Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(4):845-849

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Research on hydration mechanism of slag composite cementitious material mixed with NaCl

Chengbin Liu[1,2*], Xiuqing Gao[1] and Yichao Zhou[2]

[1]*Department of Hydraulic and Architectural Engineering, Beijing Vocational College of Agriculture, Beijing, China*
[2]*School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing, China*

ABSTRACT

The main purpose of this article is to replace NaOH with NaCl as slag hydration activator, and preliminarily study the hydration mechanism. By strength test, EDS and XRD analysis, we studied the hydration products of slag composite cementitious material mixed with NaCl. The strength test results showed that the N-SM agent's strength can reach 32.5 P•S standard. The EDS test results proved that the Cl^- in NaCl reacted with the slag composite cementitious material and generated crystal of $3CaO•Al_2O_3•(0.5CaCl_2•0.5CaSO_4)•12H_2O$. At the same time, the Na^+ generated NaOH and provided better alkaline environment to hydration of slag. The XRD test results proved that the slag generated zeolite mineral $0.8CaO•0.2Na_2O•Al_2O_3$ and C-S-H gel (Ca/Si=2) under alkaline environment.

Keywords: strength, crystal, kuzel's salt, zeolite, gel.

INTRODUCTION

Blast-furnace slag is amorphous granular particle which is produced by quickly cooling melted mineral slag by air or water, when iron ore, coke, limestone or dolomite is reacted in blast furnace under temperature of 1500℃ or so during deoxygenization process [1]. The steel production of China reached 350 million tons in 2005, and the blast-furnace slag reached 160 million tons also [2-4]. Utilizing blast-furnace slag will turn the waste to treasure and reduce environment pollution and land fill areas, and achieve economic and social benefits at the same time. This field has already attracted attention all over the world and is actively researched and developed [5]. Before the 1970s, blast-furnace slag was only stacked as industrial waste. With the development of steel industry, the amount of blast-furnace slag turns more and more, which caused serious environment pollution and wasted a lot of resources. With the increasingly world-wide resources scarceness, comprehensive utilization of blast furnace slag has become very essential [6].

The slag hydration needs an alkaline activator. Many scholars have researched the hydration mechanism of alkaline slag cementitious material [6-9], but the final hydrated products are difficult to determined [10-13]. Alkaline activator mainly adopts NaOH or KOH solution, but this article used NaCl instead of NaOH or KOH as the activator, which is not reported in other literatures yet.

This article studied the hydration mechanism of slag composite cementitious material mixed with NaCl (N-SM agent). Based on strength test, SEM test, EDS and the XRD analysis, we studied the hydration products of N-SM agent. The preliminary study found that the slag composite cementitious material reacted with NaCl, and generated flaky crystals and needle-like crystals $3CaO•Al_2O_3•(0.5CaCl_2•0.5CaSO_4)•12H_2O$, C-S-H gel and zeolite minerals, and therefore greatly increased the strength.

EXPERIMENTAL SECTION

Raw Materials

The N-SM agent is composed of slag, gypsum, lime, magnesite and NaCl in this experiment. The density of the slag is 2.79g/cm^3 and the specific surface area is around 600m^2/kg. The main chemical composition of slag is shown in Table 1.

Table 1 The Chemical Composition of Slag

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Fe_3O_4	MnO	SO_3	TiO_2
Mass(%)	34.46	13.00	3.21	8.64	38.00	0.38	0.29	0.68	0.84

Test Block Preparation

(1) Make 40mm*40mm*160mm mortar test block with N-SM agent and the tests are executed according to Chinese Standard *Method of testing cements-Determination of strength (ISO) (GB/T17671-1999).*

(2)In order to observe the microstructure more clearly, use the N-SM agent to prepare some 40mm*40mm*160mm paste block and the ratio of water to cementitious material is 0.5.

Experimental Methods

(1)Strength experiment of mortar block: Cure the mortar test block for 3d and 28d under standard conditions, and then measure the flexural strength and compressive strength.

(2)EDS analysis experiment: Calculate chemical formula of the hydration products based on EDS analysis data.

(3)XRD analysis experiment: Determine the hydration products through XRD analysis of the paste block which had been cured for 28d.

