Influence of slag on leaching behavior of cement mortar lined in ductile iron pipe under a flowing solution

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Abstract: In order to investigate the influence of slag on the leaching behavior of cement mortar lined in ductile iron pipe in a flowing solution, two types of ductile iron pipe specimens lined with ordinary- and 40% slag- cement mortar are firstly prepared, then, an accelerated leaching experiment on the prepared specimens is carried out by using a 6M ammonium chloride solution at a flow rate of 0.3m/s. The parameters of linings at different leaching times, such as porosity, pore size distribution, phase composition and Calcium-Silicon (Ca/Si) ratio, were analyzed by using the saturation-drying weighing method, mercury intrusion porosimetry (MIP), X-ray diffraction (XRD) and scanning electron microscopy in back scattered electron mode (ESEM-BSE) measurements. Results show that, the mixture of 40% slag in cement-mortar lining can reduce its initial porosity and Calcium-Silicon ratio, and improve its pore size distribution and phase composition. In the accelerated leaching process, the porosity, phase composition and Calcium-Silicon ratio of the slag-cement-mortar lining with 40% slag have smaller change than that of the ordinary-cement-mortar lining without slag, and it indicates that the addition of slag can effectively improve the calcium leaching resistance of cement-mortar lining in ductile iron pipes in water supply engineering.

Keywords: Slag; cement-mortar lining; calcium leaching; ductile iron pipe; flowing solution

1. Introduction

Ductile iron pipes lined with cement-mortar protective layer in their inner wall by the centrifugal process [1, 2] have been widely used in water supply and drainage engineering because of their large diameter, high bearing capacity, good durability and safe operation when buried deeply in underground [1-6]. However, when the soft water with low hardness (e.g. tap water and desalinated seawater) is carried by the cement-mortar-lined ductile iron pipe, it easily results in the calcium leaching of cement-mortar lining in the pipe, namely, the dissolution of calcium hydroxide(CH) and decalcification of calcium silicate hydrate(C-S-H) gel [7]. The calcium leaching causes not only the deterioration of microstructure and decrease in strength of the lining cement mortar but also the reduction of alkalinity in pore solution of mortar, which can lead to the depassivation of the ductile iron[1, 2, 8-11]. Thus, the calcium leaching caused by flowing water will gradually reduce the protective effect of cement-mortar lining on ductile iron pipes, and also reduce the durability and in-service lifetime of cement-mortar-lined ductile iron pipe [1, 2]. Design of cement-mortar lining with an excellent leaching resistance is of great importance to improve the durability of ductile iron pipes in water supply.

The blast furnace slag can effectively change the microstructure of cement-based materials and the phase composition of cement hydrated products, while enhancing its calcium leaching resistance in water environment [12-14]. Related studies have been conducted by many researchers [7, 12-14]. Taylor[12] used Scanning Electron Microscope(SEM) to analyze the microstructure evolution of slag-cement pastes cured in water for 20 years, and reported that the calcium hydroxide content has a gradual decrease while the

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hydration degree of slag has a slight increases in the slag-cement matrix. Liu [14] utilized SEM for observing the microstructure morphology of leached slag-cement pastes under the attack of flowing deionized water, and also analyzed the evolution characteristics of its microstructure in the long-term process of leaching. Jain et al. [13] investigated the changes of the porosity and calcium hydroxide content in plain and slag- and fly ash-modified cement pastes in pure water with the leaching time by the weighting and thermogravimetric methods respectively, and it can be obtained that, with the addition of slag and fly ash, the microstructure of specimens became more dense and the Ca-Si molar ratio became lower, while the slag-modified cement pastes showed better leaching resistance than the plain paste. However, because the natural calcium leaching in water is a very slow process, some accelerated leaching tests have been conducted to investigate the influence of calcium leaching on cement-based materials' performance [15-19]. Yang et al. [16] used 6M ammonium chloride solution to accelerate the calcium leaching of cement pastes and investigated the influence of leaching on its mechanical properties, such as the hardness and compressive strength. Wan [19] experimentally investigated the equilibrium curve of Ca in 6M ammonium nitrate solution to clarify the accelerated leaching mechanism in cement-based materials, and it can be obtained from comparison with the equilibrium curve in water that their dissolution and leaching mechanisms are similar.

