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Study on the properties of chromium residue-cement matrices (CRCM) and the influences of superplasticizers on chromium(VI)-immobilising capability of cement matrices

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ABSTRACT

The study of cementitious activity of chromium residue (CR) was carried out to formulate the properties of chromium residue-cement matrices (CRCM) by blending CR with Ordinary Portland Cement (OPC). The particle size distribution, microstructures of CR were investigated by some apparatuses, and physical properties, leaching behavior of hexavalent chromium [Cr(VI)] of CRCM were also determined by some experiments. Three types of commonly used superplasticizers (sulphonated acetone formaldehyde superplasticizer (J1), polycarboxylate-based superplasticizer (J2) and naphthalene superplasticizer (J3)) were chosen to investigate their influences on the physical properties and the Cr(VI)-immobilisation in the leachate of the CRCM hardened pastes. The results show that the CR has a certain cementitious activity. The incorporation of CR improves the pore size distribution of CRCM. The Cr(VI) concentrations in the leachate of CRCM significantly decrease by incorporation of J2. Among three superplasticizers, J2 achieves lowest Cr(VI) leaching ratio. Based on this study, it is likely to develop CR as a potential new additive used in cement-based materials.

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1. Introduction

As a result of industrial development, many chemical substances have generated pollution in air, water, and soil. At least 20 metals including chromium are classified as toxic and half of these emitted into the environment in higher quantities that pose risks to human health [1]. Chromium has both beneficial and detrimental properties. In the environment, chromium usually exists in its compounds in the forms of hexavalent chromium [Cr(VI)] or trivalent chromium [Cr(III)], which have different toxicities, mobilities and bioavailabilities [2,3]. Cr(III) is essential in human nutrition (specially in glucose metabolism) as well as for plants and animals at trace concentrations. It is recommended that a daily uptake of 50-100 mg is helpful for human beings, without toxic effects observed even at a higher dosage [4]. It is relatively innocuous and immobile in most environmental systems [5]. In contrast, Cr(VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin [6]. It is known to

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be toxic to human, animals and plants and classified as a carcinogen associated with the risk of respiratory tract cancer [7–11]. Unfortunately, In recent years, due to the extensive use of chromium in industrial processes (such as electroplating, leather tanning, paints and pigments, textile, steel fabrication and production of chromium chemicals), large quantity of Cr(VI)-containing wastes that lead to serious problems and hazardous risks for human health are discharged into the environment. Chromium residue (CR) from chromate plant and metallic chromium production is one of the most hazardous solid wastes because of its high content of dissolvable Cr(VI). The continuous Cr(VI) leaching from CR could cause sustainable contamination to its surrounding.

It was reported that 7 tonnes of CR was produced when 1 tonne of metallic chromium was manufactured, and 1.7–4.2 tonnes of CR were produced when 1 tonne of sodium dichromate was manufactured [12]. Each year, 200–300 thousand tonnes of CR are discharged and the accumulative total amount is no lower than 2 million tonnes [13]. Thus, there is an urgent requirement to treat CR for environmental protection and human health concern.

Many countries have adopted severe restrictions on disposals of CR. Various strategies had been evaluated to deal with the problem of CR waste accumulation and the associated health hazards. Some of the approaches included biosorption, ion exchange, solvent extraction, micelle-enhanced ultra filtration, nanofiltration,

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Fig. 1. XRD spectrum of chromium residue.

adsorption with inorganic sorbent materials, precipitation, stabilization/solidification (S/S), reduction and complexation [14–16]. Among them, S/S technology is favorable [17–21]. In recent years, the most widely used S/S systems are the cement-based materials [22,23]. A major factor is that cement is easy to form a durable, monolithic material that will not leach hazardous components under the disposal conditions [24,25]. Using cement to dispose CR has been investigated in recent years. However, the potential of reusing CR in construction materials are less studied. Some researches show the CR has similar chemical and mineralogical compositions to cement [26-31]. It is possible that CR could be utilized as a kind of resource and developed into a new auxiliary cementitious material in construction engineering. Currently, with the rapid development of construction projects, superplasticizers are widely used in concrete and have become common components of concrete. For the goal of disposal and reuse of CR, the purpose of this study is to investigate the effect of CR on the properties of CRCM and superplasticizers on Cr(VI)-immobilising capability of cement matrices.

