shale ash, in its nature, is a porous pozzolanic material requiring higher amount of water.

From Figure 5, it can be found that the strength of concrete with YG3 was 15% higher than that of control concrete at 28 days.

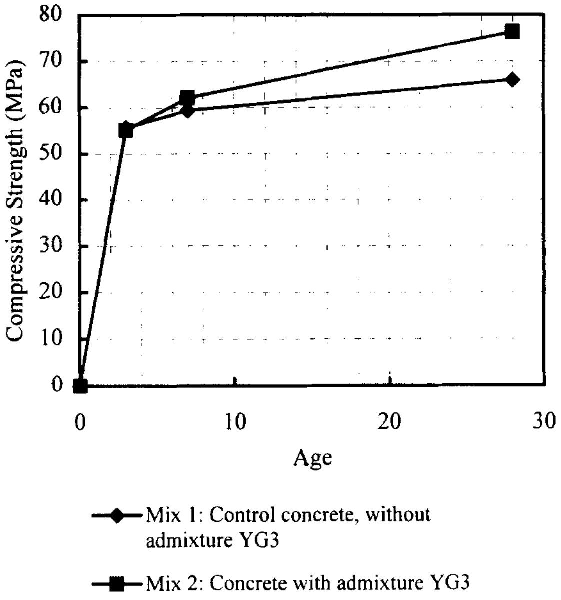


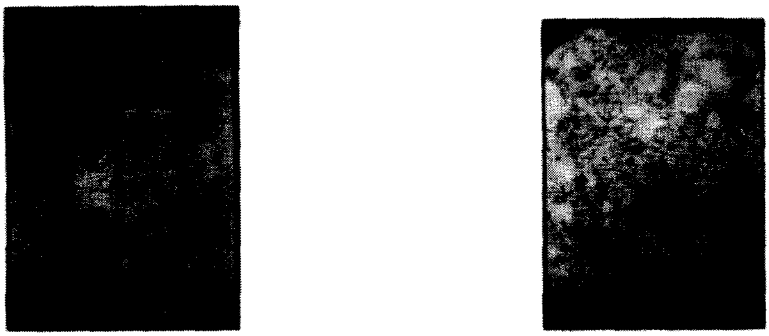
FIG. 5.
Strength development of concretes.

An optical microscope was used to observe and compare the dispersion and coalescence of fresh cement paste with and without the shale ash carrier fluidifying agent. It can be seen from Figure 6 that one hour after mixing, the cement paste containing 1.5% of shale ash carrier fluidifying agent was still in dispersed state (photographs No. 2 and No. 4 in Figure 4); but as for the cement paste without carrier fluidifying agent, it has coalesced (photographs No. 1 and No. 3 in Figure 6). The reason is that the shale ash carrier fluidifying agent can release the superplasticizer gradually and continuously to the paste, hence maintaining the zeta potential between the cement particles and keeping the cement paste in dispersed state.

Strengthening Mechanism of Shale Ash Strengthening Agent

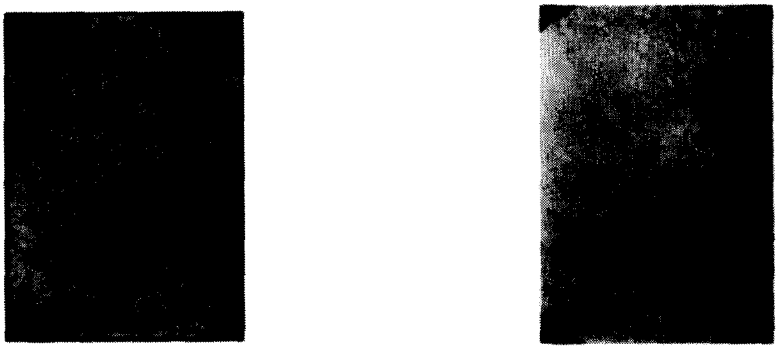
To explore the strength enhancing mechanism of shale ash mineral admixture in concrete, the technique of XRD was used to analyse the quantities of $Ca(OH)_2$, and SiO_2 in hardened cement paste (hcp) with different dosages of shale ash strengthening agent. Photographs of SEM were taken to reveal the hydrates formed from the reaction between the soluble SiO_2, Al_2O_3 and $Ca(OH)_2$ and the products in the vicinity of the interface between hcp and aggregate MIP technique was used to determine the pore volume in hcp. In this research, the ratios of SiO_2/CaO in the transition zones were determined by means of EDAX.

Enhancement of Structure of hcp by Shale Ash. Specimens were made of cement paste with shale ash mineral admixture dosed to replace 0%, 10%, 20% and 30% of cement, and were cured for 28 days. XRD technique was used to determine the quantities of $Ca(OH)_2$, and SiO_2, the results are presented in Figure 7.



No.1: Original state of pure cement paste

No.2: Original state of cement paste with carrier fluidifying agent



No.3: Pure cement paste has coalesced one hour after mixing

No.4: The cement paste with carrier fluidifying agent is still in dispersive state one hour after mixing

FIG. 6.
Dispersion and coalescence of cement paste.