The current researches reveal the influence of slag on hydration characteristics, microstructure evolution and leaching mechanism of cement-based materials in water environments or accelerated solutions, and further demonstrate that the mixture of slag in cement mortar can improve its calcium leaching resistance in water environment. However, the cement-mortar lining in ductile iron pipe produced by the centrifugal process has two components, namely cement paste and mortar, which have greatly gradient distributions of microstructure and compositions. Therefore, the leaching behavior of the specimen of cement-mortar lining should be different from that of the ordinary mortar specimen. But, very limited study has been conducted on the leaching behavior of cement mortar lined in ductile iron pipe under flowing water, and there is hardly any substantial design basis for the durability improvement of cement-mortar lining by the mixture of slag in ductile iron pipe.

In this paper, two kinds of specimens of ductile iron pipes, lined with ordinary- and 40% slag- cement mortar, are designed and produced to carry out the accelerated leaching experiment for investigating their leaching behavior under the flowing solution. Some measurements such as the saturation-drying weighing method, MIP, XRD and ESEM-BSE are used to analyze the influence of slag on the calcium leaching process of the cement-mortar lining with/without slag in ductile iron pipe.

2. Experiments

2.1 Materials

The cement used in this study was the 52.5-grade ordinary portland cement (P.O 52.5), whose chemical compositions are listed in Table 1, with a density of 3150 kg/m^3 and specific surface area of $369.6 \text{ m}^2/\text{kg}$. The initial and final setting times are 72min and 290min respectively, while its normal compression strength and flexural strength for 28days curing are 60.5MPa and 8.7MPa respectively. S95-grade blast furnace slag powder with a density of 2900 kg/m^3 and specific surface area of $435 \text{ m}^2/\text{kg}$ was used as an additive mixture. River sand with a fineness modulus of 2.44, apparent density of 2600 kg/m^3 and water content of 3.6% was used. Tap water and purified water were respectively used to mix the slag-cement pastes and prepare the ammonium chloride solution. Table 2 lists the mixture proportions of the slag- and ordinary- cement mortar linings.

Table 1

Characteristic of cementitious materials

Material	Chemical composition (%)						Compound composition of clinker (%)				
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Total
Cement	21.10	5.56	3.98	62.48	1.76	2.59	55.10	19.10	6.50	8.50	89.20
Slag	32.70	16.10	5.54	38.70	5.50	1.46	-	-	-	-	

Table 2

Mixture proportions of slag- and ordinary- cement mortar linings.

Species	Water-binder ratio	Mass fraction/%			
		cement	slag	sand	water
Slag-cement mortar lining	0.4	60	40	130	40
Ordinary cement-mortar lining	0.4	100	0	130	40

Ammonium chloride reagent with a solubility of 37.2g/100ml at room temperature was used to prepare the accelerated leaching solution with the concentration of 6M. Similar to the accelerated leaching mechanism of ammonium nitrate solution, the ammonium chloride solution can be also used to perform the chemically accelerated leaching on cement-based materials to reveal its leaching mechanism in a relatively short time [16, 20, 21], and the accelerated leaching principle is to promote chemical reaction between calcium hydroxide and ammonium chloride in the leachant solution, forming gaseous ammonia and calcium chloride, which is highly soluble in water (see Eq. (1)) [16].

2.2 Preparation of specimens

The cement-mortar-lined ductile iron pipe specimen was produced by the centrifugal process [3], as follows: the cement mortar was firstly prepared according to the mixture proportion in Table 2, and then injected into the ductile iron pipe. Next, the ductile iron pipe with the injected cement mortar was installed on the centrifugal machine with an operating speed of 2600 rpm. After the revolutions lasting 5 minutes, the injected cement mortar was evenly spread along the inner wall of the ductile iron pipe under the centrifugal force, and the extra water produced by the centrifugal process was discharged, so it results in the reduction of the water-cement (binder) ratio of cement-mortar lining, and its actual water-cement (binder) ratio is 0.3 by the measurement on the extra water.

Afterwards, the prepared cement-mortar-lined ductile iron pipe specimen was put into the curing room, and began to cure according to the following steps [22]: Firstly, the specimen was naturally cured in the curing room for 2 hours while the temperature was kept at 25°C; Secondly, the steam with the moisture of 90% was filled in the room for curing the specimen while the temperature was raised from 25°C to 60°C by heating for 4 hours, and then continue to cure for 4 hours at 60°C. Finally, the heating was stopped, and the specimen was naturally cooled for an hour again, so the cement-mortar-lined ductile iron pipe specimen was completed, as shown in Fig.1(a). Fig.1(b) shows the stratification of cement-mortar lining in the pipe, and a cross-sectional view of cement-mortar lining in ductile iron pipe is presented in Fig.1(c). Table 3 lists the structural parameters of the cement-mortar-lined ductile iron pipe for the leaching experiment.

