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Properties and microstructure of the hardened alkali-activated red mud–slag cementitious material

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Abstract

A new kind of alkali–slag–red mud cementitious (ASRC) material, with both high early and ultimate strength and excellent resistance against chemical attacks, has been developed by the introduction of composite solid alkali activator into slag–red mud mixture system. Tests on strength development and other properties such as resistance against carbonation, simulated seawater, diluted acid, sulfate solution and freeze and thaw cycles of the ASRC cement were carried out and the results were reported in this paper. Meanwhile, the microstructure of the hardened ASRC cement paste, such as porosity and pore size distribution, and morphological characteristics of the resultant cement stone were also analyzed with the aid of MIP, SEM, etc. The results showed that the hardened cement paste had almost integrated and very compacted structure, more appropriate pore structure and less coarse crystallized products, which were believed to be the physical reasons for its high early and ultimate strength and good resistance against chemical attacks.

Keywords: Alkali-activated cement; Hydration products; Granulated blast-furnace slag; Red mud; Microstructure

1. Introduction

The titled alkali–slag–red mud cement (ASRC) belongs to clinker free cementitious material, which is made from alkali activator, blast-furnace slag and red mud in designed proportion. The similar cementitious material includes alkali-activated slag cement, alkali-activated phosphorous slag cement, alkali-activated slag–fly ash cement and alkali-activated slag–pozzolan cement. It was believed that the alkali-activated cementitious material was first investigated and invented by Glukhovsky [1]. Research activities in this area were carried out later in France, America, Poland, etc. [2–4] and also carried out in China in 1980s [5–8]. So far, some special characteristics of the alkali-activated cementitious material much different from the Portland cement, such as high early and ultimate strength development and excellent resistance to chemical attacks, have been recognized and paid a lot of interest by scientists in cement and concrete research area. However, the research activities so far were mostly concentrated on the alkali-activated slag cement system compared with other similar systems. On other hand, the high price and shortage in supply of blast-furnace slag as the major raw material of the alkali-activated slag cement became a big obstruction to the large-scale application of alkali-activated slag cement in China. The attempt to use other kinds of industrial waste materials as the replacement of blast-furnace slag for making low slag content alkali-activated cementitious materials, therefore, becomes an interesting and practical research subject in China. Meanwhile, the red mud discarded from alumina refining plant was almost remaining in nonrecycled state, except very little use in the manufacture of Portland cement clinker as the replacement for clay. Gong and Yang [9] reported that ASRC was developed using liquid state water glass as an alkali activator and sodium phosphate as a setting retarder. The present authors developed ASRC cement by the introduction of solid composite alkali activator into slag–red mud mixture system instead of the liquid water glass, based on the previous experiments [9–13]. It was suggested [14] that the low Ca/Si ratio of C-S-H and lack of $Ca(OH)_2$ and AFt-like hydration products in hardened cement paste is a major chemical reason for the good physical properties and

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Table 1
Chemical composition of slag and red mud used in experiments (%)

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	Ig.loss	$\sum$
Slag	33.80	14.14	1.22	42.82	5.42	0.34	–	–	0.44	98.78
Red mud	17.75	7.17	9.46	38.69	1.51	2.41	3.23	0.50	16.38	97.10

excellent chemical resistance of the ASRC cement. This paper here reported the experimental results on the physical properties and the microstructure of the hardened ASRC cement paste. The relationships between the good performance of the ASRC hardened cement paste and its microstructure are discussed.

2. Raw materials and test methods

2.1. Raw materials

Red mud used in experiments was an industrial waste from Shan Dong alumina refining plant, with 0.080 mm sieve residue 4.0% and Blaine specific surface area 380 m^2/kg. Slag was granulated blast-furnace slag from Jinan steel refining plant, with 0.080 mm sieve residue 6.0% and Blaine specific surface area 355 m^2/kg. The chemical composition of slag and red mud is listed in Table 1. X-ray diffraction and electron microscopy analysis showed that the slag mostly comprised a vitrified phase, and the red mud (RM) contained amorphous silica aluminate phase and β-C_2S, α-Fe_2O_3, calcite and $CaTiO_3$. The alkali activator is composed of solid water glass (NS) with modulus 1.2 and sodium aluminate clinker (NA), with 0.080 mm sieve residue 5.0%.