2. Experimental

2.1. Raw materials and preparation

The CR was collected from a chemical and industrial plant (Hangzhou, Zhejiang province, China). Its X-ray diffraction (XRD) spectrum is shown in Fig. 1. A class P II 42.5 Ordinary Portland Cement (OPC) was used in this study. The chemical compositions of OPC and CR are given in Table 1. The particle size distribution of CR is given in Fig. 2 and Table 2. As shown in Fig. 2 and Table 2, more than 90% of the particles have a smaller size of 40.690 μ m. Superplasticizers were brought on the market and their properties are reported in Table 3. The mix designs of all samples in this research are listed in Table 4.

Table 1

Main chemical compositions of OPC and chromium residue (wt.%)



Fig. 2. Granularity distribution of chromium residue.

2.2. Experimental procedure

2.2.1. Physical properties test

The water demand for normal consistency and setting time were tested according to Chinese National Standard GB/T1346–2001. For the compressive strength, these pastes were mixed in a standard laboratory mixer, casted into molds of $20 \text{ mm} \times 20 \text{ mm} \times 20 \text{ mm} \cos 20 \text{ mm} \sin 20 \text{ mm} \cos 20$

2.2.2. Leaching test

The leachate was prepared in accordance with Chinese National Standard GB5086.2–1997. Coarse grains were chosen by a 5-mm sieve from the crashed pastes samples after the compressive strength test. Hundred grams coarse grains then were placed into

Table 2

Particle size distribution of chromium residue

Particle diameter (µm)	Volume (%)
<1.336	10
<2.575	25
<6.008	50
<18.840	75
<40.690	90

Table 3

Basic property parameters of superplasticizers

Sample	Color of liquid	Solid content (%)	Commend volume (%)
Sulphonated acetone formaldehyde superplasticizer (J1)	Wine	33	1.0-2.0
Polycarboxylate-based superplasticizer (J2)	Yellow	20	0.5–1.0
Naphthalene superplasticizer (J3)	Brown	40	1.0-2.0

Sample	SiO ₂	Al_2O_3	CaO	MgO	K ₂ O	Fe_2O_3	TiO ₂	SO ₃	T ^a Cr	Cr(VI)
CR ^b	13.10	4.51	22.96	19.68	-	7.89	0.28	-	2.57	0.192
OPC ^c	21.1	5.3	64	1.7	0.7	2.6	0.3	1.7		-

^a T, total.

^b CR, chromium residue.

^c OPC, Ordinary Portland Cement.

Table 4Mixing proportion of samples (%)

Sample	Mixing proportion of sample							
	Cement	Chromium residue	Superplasticizer					
RO	100	0	-					
R1	90	10	-					
R2	80	20	-					
R3	70	30	-					
R4	60	40	-					
R0-J1	100	0	2.0					
R1-J1	90	10	2.0					
R2-J1	80	20	2.0					
R3-J1	70	30	2.0					
R4-J1	60	40	2.0					
R0-J2	100	0	1.0					
R1-J2	90	10	1.0					
R2-J2	80	20	1.0					
R3-J2	70	30	1.0					
R4-J2	60	40	1.0					
R0-J3	100	0	1.6					
R1-J3	90	10	1.6					
R2-J3	80	20	1.6					
R3-J3	70	30	1.6					
R4-J3	60	40	1.6					

a 2000-mL lidded polythene bottle containing 1000 mL of distilled water. The suspension was fixed onto a horizontal vibrator and shook for 8 h at the frequency of 110 ± 10 times per min and with the amplitude of 40 mm. The solution was filtrated with a medium-speed quantitative filter paper after the sedimentation period of 16 h. The pH value of the filtrate was tested immediately and Cr(VI) concentrations were analyzed by a TU-1800PC UV–vis spectrophotometer. The Cr(VI) leaching concentrations test method applied in this research corresponds to the describing in the GB/T15555.4–1995.

2.2.3. pH value test

The pH value of the CR was 10.58, which was experimental determined according to the following EPA Method SW-846 9045C. Five grams of CR was added to 100 mL of distilled water, continuously stirred for 5 min then settled for 15 min. The pH value was tested immediately by Phs-25 Meter.