RESULTS AND DISCUSSION

The Strength Feature

Cure the mortar test block for 3d and 28d under standard conditions, and then measure the flexural strength and compressive strength. The test results are shown as Table 2.

Table 2 The Strength of Mortar Test Block

Item	Compressive strength(MPa)		Flexural strength(MPa)	
	3d	28d	3d	28d
N-SM agent	10.84	34.58	3.15	6.82

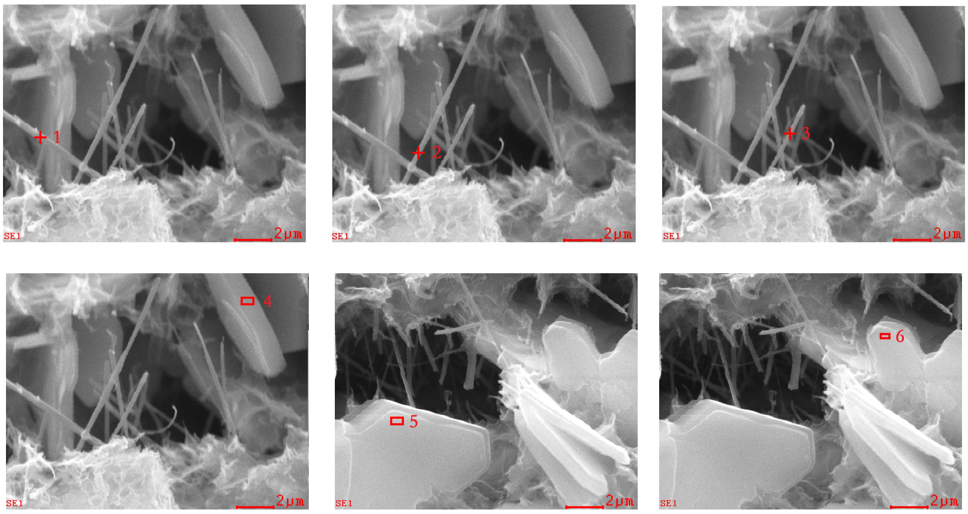

Fig. 1 The energy-dispersive X-ray analysis photos

Table 2 shows that the compressive strength and flexural strength of the mortar test block are growing with the increasing age. The N-SM agent’s strength can reach the 32.5 P•S standard according to Chinese Standard *Common Portland Cement (GB175-2007).*

EDS Analysis Result

Do EDS analysis to the block and the test results are as shown as Fig.1 and Fig. 2.

Measure and calculate the chemical composition of the flaky crystals and needle-like crystals in Fig.1 and the results are shown in Fig.2 and Table 3.

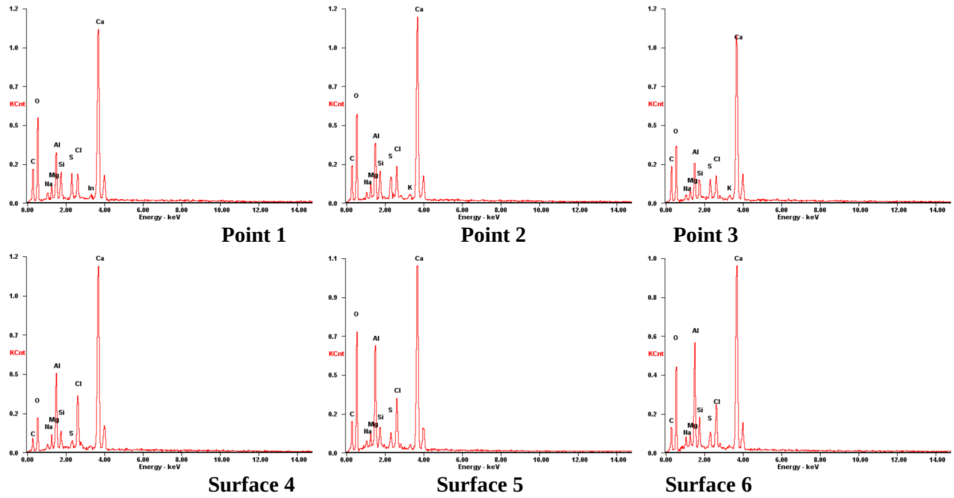

Fig. 2 The energy-dispersive X-ray analysis patterns

Table 3 The energy-dispersive X-ray analysis results of point 1-3 and surface 4-6 (Weight%)