As indicated in Figure 7, for concrete with 10% shale ash replacement, due to the reaction between the soluble SiO_2, soluble Al_2O_3 and $Ca(OH)_2$ precipitated during the hydration of cement which produced C-S-H gel and aluminates (SEM photograph for the hydration products is given in Figure 8), the content of $Ca(OH)_2$ was decreased when comparing with the control concrete. In contrast, the content of SiO_2 was increased. When the shale ash content was further increased, the content of $Ca(OH)_2$ in hcp was decreased and the quantity of SiO_2 continued to increase. However, when the shale ash content was excessive, the strength, especially the early strength of concrete was decreased (8).

The reason is that the shale ash, though pozzolanic in its nature, is not cementitious and its reactivity is far below that of cement. This was confirmed by the comparative test results of pore structures between pure hcp and hcp with shale ash mineral admixture. For mixes with constant water to total cementitious materials ratio of 0.30, the shale ash was used to replace 5% of cement. The pore volume and pore size distribution in the hcp of both the shale ash concrete and the control concrete were determined at the ages of 3 days, 7 days and 28 days. The results are summarized in Table 6.

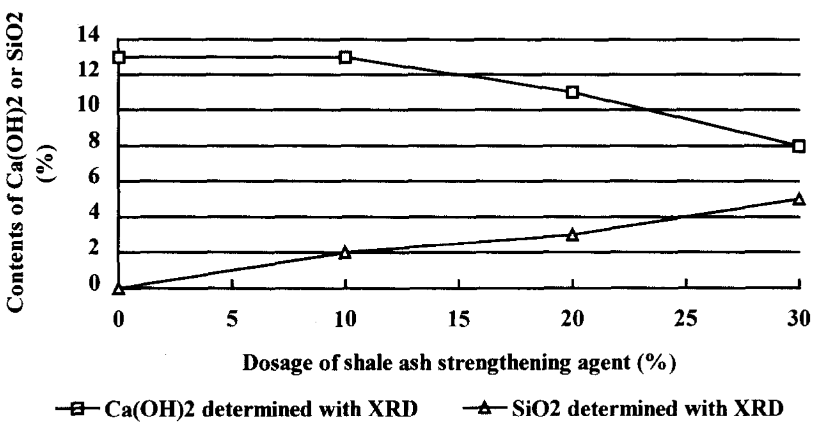


FIG. 7.
Relationship between content of $Ca(OH)_2$ and SiO_2, and dosage of shale ash strengthening agent in hcp.

The data in Table 6 indicate that the accumulative volume of pores larger than 100nm in hcp with shale ash at 3 days, 7 days and 28 days is less than that in pure hcp respectively, while the volume of pores smaller than 50nm, which reflect the quantity of C-S-H gel formed in hcp, are greater than that in pure hcp. The MIP test results show that the shale ash mineral admixture agent can increase the formation of hydrates, reducing the content of harmful large pores, so the strength and impermeability of hcp are enhanced.

Improvement of Interface between hcp and Aggregate by Shale Ash. The specimens were made of limestone aggregate and cement pastes with water to total cementitious materials ratio of 0.30. Beginning from the edge of aggregate, the EDAX point analysis was conducted with an electronic probe to determine the content of elements CaO and SiO_2, and the ratios

FIG. 8.
SEM photograph for the products formed from the reaction between shale ash and lime (specimen cured for 28 days).

TABLE 6

Pore Size Distribution and Pore Volume in hcp with and without Shale Ash Admixture

Age	3 days			7 days			28 days		
Pore Size Distribution	<50nm (%)	>100nm (%)	Pore Volume (ml/g)	<50nm (%)	>100nm (%)	Pore Volume (ml/g)	<50nm (%)	>100nm (%)	Pore Volume (ml/g)
hcp	93.21	4.96	0.1117	96.24	3.29	0.1032	96.02	2.93	0.0947
hcp with Shale Ash	95.16	3.86	0.1165	96.64	2.51	0.1007	96.41	2.66	0.0913

of SiO_2/CaO (by weight) at the interface between cement paste and aggregate were calculated. It can be shown from Figure 9 that the ratios of SiO_2/CaO at the interface of the specimen with shale ash are higher than those without shale ash. High content of Si^{4+} existing at the interface with shale ash leads to the increase of content of C-S-H gel, and in the mean time, the decrease of content of the orientational flake like $Ca(OH)_2$. In the probed points of distance 20 μm and 40 μm from the side of aggregate there are two low points of ratio SiO_2/CaO. This is possibly because at these two locations there existed the crystallization centres provided by the aggregates and the cement paste respectively where the hydrates formed first and gradually filling the rest of the interface. Hence resulting in the special changes of ratios of SiO_2/CaO in these two points (20 μm and 40 μm from the edge of aggregate). Furthermore, as shown in Figure 9, with the SiO_2/CaO ratio near the surface of the aggregate not less than that in the cement paste matrix, it indicates that the transition zone was absent in the sample with W/(C + M) of 0.3 (9).