2.2.4. Pore size distribution

The test for pore size distribution was carried out at the hydration of 28 days. Pore structure was experimental investigated with mercury intrusion porosimeter (MIP). Samples of R0 (control cement matrix) and R3 (matrix contains 30% CR) were collected from the crashed cubes after the compressive strength test. The MIP apparatus was used to determine pore size distribution within a range of 0.002–213 μ m radius.

3. Results and discussion

3.1. Study on cementitious activity of CR

As shown in Table 1, the CR belongs to the system of $CaO-SiO_2-Al_2O_3-Fe_2O_3$, which is quite similar to those of complementary cementitious materials presently commonly used such as granulated blast-furnace slag and coal fly ash. Experimental test result is shown in Fig. 1, the main minerals in chromium residue include: alpha quartz, portlandite, calcite, chromite, periclase, brucite, eskolaite, etc. Some researches reported (Table 5 [32,33]) the mineralogical compositions also include dicalcium silicate (C₂S), calcium aluminoferrite (C₄AF), which are the main cementing activity components of cementitious materials. From the angle of the chemical and mineralogical compositions, CR con-

3.1.1. Method of chemical compositions analysis

The coefficient *K* of granulated blast-furnace slag was calculated based on Chinese National Standard GB/T203–1994:

$$K = [m(\text{CaO}) + m(\text{MgO}) + m(\text{Al}_2\text{O}_3)]/$$
$$[m(\text{SiO}_2) + m(\text{MnO}) + m(\text{TiO}_2)]$$
(1)

where *m* was given in wt.%. According to GB/T203–1994, granulated blast-furnace slag can be regarded as cementitious activity when K > 1.2. Higher *K*-value indicates higher cementitious activity.

K-value of CR was calculated as

$$K = \frac{22.96 + 19.68 + 4.51}{(13.10 + 0.28)} = 3.52 > 1.2$$

As an adoption of the rule above, CR could be regarded as a certain cementitious activity from the point of view of chemical compositions.

3.1.2. Method of compressive strength analysis

According to the test method in Chinese National Standard GB/T2847–2005, the activity coefficient *R* of CR was calculated:

$$R = \left(\frac{f_{c3}}{f_{c0}}\right) \times 100\% \tag{2}$$

where f_{c3} is the compressive strength containing 30% CR at hydration of 28 days and f_{c0} is the compressive strength of OPC at hydration of 28 days.

So, the activity coefficient of CR was calculated as

$$R = \left(\frac{f_{c3}}{f_{c0}}\right) \times 100\% = \left(\frac{72.4}{107.0}\right) \times 100\% = 67.7\%$$

On the basis of the GB/T2847–2005, pozzolanic materials can be regarded as active additive when R > 65%. Thus, the CR could be regarded as cementitious activity from the point of view of compressive strength.

Based on the above discussion, it is likely to think the CR has the potential of cementitious activity. It can be proposed as an activating admixture used in cement-based materials.

3.2. Effect of CR on the physical properties of cement-based materials

The water demand for normal consistency, setting time and compressive strength developments of CRCM are illustrated in Table 6.

Table 5

Main mineralogical compositions of chromium residue [32,33]

Mineralogical name	Formula	Content (%)
Periclase	MgO	20
Dicalcium silicate	β-2CaO·SiO ₂	25
Calcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	25
Calcium chromate	α -Ca(CrO ₂) ₂	5-10
Chrome spinel	(Mg·Fe)(CrO ₂) ₂	5-10
Calcium chromate	CaCrO ₄	1
Sodium chromate, tetrahydrate	$4Na_2CrO_4 \cdot 4H_2O$	2-4
Calcium chromate aluminate	$4CaO \cdot Al_2O_3 \cdot Cr_2O_3 \cdot 12H_2O$	1-3
Basic ferric chromate	Fe(OH)CrO ₄	0.5
Calcium carbonate	CaCO ₃	2-3
Calcium hydrate calcium aluminate	$3CaO \cdot Al_2O_3 \cdot 6H_2O_3$	1

Table 6

Samples	Water demand for	Setting tir	Setting time (min)		^c f _c (MPa)			Ratio of ^c f _c (%)		
	normal consistency (%)	Initial	Final	3 days	7 days	28 days	3 days	7 days	28 days	
RO	25	153	240	66.4	96.2	107.0	100.0	100.0	100.0	
R1	25	174	225	73.4	84.6	93.1	111.0	87.9	87.0	
R2	25	172	262	60.7	72.6	85.9	91.4	75.5	80.3	
R3	24	177	261	58.8	61.5	72.4	88.6	63.9	67.7	
R4	23	172	262	52.2	57.5	66.0	78.6	59.8	61.7	

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 $^{c}f_{c}$, compressive strength.

