

INVESTIGATION ON THE PORTLAND POZZOLANA  
CEMENT WITH MORE SHALE ASH CONTENT

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ABSTRACT

The retort residue abandoned by shale oil plant of Maoming Petroleum Industry Corporation is burnt again at 800~1000°C, makes a high activity admixture applied in cement industry. During grinding cement, putting in 40~50% high activity shale ash as an admixture and adding a kind of surface active agent, a portland pozzolana cement that conform to the Chinese State Standard is produced.

Producing this portland pozzolana cement with more shale ash possesses the better economic and environmental effect, benefits the development of oil shale industry.

1. PROBLEM REPRESENTED

In China, producing portland pozzolana cement with retort residue abandoned by shale oil plant, as an admixture, has had many years. Experience represents there are mainly two existent problems in producing portland pozzolana cement with the reburned retort residue of oil shale; 1. The pozzolanic activity of the retort residue is lower.

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★ This project is completed by Oil Shale Ash Research Group of Engineering Construction Technology Institute of Petroleum Industry Ministry and Maoming Petroleum Industry Co. of China General Petrochemistry Co.

As an admixture, putting it in cement will decrease mostly the cement mark. It isn't benefit in economy. 2. Because the retort residue has porous structure and bigger inner specific surface, it affects the water requirement, drying-shrinkage and abrasion resistance of cement after putting it into cement. Therefore, the shale ash of shale ash portland cement in China is not over 30% as the same content as "Oil Shale Cement" in Germany and "Shale Ash Cement" in the Soviet Union.

In order to increase the economic effect of oil shale industry and improve environment and the utilization efficiency of shale ash, we increase shale ash content of portland pozzolana cement to 40~50% and at the same time, improve the defect of the lower early strength of cement, more drying-shrinkage and lower abrasion resistance etc. by using of activated shale ash and surface activator and produce a type of shale ash pozzolana cement with more shale ash which meets Chinese State Standard GB 1344.

## 2. THE THERMAL ACTIVATING ON RETORT RESIDUE OF OIL SHALE ASH

We take the retort residue from the bottom of furnace of Maoming Petroleum Industry Corporation, the brick red shale ash of passing through self-burning and oxidation which is abandoned and the specimen of the retort residue burned at 600~1000°C in electric oven to carry on physical, chemical tests; x-ray diffraction, DAT, infrared spectrometry, scanning electron microscope, photomicroscope analyses and pozzolanaic activity tests. The results are shown in Table 1, 2 and Fig 1, 2, 3.

Table 1, The chemical compositions of Maoming shale ash(%)

No	Sampling position	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	LOI
M	Shale oil plant	51.7	9.21	20.10	0.66	1.02	14.46
C1	South abandoned-field	56.87	10.26	22.23	0.46	1.08	3.08
C3	North abandoned-field   Lu Chuang	58.56	10.72	22.23	0.57	0.86	2.00
C6	North abandoned-field   Tian An	58.56	10.3	21.03	0.60	0.97	5.33

Table 2. The mineral compositions of Maoming shale ash

No	Sampling position and treating temperaure	qua- rtz	hema- tite	kaoli- nite	mica	feld- spar	mull- ite	cristo- balite
M	Shale oil plant	+	-	+	+	+	-	-
C3	North abandoned-field Lu chuang	+	+	-	+	-	+	+
M6	M(burnt at 600°C)	+	+	-	+	+	-	-
M7	M(burnt at 700°C)	+	+	-	+	+	-	-
M8	M(burnt at 800°C)	+	+	-	-	+	-	-
M9	M(burnt at 900°C)	+	+	-	-	-	-	-
M10	M(burnt at 1000°C)	+	+	-	-	-	+	-

The research represents the mineral compositions of Maoming shale ash mainly contain kaolinite. Its SO<sub>3</sub> content and LOI meet the needs of pozzolanic admixture of Chinese Standard GB2847-81, but its compressive strength ratio is so lower that it can't directly applied to produce the shale ash cement with more shale ash content. The crystal phases are inversed; The kaolinite is decomposed at 600°C; the mica is decomposed at 800°C; the feldspar is decomposed at over 800°C; the mullite appears at 1000°C. Its best activation temperature is at the inert phases of lower temperature of kaolinite, mica, feldspar etc. being decomposed and the inert phases of higher temperature of mullite, cristobalite etc. having not separated out. At the same time, we can observe that the agglomeration increases, the specific surface decrease, the bulk density is changed more heavily, the colour is changed to darker as the activation temperature increases. By the determination of pozzolanic activity of these shale ash specimen, we have got that there is a activation temperature range at 600~1000°C. The best activation temperature is 850°C. Treating shale ash at this temperature range may increase its compressive strength ratio to 70 %, or more, become a kind of high activated pozzolanic admixture.