A 525 ordinary Portland cement (OPC) in accordance with China standard GB 175-1992 was selected as the reference in all the tests of strength development and resistance against various chemical attacks of ASRC cement. The physical properties and some technical parameters of the selected Portland cement are listed in Table 2.

2.2. Specimen preparation and testing conditions

2.2.1. Preparation of hardened cement paste

ASRC cement with the proportion as listed in Table 3 was used for preparation of hardened cement paste specimens. It was also used in tests of strength development and resistance to various chemical attacks.

Table 3
Raw material proportion of ASRC cement used in experiments (%)

Blast-furnace slag	Red mud	NS[a]	NA[a]
70	30	8	6

[a] Activators are measured on the base of sum of slag and red mud.

Hardened cement paste specimens were prepared from both ASRC cement and Portland cement in water/cement ratio 0.5 and curing in fog room at 20±3 °C first for 24 h followed by curing in water at 20±2 °C. The hydration process of the specimens was stopped by alcohol drenching at different prescribed curing ages, and the hardened cement paste specimens were analyzed by means of SEM observation and MIP measurement.

2.2.2. Testing conditions

(1) SEM observation was carried out on H-800 analysis electron microscope for morphology observation of hardened cement paste.
(2) MIP measurement was carried out on Quantanchrome Auto/60 automatic mercury scanning porosimeter, with scanning range of 0–60 kPa in pressure and 4 nm to 15 μm in pore size.
(3) Tests on strength development were carried out according to China Standard GB 177-85, with water/cement ratio 0.46 for ASRC cement and 0.44 for Portland cement and cement/sand ratio 1:2.5. Mortar specimens in size 40×40×160 mm were first cured in fog room at 20±3 °C for 24 h after demoulding and then followed by water curing at 20±2 °C until the prescribed curing age.

3. Results and discussion

3.1. Strength development and resistance against chemical attacks

3.1.1. General physical properties

The general physical properties of ASRC cement are listed in Table 4.

The ASRC cement shows a lower density, a larger amount of water demand, a larger ignition loss, a shorter

Table 2
Physical properties and technical parameters of the 525 OPC used as reference in tests

Additive (%)	Acid residue (%)	MgO (%)	SO_3 (%)	Ig.loss (%)	Fineness ($R_{80\mu}$) (%)	Soundness	Setting time		Strength (MPa)			
							Initial	Final	Bending		Compressive	
									3 days	28 days	3 days	28 days
6.5	0.55	1.3	1.9	1.5	2.0	Good	3:01	4:17	5.8	8.9	26.2	58.2

Table 4
Physical properties of the alkali-activated slag–red mud cement

Cement	Color	Density (kg/m^3)	Specific surface area (m^2/kg)	Consistency (%)	Initial setting	Final setting	Soundness	Ig.loss (%)
ASRC	Red gray	2.80	370	27	1:02	1:35	Good	5.5

setting time and interval between initial and final setting as compared with OPC.

3.1.2. Strength development

Test results on the strength development of ASRC cement according to the China standard GB177-85 are listed in Table 5.

3.1.3. Resistance to carbonation

Enhanced carbonation condition was employed in the test of carbonation of ASRC cement, with the surrounding air relative humidity 52% and supersaturation of CO_2 concentration maintained by the continued supplementation of CO_2 gas as compared with the 525 OPC. The resistance of the cement against carbonation attack was judged according to both the ratio of the compressive and bending strength after enhanced carbonation for 28 days to those before carbonation and the depth of the carbonation frontier entered from the surface of the tested specimen, which are both listed in Tables 6 and 7, respectively.

3.1.4. Resistance to various corrosive media

Tests on the resistance of ASRC cement to the chemical attacks caused by various corrosive media in state of water solution were carried out. Corrosive media used in tests include 3% Na_2SO_4 water solution, 3% $MgSO_4$ water solution, 3% $MgCl_2$ water solution, 3% NaCl water solution and simulated seawater with composition of 0.7% NaCl, 0.32% $MgCl_2$, 0.22% $MgSO_4$ and 0.13% $CaSO_4$. The resistance of the tested specimen was evaluated by the ratio of its fractural strength cured in water to that subjected to corrosive solution, i.e., $F=R_{f\ solution}/R_{f\ water}$, which is defined as resistance coefficient. The test results are listed in Table 8.

3.1.5. Resistance to freeze and thaw cycles

Test results of the resistance against freeze and thaw of ASRC cement after 13, 25, and 50 cycles are listed in Table 9.