As shown in Table 6, the CRCM hardened pastes had a slightly lower water demand for normal consistency and a modest retardation of setting time when the proportion of CR rose. The reason could be the cementitious activity of CR was lower than clinker. In addition, compressive strength of matrix R4 with 40% CR was 66.0 MPa at 28 days, 61.7% of control matrix R0, and 52.2 MPa at 3 days, 78.6% of control matrix R0, respectively. It is suggested that CR has a worse influence on compressive strength at 28 days than 3 days.



Fig. 3. Pore size distribution of hardened pastes at the hydration of 28 days ages.

3.3. Pore size distribution of CRCM

The total porosity is an important indicator for evaluating the mechanical properties and leaching potential of solidification matrices. Fig. 3 shows the cumulative pore size distribution of R3 (with 30% CR) in comparison with the control matrix R0, which were cured for 28 days. This is in accordance with the classification of pore size distribution by Feldman [34]. As shown in Fig. 3, the pore size distribution of CRCM shifted toward smaller pores as CR was incorporated into cement matrices. The control matrix R0 had bigger pores above 500 nm of 7.73%, while matrix R3 decreased to 5.88%. The gel pores of less than 10 nm of R0 was 39.81%, but it was as high as 72.58% for the matrix R3. Based on the experimental results, the porosity of R3 decreased to 6.6% and total specific surface area increased to 42.7%. compared with the control matrix R0. The incorporation of CR improved the pore size distribution of the matrices. It is implied that the average pore diameter becomes closer due to the incorporation of CR.

3.4. Effect of three different types of superplasticizers on physical properties of CRCM hardened pastes

In order to expand the application scope of CR in concrete, the influences of superplasticizers on physical properties and Cr(VI)-immobilising capability of cement matrices were experimental studied. Sulphonated acetone formaldehyde superplasticizer (J1), polycarboxylate-based superplasticizer (J2) and naphthalene superplasticizer (J3) were used in the research. The difference of physical properties caused by the three different types of superplasticizers is shown in Table 7.

As the increasing of CR, the setting time was shorted. Combined with Table 6, the initial setting and final setting time of CRCM with

Table 7

Effects of three different types of superplasticizers on physical properties of chromium residue-cement matrices hardened pastes