Eelement	O	Na	Mg	Al	Si	S	Cl	Ca
Point 1	34.25	1.28	1.76	6.25	3.20	2.54	3.56	28.52
Point 2	33.48	1.28	2.00	5.34	3.06	2.41	3.32	29.06
Point 3	30.01	0.96	1.64	4.62	2.60	2.36	3.63	33.15
Surface 4	23.30	1.18	1.96	9.61	2.71	1.42	9.09	40.39
Surface 5	38.44	1.07	1.15	9.15	2.00	1.25	5.20	26.26
Surface 6	35.10	1.39	1.30	9.33	2.78	1.83	4.95	28.77

Judging from data in table 3, the Si content is quite high, which is quite possibly due to that the measurement point diameter of spectrum analyzer is larger than the compounds containing Cl^-, so each testing region is mixed with other compounds containing C-S-H gel and therefore the elements mass presents some errors. We need to eliminate the influence of this cause as much as possible[14]. According to Chemistry of Cement and Concrete[15], the Ca/Si in C-S-H gel is 0.8-2, thus we assume that all Si ions are turned to C-S-H gel (Ca/Si=2) and subtract the mass of corresponding Si, Ca, and then calculate the remaining mass ratio of Al, Cl, and Ca. The calculated results are shown in Table 4.

Table 4 shows that if the hydration product is $3CaO{\bullet}Al_2O_3{\bullet}CaCl_2{\bullet}10H_2O$, the mass ratio of Al: Cl: Ca is 1: 1.31: 2.97, and if the hydration products is $3CaO{\bullet}Al_2O_3{\bullet}CaSO_4{\bullet}12H_2O$, the mass ratio of Al: S: Ca is 1: 0.59: 2.97, so the hydration products containing Cl^- are Calcium Aluminate Chlorine ($3CaO{\bullet}Al_2O_3{\bullet}CaCl_2{\bullet}nH_2O$) and C-S-H gel (Ca/Si=2) at point 1, 2, 3 and the surface 4, 5, 6[15]. The flaky crystals and the needle-like crystals are very close to $3CaO{\bullet}Al_2O_3(0.5CaCl_2{\bullet}0.5CaSO_4){\bullet}12H_2O$ (called Kuzel's salt) and the mass ratio of Al: S: Cl: Ca is 1: 0.30: 0.66: 2.97, the result is relatively close to the calculated results in Table 4.

According to related literature[16], the Cl^- reacts with mineral admixture and generates chloroaluminate, whose theoretical composition is $3CaO{\bullet}Al_2O_3{\bullet}CaCl_2{\bullet}10H_2O$ which is also known as Friedel's salt and is a compound of AFm family. The AFm family has various compounds whose compositions are very different. The typical compounds include $3CaO{\bullet}Al_2O_3{\bullet}CaCl_2{\bullet}nH_2O$, $3CaO{\bullet}Al_2O_3{\bullet}CaSO_4{\bullet}nH_2O$ and $3CaO{\bullet}Al_2O_3{\bullet}CaCO_3{\bullet}nH_2O$, etc.. In actual hydration process, because there are various ions, the hydration products might have several kinds of compounds and might also include several complex compounds whose ions are substituted with each other. Under ideal conditions, the large crystal of AFm is a six-square flake and if it is not formed completely, the crystal would be small needle-like and flaky body. However in any case, the Cl^- in the NaCl has been reacted with the slag composite cementitious material, and generated the compound containing Cl^- in the experiment. At the same time, the Na^+ generated NaOH and provided better alkaline environment to the hydration of slag. This may be one of the causes that the N-SM agent has high strength.