It is obvious that the titled ASRC cement stone has almost comparable properties of strength development with 525 OPC and better other properties such as

Table 5
Mortar strength development of ASRC cement with curing age

Bending strength (MPa)						Compressive strength (MPa)					
1 day	3 days	7 days	28 days	90 days	180 days	1 day	3 days	7 days	28 days	90 days	180 days
3.3	4.9	5.5	8.4	9.1	9.9	20.0	28.1	36.5	56.0	65.0	66.5

Table 6
Strength changes of ASRC cement after 28 days enhanced carbonation

Cement	Bending strength (MPa)			Compressive strength (MPa)		
	Before	After	Ratio	Before	After	Ratio
ASRC	7.6	6.9	0.91	48.6	47.6	0.98
Ref.	7.7	6.8	0.88	44.4	40.4	0.91

Table 7
Carbonation depth of ASRC cement after 7, 14 and 28 days enhanced carbonation

Cement	Carbonation depth (mm)		
	7 days	14 days	28 days
ASRC	1.0	1.5	1.7
Ref.	1.5	1.9	2.2

Table 8
Resistance of the ASRC against chemical attacks caused by different corrosive solutions

Cement		H_2O	Na_2SO_4	$MgSO_4$	$MgCl_2$	NaCl	Simulated seawater	Diluted HCl
ASRC	Bending strength (MPa)	7.6	7.7	9.0	8.3	7.3	8.9	7.7
	Resistance coefficient	–	1.01	1.19	1.09	0.96	1.17	1.01
Ref.	Bending strength (MPa)	7.7	7.3	8.7	8.6	6.5	7.9	7.3
	Resistance coefficient	–	0.95	1.13	1.12	0.84	1.03	0.95

Table 9
Mass loss and strength loss of the ASRC cement mortar after varied cycles of freeze and thaw (%)

Cement	After 13 cycles		After 25 cycles		After 50 cycles	
	Mass loss	Rate of mass loss	Mass loss	Rate of mass loss	Mass loss	Rate of mass loss
ASRC	0.9	0.8	1.1	1.0	2.0	2.7
Ref.	1.2	1.3	1.8	1.5	2.9	3.3

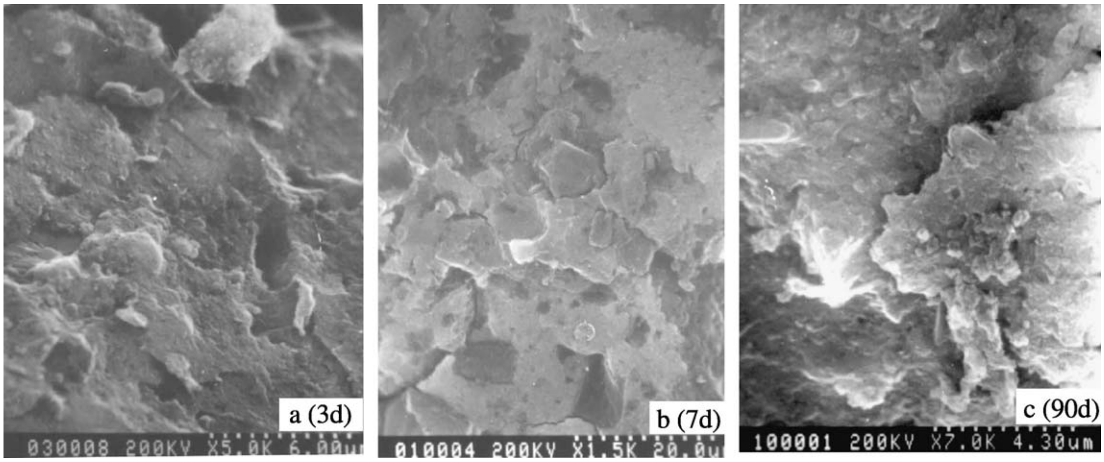

Fig. 1. Microstructure of the hardened ASRC cement paste with different curing ages under SEM observation.

resistance against carbonation, simulated seawater, diluted acid, sulfate solution and freeze and thaw cycles.