Water demand for	Setting tir	ne (min)	<i>f</i> _c (MPa)	f _c (MPa)			Ratio of ^c f _c (%)		
normal consistency (%)	Initial	Final	3 days	7 days	28 days	3 days	7 days	28 days	
22	186	289	56.7	73.9	85.1	100.0	100.0	100.0	
20	181	283	59.6	67.4	82.0	105.0	91.2	96.4	
19	140	243	45.2	63.2	80.1	79.7	85.5	94.1	
18	84	177	44.3	51.1	79.5	78.1	69.1	93.4	
17	72	178	45.6	50.8	74.1	80.4	68.7	87.1	
18	290	384	72.5	76.2	106.1	100.0	100.0	100.0	
17	240	315	65.4	84.6	95.9	90.2	111.0	90.4	
16	223	290	55.9	75.2	87.8	77.1	98.7	82.8	
16	198	273	52.9	69.5	76.8	73.0	91.2	72.4	
15	181	252	50.2	56.5	71.2	69.2	74.1	67.1	
18	229	320	58.8	96.3	111.7	100.0	100.0	100.0	
18	218	293	56.3	83.8	85.3	95.7	87.0	76.4	
17	170	259	47.6	80.8	81.4	81.0	83.9	72.9	
16	149	245	45.5	78.7	80.9	77.4	81.7	72.4	
15	107	222	41.5	72.4	75.6	70.6	75.2	67.7	
	Water demand for normal consistency (%) 22 20 19 18 17 18 17 16 16 16 15 18 18 17 16 15 18 18 17 16 15	Water demand for normal consistency (%) Setting tin Initial 22 186 20 181 19 140 18 84 17 72 18 290 17 240 16 223 15 181 18 229 18 218 177 170 16 149 15 107	Water demand for normal consistency (%) Setting time (min) 1nitial Final 22 186 289 20 181 283 19 140 243 18 84 177 17 72 178 18 290 384 17 240 315 16 223 290 16 198 273 15 181 252 18 218 293 17 170 259 16 149 245 15 107 222	Water demand for normal consistency (%)Setting time (min) Initial f_c (MPa) 3 days2218628956.72018128359.61914024345.2188417744.3177217845.61829038472.51724031565.41622329055.91518125250.21821829356.31717025947.61614924545.51510722241.5	Water demand for normal consistency (%)Setting time (min) Initial f_c (MPa)2218628956.773.92018128359.667.41914024345.263.2188417744.351.1177217845.650.81829038472.576.21724031565.484.61622329055.975.21619827352.969.51518125250.256.51821829356.383.81717025947.680.81614924545.578.71510722241.572.4	Water demand for normal consistency (%)Setting time (min) Initial f_c (MPa)2218628956.773.985.12018128359.667.482.01914024345.263.280.1188417744.351.179.5177217845.650.874.11829038472.576.2106.11724031565.484.695.91622329055.975.287.81518125250.256.571.21822932058.896.3111.71822932058.896.3111.71821829356.383.885.31717025947.680.881.41614924545.578.780.91510722241.572.475.6	Water demand for normal consistency (%)Setting time (min) Initial f_c (MPa)Ratio of cf_a 3 daysRatio of cf_a 3 days2218628956.773.985.1100.02018128359.667.482.0105.01914024345.263.280.179.7188417744.351.179.578.1177217845.650.874.180.41829038472.576.2106.1100.01724031565.484.695.990.21622329055.975.287.877.11619827352.969.576.873.01518125250.256.571.269.21822932058.896.3111.7100.01821829356.383.885.395.71717025947.680.881.481.01614924545.578.780.977.41510722241.572.475.670.6	Water demand for normal consistency (%)Setting time (min) Initial f_c (MPa)Ratio of cf_c (%)2218628956.773.985.1100.0100.02018128359.667.482.0105.091.21914024345.263.280.179.785.5188417744.351.179.578.169.1177217845.650.874.180.468.71829038472.576.2106.1100.0100.01622329055.975.287.877.198.71619827352.969.576.873.091.21518125250.256.571.269.274.11822932058.896.3111.7100.0100.01821829356.383.885.395.787.01614924545.578.780.977.481.71510722241.572.475.670.675.2	

Table 8 Effects of three different types of superplasticizers on the Cr(VI) concentrations in the leachate								
Sample	pH value of t	he leaching	Leaching ra	Leaching ratio of Cr(VI)/%				
	7 days		28 days		7 days			
	рН 3	pH 7	pH 3	pH 7	рН 3	pH 7		
R1-J1	11.74	12.38	11.94	12.15	20.7	12.7		
R2-J1	11.77	12.29	11.75	12.20	12.7	7.9		

	рН 3	pH 7	рН 3	pH 7	рН 3	pH 7	pH 3	pH 7
R1-J1	11.74	12.38	11.94	12.15	20.7	12.7	5.5	3.0
R2-J1	11.77	12.29	11.75	12.20	12.7	7.9	7.8	4.5
R3-J1	11.66	12.02	11.68	12.25	13.2	6.6	8.5	4.4
R4-J1	11.50	12.30	11.70	12.23	16.4	9.1	7.0	5.0
R1-J2	11.50	12.25	11.86	12.18	15.2	8.0	6.9	3.1
R2-J2	11.58	12.05	11.84	12.30	11.3	5.2	4.6	1.7
R3-J2	11.50	12.05	11.66	12.10	8.8	5.4	4.9	2.0
R4-J2	11.50	12.20	11.41	12.01	8.4	4.8	5.4	1.9
R1-J3	11.47	12.23	11.55	12.24	8.1	1.4	11.6	5.0
R2-J3	11.70	12.19	11.33	12.24	4.5	1.7	14.5	3.2
R3-J3	11.75	12.30	11.48	12.24	5.7	1.4	12.1	4.1
R4-J3	11.44	12.06	11.76	12.30	7.7	1.4	10.4	4.8

J2 were retarded than ones without J2. When the volume of CR in the matrices exceeded 10%, the setting time of CRCM with J1 were shorted than ones without J1. J3 matrices had similar experimental results to J1. At the same time, it revealed that the compressive strength decreased while the CR volume increased. The difference between the effects of three types of superplasticizers on compressive strength of CRCM was not significant. Compared with others, J2 had slight advantage in improving the compressive strength of CRCM hardened pastes.