Table 4 The chemical composition of point 1-3 and surface 4-6 (Weight%)

	Element	O	Na	Mg	Al	Si	S	Cl	Ca
Point 1	Mass of each element	34.25	1.28	1.76	6.25	3.20	2.54	3.56	28.52
	Mass of Si and Ca in the C-S-H					3.20			9.14
	Mass of remaining elements	34.25	1.28	1.76	6.25	0	2.54	3.56	19.38
	Mass ratio of some elements				1		0.41	0.57	3.10
Point 2	Mass of each element	33.48	1.28	2.00	5.34	3.06	2.41	3.32	29.06
	Mass of Si and Ca in the C-S-H					3.06			8.74
	Mass of remaining elements	33.48	1.28	2.00	5.34	0	2.41	3.32	20.32
	Mass ratio of some elements				1		0.45	0.62	3.81
Point 3	Mass of each element	30.01	0.96	1.64	4.62	2.60	2.36	3.63	33.15
	Mass of Si and Ca in the C-S-H					2.60			7.43
	Mass of remaining elements	30.01	0.96	1.64	4.62	0	2.36	3.63	25.72
	Mass ratio of some elements				1		0.51	0.79	5.57
Surface 4	Mass of each element	23.30	1.18	1.96	9.61	2.71	1.42	9.09	40.39
	Mass of Si and Ca in the C-S-H					2.71			7.74
	Mass of remaining elements	23.30	1.18	1.96	9.61	0	1.42	9.09	32.65
	Mass ratio of some elements				1		0.15	0.95	3.40
Surface 5	Mass of each element	38.44	1.07	1.15	9.15	2.00	1.25	5.20	26.26
	Mass of Si and Ca in the C-S-H					2.00			5.71
	Mass of remaining elements	38.44	1.07	1.15	9.15	0	1.25	5.20	20.55
	Mass ratio of some elements				1		0.14	0.57	2.25
Surface 6	Mass of each element	35.10	1.39	1.30	9.33	2.78	1.83	4.95	28.77
	Mass of Si and Ca in the C-S-H					2.78			7.94
	Mass of remaining elements	35.10	1.39	1.30	9.33	0	1.83	4.95	20.83
	Mass ratio of some elements				1		0.20	0.53	2.23

XRD Analysis Result

Use the above test block to do the XRD analysis experiment and the test results are shown in Fig. 4.

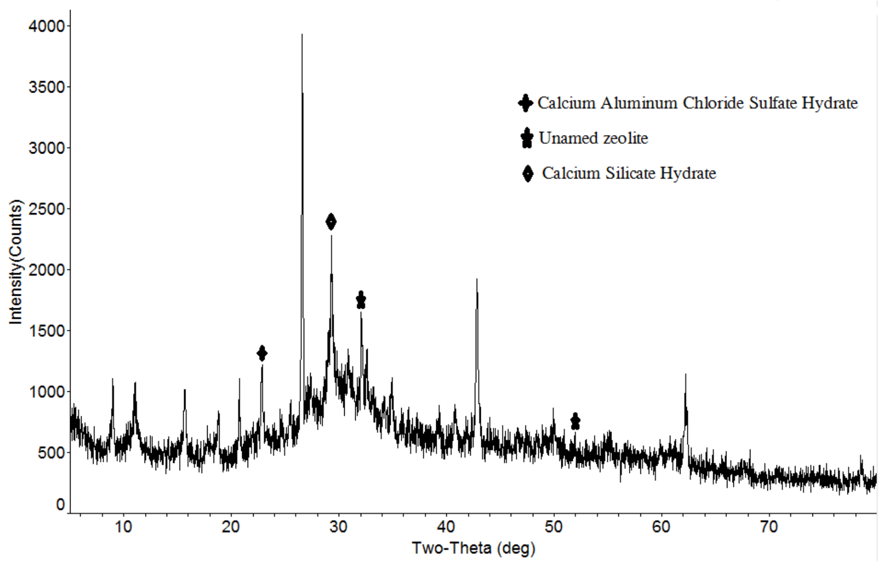

Fig. 4 The X-ray diffraction of N-SM paste block

Fig. 4 shows that the hydration products of the N-SM agent contain $3CaO•Al_2O_3•(0.5CaCl_2•0.5CaSO_4)•12H_2O$ (Calcium Aluminum Chloride Sulfate Hydrate), $Ca_2SiO_4•nH_2O$ (Calcium Silicate Hydrate), and $0.8CaO•0.2Na_2O•Al_2O_3•3SiO_2•6H_2O$ (Unamed zeolite), etc. . The results verify the correctness of the EDS analysis.