3.2. Microstructure of the hardened cement paste

3.2.1. Results of SEM observation

Fig. 1a–c shows the microstructure of the hardened ASRC cement paste. As a comparison, Fig. 2a–c shows the microstructure of the hardened Portland cement paste with different curing ages. It can be obviously noticed that there exists quite large difference in the microstructure of the hardened cement paste between ASRC cement and OPC. The former generally exhibits compacted and continued integrated morphological characteristics, while the latter exhibits some incompact area, i.e., remains some porous area that may be caused by the coarse hydration products such as AFt and $Ca(OH)_2$. Investigations [14] on the hydration products have also proved that ASRC cement generally yields C-S-H with lower Ca/Si molar ratio, nearly amorphous and with very fine particle size as its major products, but does not form coarse hydration products like AFt and $Ca(OH)_2$, which are generally formed in the hydration system of Portland cement.

It is believed that this morphological characteristic of the hardened ASRC cement paste may comprise another major physical reason contributing to its good strength performance and excellent resistance against various chemical attacks besides the chemical reason relative to the composition of C-S-H gel and microstructure of its hydration products.

3.2.2. Results of MIP measurements

MIP measurement was applied to determine the pore structure difference, i.e., difference in porosity and pore size distribution, to see the difference between the microstructure of the hardened cement paste of ASRC cement and OPC. Table 10 shows the results of the MIP measurements on the hardened cement paste specimens

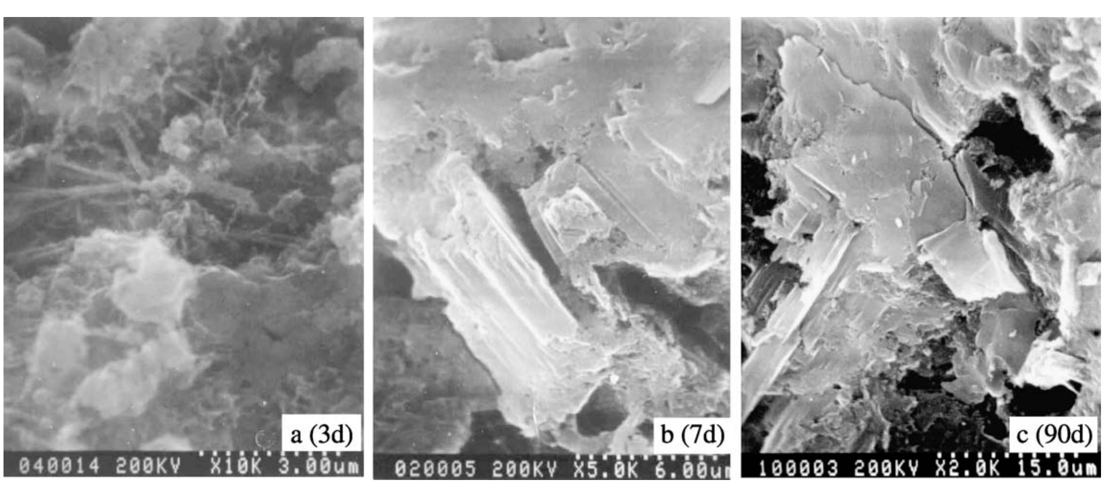

Fig. 2. Microstructure of the hardened Portland cement paste with different curing ages under SEM observation.

Table 10
Porosity and pore size distribution of hardened ASRC cement paste at different curing ages

Curing ages and type of cement		3 days		7 days		28 days	
		Ref.	ASRC	Ref.	ASRC	Ref.	ASRC
Porosity (%)		37.42	36.12	28.42	26.82	24.25	23.30
Pore size distribution	>50 nm	32.54	30.22	30.76	27.12	20.88	15.05
	10–50 nm	42.21	43.24	38.00	39.42	43.91	44.63
	<10 nm	25.25	26.34	31.24	33.46	35.21	40.32

with different curing ages of both ASRC cement and OPC.

Data in Table 10 indicate that hardened ASRC cement paste has lower total porosity, less portion of larger pore and more portion of smaller pore, as compared with those of hardened Portland cement paste, which is in a very good coincidence with the above test results from SEM observation.

4. Conclusions

(1) The titled ASRC cement has high early and ultimate strength and a good strength development, without any trend of strength rebounding with curing ages.
(2) ASRC cement has good resistance against various chemical attacks and freeze and thaw cycles.
(3) The hardened ASRC cement paste has lower total porosity, less portion of larger pore and more portion of smaller pore, as compared with those of hardened Portland cement paste.
(4) The hardened ASRC cement paste has more compacted and continued more integrated microstructure than hardened Portland cement paste.
(5) The denser microstructure and the better pore structure are the physical reasons contributing to the good strength performance and resistance against chemical attacks.

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