3.5. The influence of superplasticizers on Cr(VI)-immobilising capability of cement matrices

The influence of superplasticizers on Cr(VI)-immobilising capability of cement matrices was studied by analysis the Cr(VI) concentrations in the leachate of CRCM hardened pastes. Based on the leaching concentrations, leaching ratio were calculated through the ratio of Cr(VI) quantities in the leachate of CRCM to the total Cr(VI) quantities of the pastes multiplied by 100%. The pH value



Fig. 4. A^d: the limit concentration for Cr(VI) based on Chinese National Standard GB 5085.3-1996. Effects of different types of superplasticizers on Cr(VI) concentrations in the leachate of CRCM hardened pastes.

28 days



Fig. 5. Effects of with and without J2 on the compressive strength of CRCM hardened pastes at 28 days ages.

of the solution medium in the leaching test has an obvious effect on the Cr(VI) concentrations of the leachate. Detailed results were reported in Table 8 and Fig. 4.

As shown in Table 8, the pH value of CRCM leachate at the curing age of 1, 28 days were between of 11.30 and 12.00 at pH 3, and between 12.00 and 12.30 at pH 7.

Based on the leaching experimental results, Cr(VI) concentrations of the leachate from CR was 332 mg/L at pH 7 and 413 mg/L at pH 3. The allowable concentration given by WHO [35] for Cr(VI) in drinking water is 0.05 mg/L. There are many different types of standards concerning the limit concentration of Cr(VI) in China. On the basis of Chinese National Standard GB3838–2002 (Environmental quality standards for surface water), the limit concentration of Cr(VI) for type I surface water is 0.01 mg/L, and 0.05 mg/L for types II, III and IV, 0.1 mg/L for type V. The Integrated wastewater discharge standard (GB8978–1996) is 0.5 mg/L. Complying with Chinese National Standard GB5085.3–1996 (identification standard for hazardous wastes-identification for extraction procedure toxicity), the allowable regulatory limit for Cr(VI) is below 1.5 mg/L. In this research, we discussed the leaching results according to the



Fig. 6. Effects of with and without J2 on the Cr(VI) leaching ratio in the leachate of CRCM hardened pastes at 28 days ages.



Fig. 7. SEM micrograph of R3-J2 (28 days).

limit concentration of 1.5 mg/L, which was adopted widely in many studies [36,37].

As shown in Fig. 4, whether pH 3 or pH 7, the Cr(VI) concentrations in the leachate of CRCM with J1 or J2 were lower than with J3, and they decreased as the hydration period was delayed. However, the Cr(VI) concentrations in the leachate of CRCM with J3 at 28 days were higher than at 7 days, which deteriorated the long security. Compared with others, J2 had a better effect on Cr(VI)immobilising capability. When CR volume rose to 40% at 28 days with pH 7, the Cr(VI) concentration in the leachate was still below the limit concentration. While CR volume could be attain 20% with pH 3 at hydration of 28 ages, the Cr(VI) concentration was just close to the limit of 1.5 mg/L. Additionally, compared with the experimental condition, Cr(VI) leaching in situ is a slow and diluting process and only few grains are below 5 mm, so the Cr(VI)-immobilising capability of J2 could be more reliable in the practical environment.

3.6. Further comparison of J2's influence on the compressive strength and leaching ratio of Cr(VI) of CRCM hardened pastes at 28 days ages

Based on the above discussion, it was revealed that some benefit of chromium(VI)-immobilising capability of cement matrices was achieved in the presence of J2. For further research, we compared with the compressive strength and Cr(VI) leaching ratio of CRCM hardened pastes with J2 and ones without it at the hydration of 28 days. The results were reported in Figs. 5 and 6.