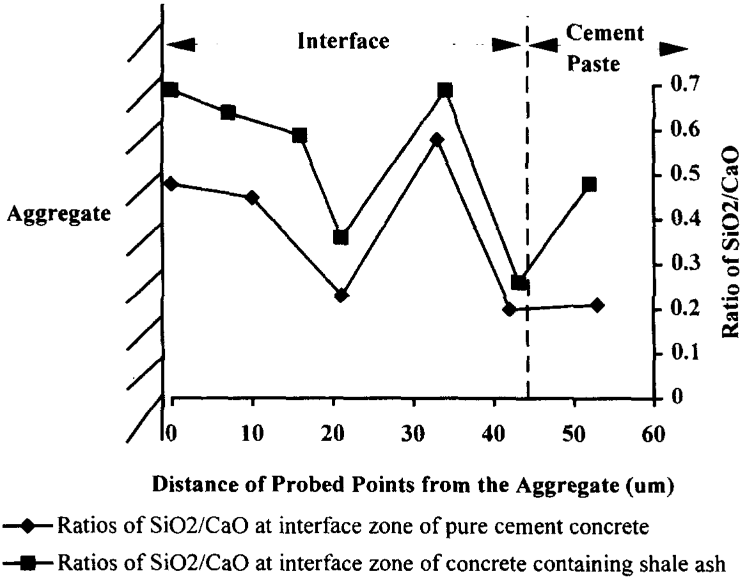
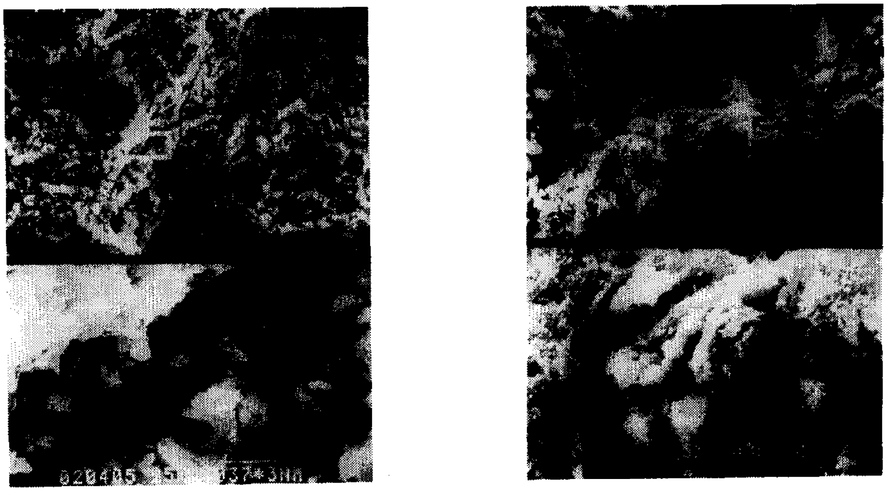


FIG. 9.

Ratios of SiO_2/CaO (by mass) at interface zone.



(a) Pure hcp without shale ash (b) hcp with shale ash

FIG. 10.
SEM photographs for interface structure between aggregate and hcp with and without shale ash strengthening agent.

The interface structure between aggregate and hcp was also observed by means of SEM (Photographs are give in Figure 10). It is shown in Figure 10 that high quantity of $Ca(OH)_2$ (the white hexagonal flake liked crystal in photograph (a)) was found to exist in the interface between the aggregate and the hcp without the shale ash mineral admixture, but for the specimen with mineral admixture (photograph (b)), the phenomenon is not apparent.

The analysis above testifies that the shale ash mineral admixture can enhance the hcp-aggregate interface, hence the increase in the strength of concrete.

Conclusions

1. The shale ash is a type of pozzolanic material, it contains soluble SiO_2 and soluble Al_2O_3, and is chemically reactive. When its specific surface area is up to 6000-8000 cm^2/g, it can increase the strength of concrete.
2. When the admixture is made of shale ash and $CaSO_4 \cdot \frac{1}{2} H_2O$and is used to replace up to 10% by weight of cement, it can increase the strength of concrete by 5 to 10% at 7 days and 28 days, by 10 to 15% at 56 days as compared with the control concrete.
3. Shale ash is effective in acting as the carrier for superplasticizer and other chemical admixtures to produce carrier fluidifying agent which retains the slump of concrete. When 1.5% of carrier fluidifying agent was added to the concrete, the slump can be maintained for 90 minutes.
4. The main strengthening mechanism of shale ash in concrete is that the soluble SiO_2 and Al_2O_3 can react with $Ca(OH)_2$ released during the hydration of cement to produce C-S-H gel and aluminate gel, thus enhancing the inner structure of hcp, decreasing the volume of pores larger than 100nm, and raising the content of micro-pores less than 50nm in

hcp and densifying the hcp structure. Furthermore, it can also improve the interface structure between the aggregate and hcp, minimizing the accumulation and orientation of the crystal $Ca(OH)_2$ in the interface, hence increasing the strength of concrete.

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