Hydration Mechanism Analysis

The hydration reaction of the N-SM agent uses NaCl as main activator. Based on the hydration products, the whole reaction process is given as below:

(1)The NaCl reacts with slag and gypsum:

$NaCl + CaO + Al_2O_3 + CaSO_4 + H_2O \rightarrow 3CaO•Al_2O_3•(0.5CaCl_2•0.5CaSO_4) •12H_2O + NaOH$.

The hydration process generates not only the flaky crystals and needle-like crystals $3CaO•Al_2O_3•(0.5CaCl_2•0.5CaSO_4)•12H_2O$ which contributes to the strength, but also generates the alkali NaOH which provides the alkaline environment to the slag hydration.

(2)The hydration process of slag under alkaline environment:

According to the hydration product $0.8CaO \cdot 0.2Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 6H_2O$, the slag reacting with the NaOH is as below:
$CaO + SiO_2 + Al_2O_3 + NaOH + H_2O \rightarrow 0.8CaO \cdot 0.2Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 6H_2O$.

(3)The slag reacts with active SiO_2 and Al_2O_3:
$2CaO + SiO_2 + n\ H_2O \rightarrow Ca_2SiO_4 \cdot nH_2O$.

The three hydration processes of the N-SM agent generates Kuzel's salt, zeolite and C-S-H gel and these hydration products make the N-SM agent to have high strength.

CONCLUSION

To sum up, the conclusions are as below:
(1)The N-SM agent's strength can reach the 32.5 P•S standard.

(2)The EDS test results prove that the Cl^- in the NaCl reacted with the slag composite cementitious material and generated the flaky crystals and needle-like crystals $3CaO \cdot Al_2O_3 \cdot (0.5CaCl_2 \cdot 0.5CaSO_4) \cdot 12H_2O$. At the same time, the Na^+ generated NaOH and provided better alkaline environment to the slag hydration.

(3) The XRD test results prove that the slag generated zeolite mineral $0.8CaO \cdot 0.2Na_2O \cdot Al_2O_3$ under alkaline environment and generated C-S-H gel (Ca/Si=2) at the same time.

Acknowledgements
All of the authors are financially supported by the School-level Research Project of Beijing Vocational College of Agriculture (No. XY-YF-13-28) and the Civil Engineering Professional Group Construction Project of Beijing Vocational College of Agriculture (2013).

REFERENCES

[1]Zhao Qing-lin; Zhou Ming-kai; Xu Mu-hui. *Cement Guide for New Epoch*, **2008**, (6), 13-15.
[2]CAO De-qiu; LI Can-hua. *Iron & Steel Scrap of China*, **2006**, (5), 26-29.
[3]ZHU Gui-lin; SUN Shu-shan. *China Cement*, **2006**, (7), 33-35.
[4]HUANG Wen-qiao. *Concrete*, **2006**, (2), 66-69.
[5]Slot R J; John A. *Journal of the Canadian Ceramic Society*, **1976**, (45), 63-67.
[6]Liu Chengbin. *Advanced Materials Research*, **2012**, 518-523, 3496-3500.
[7]Purdon A O. *J Soc Chem Ind*, **1940**, (59), 191
[8]Jiang Weimin. *The Pennsylvania State University*, **1997**.
[9]Krivenko P V. *Cem, New Delhi*, **1992**, 4, 482.
[10]Richardson I G. *Cement & Concrete Composites*, **2000**, (22), 97-113.
[11]Kutti T. *Proc Int Congr, On the Chemistry of Cement, New Delhi*, **1992**, 4, 468-474.
[12]Yu Shangren; Wang Wumin. *Journal of The Chinese Ceramic Society*, **1990**, 18(2), 19-25.
[13]Wu Chengning; Zhang Yanchi; Hu Zhinong. *Journal of The Chinese Ceramic Society*, **1993**, 21(2), 176-179.
[14]CHENG Yin; LI Zhan-guo; DENG xiao-xuan, et al. *Chinese Journal of Geotechnical Engineering*, **2011**, 33(8), 1240-1245.
[15]LEA F M. The chemistry of cementand concrete, 3rd Edition, China Architecture &Building Press, Beijing, **1980**; 189-194
[16]WANG Fu-sheng; ZHU Yuan-na; MA Jin-long, et al. *Bulletin of the Chinese Ceramic Society*, **2009**, 28(4), 784-791.