As shown in Fig. 5, the incorporation of J2 increased the compressive strength of matrices at 28 days while the pore size distribution of CRCM became closer (result from Section 3.3), compared with ones without J2. For example, the compressive strength of R1-J2 was 95.9 MPa, which was an increase of 3.0% to R1 matrix. The compressive strength with R4-J2 matrix increased to 7.9%. Obviously, the benefit of J2 on compressive strength of CRCM was higher with increasing of CR volume. In addition, it was observed from Fig. 6 that under the same CR volume condition, whether pH 3 or 7, the Cr(VI) leaching ratio from CRCM with J2 was lower than ones without it. When we took 40% CR volume as an example, Cr(VI) leaching ratio with J2 in the leachate decreased by 60% than matrix without J2 at pH 7, and by 34% at pH 3. Also, as shown in Fig. 7, the scanning electron microscope (SEM) micrograph of R3-[2 indicates that the microstructure of paste is closer and produces more hydration product C-S-H gel. In accordance with the above experimental results, the compressive strength was increased and the Cr(VI) leaching behavior was improved by incorporation of J2. It is obvious that J2 is a good material that effectively immobilized the leaching of Cr(VI) from CRCM hardened pastes. Further investigation of the mechanism of superplasticizers on Cr(VI)-immobilising capability in the leachate of CRCM hardened pastes was needed.

4. Conclusions

Based on the analysis of chemical, mineralogical components of CR and the experiment of compressive strength of CRCM hardened pastes, CR has a certain cementitious properties. The incorporation of CR modestly retards the setting time, slightly decreased the compressive strength and the water demand for normal consistency. Overall, the CR has less influence on the early compressive strength. The CR can improve the pore size distribution of the matrices. Compared with the control matrix, the incorporation of CR makes the porosity and bigger pores above 500 nm decrease, but the total specific surface area and gel pores below 10 nm increase. The Cr(VI) concentrations in the leachate of CRCM are increased with the incorporation of the CR volume. Among the three superplasticizers, J2 has an advantage on Cr(VI) immobilization. Under the hydration of 28 days, CR maximum volume attains 40% with pH 7, for 20% with pH 3 when the Cr(VI) concentration of R3-J2 cement matrices was close to the limit of 1.5 mg/L.

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References

- A. Kortenkamp, M. Casadevall, S.P. Faux, A. Jenner, R.O.J. Shayer, N. Woodbridge, P. O'Brien, A role for molecular oxygen in the formation of DNA damage during the reduction of the carcinogen chromium(VI) by glutathione, Arch. Biochem. Biophys. 329 (1996) 199–208.
- [2] T.G. Wang, Z.H. Li, High-temperature reduction of chromium (VI) in solid alkali, J. Hazard. Mater. 112 (2004) 63–69.
- [3] Y. Ding, Z. Ji, Production and Application of Chromium Compounds, Press of Chemical Industry, Beijing, 2003.
- [4] K. Pohlantdt-Schwandt, Treatment of wood ash containing soluble chromate, Biomass Bioenergy 16 (1999) 447–462.
- [5] T.E. Higgins, A.R. Halloran, M.E. Dobbins, A.J. Pittignano, In situ reduction of hexavalent chromium in alkaline soils enriched with chromite ore processing residue, J. Air Waste Manage. Assoc. 48 (1998) 1100–1106.
- [6] S. Park, W.Y. Jung, Removal of chromium by activated carbon fibers plated with copper metal, Carbon Sci. 2 (2001) 15–21.
- [7] M. Costa, Potential hazards of hexavalent chromate in our drinking water, Toxicol. Appl. Pharmacol. 1 (2003) 1–5.
- [8] International Agency for Research on Cancer (IARC), Chromium and Chromium Compounds, 1997, (Accessed online: 13th February 2005). URL: http://wwwcie.iarc.fr/htdocs/monographs/vol49/.