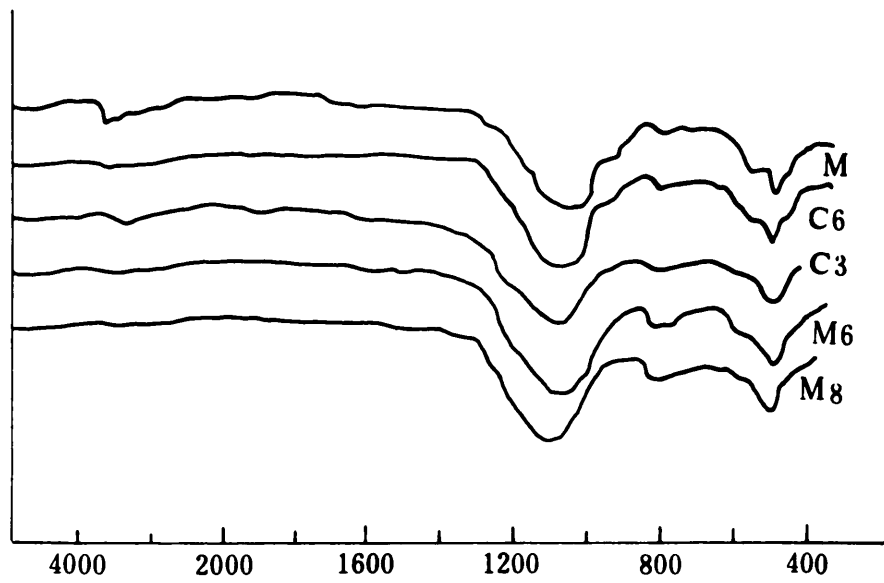


Fig 1. Infrared spectrum of Maoming shale ash

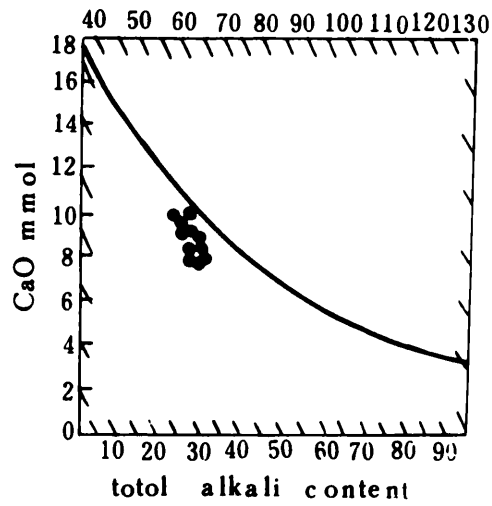


Fig 2. The pozzolanic activity of shale ash

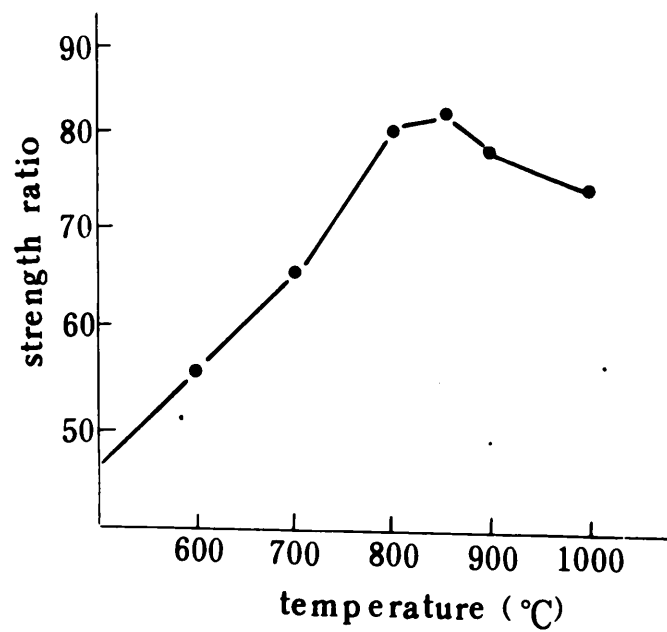


Fig 3. The Thermal activity curves of Maoming shale ash

### 3. THE APPLICATION OF THE SURFACE ACTIVE AGENT

In order to improve the properties of cement completely, we put a type of surface active agent into mill during grinding shale ash cement with more shale ash content. The composition of this type of surface active agent is a condensation compound of sodium naphthalenesulfonate and formaldehyde.

The studies represent that putting this type of surface active agent into the shale ash pozzolanic cement with more shale ash content possesses the following actions,

(1) The grinding aid action, The anionic surface active agent accelerates the grinding process of cement particles due to it adsorbs to the cement particles and its surface of micro-cracks, acts as a grinding additives. For example, the cement screenings of 0.08mm decrease from 12% to 7.7% while adding 40% shale ash, decrease from 8% to 5.2% while adding 50% shale ash.

(2) The water reducing action, The anionic surface active agent, acting as adsorption, dispersion, lubrication and moisturisation etc., is able to improve the workability of cement paste and concrete, reduces the water requirement by about 9~10%, so it solves the problem about much more water requirement of pozzolanic cement

(3) The increasing strength action, The physical and chemical studies represent that putting surface active agent in shale ash cement, its hydrated rate is accelerated, the hydrated depth is increased, the potential activity of cement clinker and latent pozzolanic activity of shale ash is taped. The 7 day's strength of this cement is over 30% higher than the basic specimen. The 28 day's strength increases over 20%. So it solves the problem concerning the slower hardening and the lower early strength.

(4) The modifying quality action, Investigation on the microstructure of hardened cement paste has shown out that the whole microcracks are almost full of the second, third hydrated products. The pore size of peak value of cement paste is 31%-34% as large as the basic specimen. Thus, the shrinkage of the pozzolanic cement with 40%-50% shale ash content decreases from 0.152-0.155% without surface active agent to 0.10-0.11% with surface active agent. The abrasion loss in

decreases from 2.34-2.98% to 1.0%, approaching that of portland cement.

Besides these, this cement possesses the lower heat of hydration and better corrosion-resisting etc.

#### 4. CONCLUSION

(1) Using the latent heat of Maoming retort residue, burning it again is able to produce a high-activated pozzolanic admixture. The burning temperature is at 800-1000°C.

(2) During grinding cement, putting 40-50% high-activated shale ash and anionic surface active agent is able to produce pozzolanic cement that conforms to Chinese Standards 425 and 525 grade of GB1344 and solve basically the problems about its lower early strength, slower hardening, much more shrinkage, lower abrasion resistance.

(3) Changing original producing process, to produce the pozzolanic cement with more shale ash content will increase 30% more cement products and reduce 20% production costs under the condition which does not increase basically the investment.

#### Reference

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