- [9] D. Bagchi, S.J. Stohs, B.W. Downs, M. Bagchi, H.G. Preuss, Cytotoxicity and oxidative mechanisms of different forms of chromium, Toxicology 180 (2002) 5–22.
- [10] M. Bock, A. Schmidt, T. Bruckner, T.L. Diepgen, Occupational skin disease in the construction industry, Br. J. Dermatol. 149 (2003) 1165–1171.
- [11] M. Hasnain-Isa, N. Ibrahim, H. Abdul-Aziz, et al., Removal of chromium (VI) from aqueous solution using treated oil palm fibre, J. Hazard. Mater. 152 (2008) 662–668.
- [12] Y. Shi, X. Du, Q. Meng, Reaction process of chromium residue reduced by industrial waste in solid phase, J. Iron Steel Res. Int. 14 (2007) 12–15.
- [13] Y. Yang, Expert warning, it is emergent to the chromium residue treatment/chromium residue pollution is astounding, Chem. Manage. 1 (2003) 4–5.
- [14] Y. Ding, Views on treatment to chromium residue, Chem. Indus. Environ. Protect. 14 (1994) 210–215.
- [15] Q. Ren, Comprehensive utilization and treatment for chromium residue, Environ. Eng. 7 (1989) 50–55.
- [16] C.Y. Wang, Y.Y. Li, Y.H. Zhao, Research on the disposal of electroplating Crcontaining wastewater, Indus. Safe. Environ. Protect. 34 (2008) 18–20.
- [17] M. Mollah, Y. Tsai, T. Hess, An FTIR, SEM and EDS investigation of solidification/stabilization of chromium using Portland cement type V and type IP, J. Hazard. Mater. 30 (1992) 273–283.
- [18] A. Kindness, A. Macias, F. Glasser, Immobilization of chromium in cement matrices, Waste Manage. 14 (1994) 3–11.
- [19] I.M.C. Lo, C.I. Tang, X.D. Li, C.S. Poon, Leaching and microstructural analysis of cement-based solidified wastes, Environ. Sci. Technol. 34 (2000) 5038–5042.
- [20] M. Allan, L. Kukacka, Blast furnace residue modified grouts for in situ stabilization of chromium-contaminated soil, Waste Manage. 15 (1995) 193–202.
- [21] A.E. Daniels, J.R. Kominsky, P.J. Clark, Evaluation of two lead-based paint removal and waste stabilization technology combinations on typical exterior surfaces, J. Hazard. Mater. 87 (2001) 117–126.
- [22] J.R. Conner, Chemical Fixation and Solidification of Hazardous Wastes, Van Nostrand Reihold, New York, 1990.
- [23] B. Batchelor, Overview of waste stabilization with cement, Waste Manage. 26 (2006) 689–698.
- [24] P.G. Baker, P.L. Bishop, Prediction of metal leaching rates from solidified/stabilized wastes using shrinking unreacted core leaching procedure, J. Hazard. Mater. 52 (1997) 311–333.
- [25] C.D. Hills, L. Koe, C.J. Sollars, R. Perry, Early heat of hydration during the solidification of a metal plating sludge, Cement Concrete Res. 22 (1992) 822–832.
- [26] H. Lv, Study on application of Cr-slag as cement raw materials and admixture, Cement 11 (2005) 8–10.
- [27] M.S. Zhang, Y. Xiao, Y.H. Zhu, et al., The disposal technology and application actuality for chromium residue, China Resour. Compr. Utilizat. 25 (2007) 16–18.
- [28] Z. Ji, A summary of the harmfulness of chrome residue and its treatment, Inorg. Chem. Indus. 35 (2003) 1–4.
- [29] Z. Ji, The composition changing of chromic residue after piled in long period and its effect on the treatment, Inorg. Chem. Indus. 38 (2006) 8–12.
- [30] J. Gu, K.W. Song, J.S. Qian, Chromium slag characteristics and applied technology for its disintoxication, Coal Ash China 02 (2007) 32–34.
- [31] K.J. Sreeram, Some studies on recovery of chromium from chromite ore processing residue, Indian J. Chem. 42A (2003) 2447–2454.
- [32] Z. Mm, Processing and Disposition of Solid Wastes, Press of Higher Education, Beijing, 1993.
- [33] X.M. Shang, Y.M. Yang, S.W. Ma, The overview of the disposal of chromium slag and resources, J. Nantong Vocation. College 22 (2008) 94–96.
- [34] W. Shen, W. Huang, P. Ming, Cement Technology, Press of Wuhan Industry University, Wuhan, 1999.
- [35] WHO, Guidelines for Drinking Water Quality, vol. 1, World Health Organization, Geneva, 1993, pp. 45–55.
- [36] X. Qu, P.J. He, L.M. Shao, D.J. Lee, Heavy metals mobility in full-scale bioreactor landfill: initial stage, Chemosphere 70 (2008) 769–777.
- [37] P.J. He, X. Zheng, L.M. Shao, J.Y. Yu, D.J. Lee, In situ distributions and characteristics of heavy metals in full-scale landfill layers, J. Hazard. Mater. 137 (2006) 1385–1394.