Fig.1 Cement-mortar-lined ductile iron pipe

Table 3

Structural parameters of the cement-mortar-lined ductile iron pipe (mm)

Specimen	Length of ductile iron pipe	Internal diameter	External diameter	Thickness of cement paste layer	Thickness of mortar layer	Thickness of cast iron layer
Slag-cement-mortar-lined ductile iron pipe	1000.0	60.0	96.0	3.0	8.5	6.5
Ordinary-cement-mortar-lined ductile iron pipe						

2.3 Experimental method

2.3.1 Experimental setup

An experimental setup for performing the accelerated corrosion of the cyclically flowing water on the specimen was designed, as shown in Fig.2. It is made up of a cement-mortar-lined ductile iron pipe with a length of 1.0m, a plastic container with 6M ammonium chloride solution of 130L, a corrosion-resistant pump with a power of 12W, a temperature controller and some connecting plastic tubes of diameter 25mm each. The specimen and pump were connected with the plastic tubes and placed together in a closed container to form the cyclic water transportation system. The flowing rate of ammonium chloride solution in the specimen is 0.3m/s, and maintained at a temperature of 25°C in the plastic container. The ammonium chloride solution is renewed once every 150 days.

2.3.2 Accelerating factor

In order to use the experimental results of accelerated corrosion on the specimen to further evaluate the performance of the cement-mortar-lined ductile iron pipe in actual water transportation, the accelerated and conventional leaching experiments of cement-mortar lining specimens in 6M ammonium chloride solution and purified water were respectively completed [23], and the leaching depth characterizing the leaching rate of cement mortar were measured by phenolphthalein method [17, 24], as illustrated in Fig.3. It can be obtained from the figure that, the leaching rate of cement-mortar lining in 6M ammonium chloride solution is about 40 times of that in purified water, namely, its accelerating factor is 40.

Fig.2 Experimental setup for simulating cyclic water transportation

Fig.3 Leaching depth-time curves of cement-mortar specimens in 6M ammonium chloride solution and purified water

2.3.3 Sample preparation

In the process of calcium leaching, the porosity, phase composition, and microstructure of cement-mortar lining in ductile iron pipe undergo different changes[25, 26], and the changes of these parameters can be measured by the saturation-drying weighing method, mercury intrusion porosimetry (MIP), X-ray diffraction (XRD) and the scanning electron microscope (SEM/BSE) to characterize the leaching behavior of the lining, and further analyze the influence of slag on its leaching process. The related measurement samples from the cement-mortar-lined ductile iron pipe specimen can be prepared according to the steps presented in Fig.4.

When the cement-mortar-lined ductile iron pipe specimen was respectively corroded for 0, 150, 300 and 450 days by the flowing ammonium chloride solution, the cyclic corrosion experiment was temporarily stopped to cut out a pipe ring with a height of 10 mm from the end of the specimen, as illustrated in Fig.4 and 5(a), and then, the experiment was continually performed to the expected corrosion time. In the meantime, some samples with the size of 10 mm × 10 mm × 18 mm were cut from the pipe ring to make the ESEM-BSE samples while the others were separated into the cement paste-and mortar- samples from the lining in the ring for MIP analysis and the preparation of XRD powder respectively, as shown in Fig.5 (b). The sample of cement paste was dried in the oven at 80 °C for 4 h, and then ground in the agate mortar so as to pass the 100 mesh size sieve. The obtained powder was used for XRD analysis. In addition, the

samples with 10mm thickness (as shown in Fig.5(b)) for ESEM-BSE analysis were freeze-dried for 24 hours, and then impregnated with epoxy resin under vacuum. After the epoxy resin had hardened at 40°C, the measured surface of samples were carefully ground on a rotary grinding/polishing machine with silicon carbide papers of different grades and polished with the different grade diamond pastes [27, 28], until no visible scratches were observed, then the samples were cleaned and stored in the vacuum dryer for the ESEM-BSE analysis. The completed sample is shown in Fig.5 (c). Table 4 lists the detailed information of the measured samples.

Table 4
The information of measured samples

Specimen	Sample		Test methods	Test time
	Name	Notation		
Slag-cement-mortar-lined ductile iron pipe	Slag-cement mortar	SCML	ESEM-BSE	0,150 and 450 days
	Cement paste layer sample	SCML-C	Saturation-drying weighing method	0,150,300 and 450 days
			MIP, XRD	0 and 150 days
	Mortar layer sample	SCML-M	Saturation-drying weighing method	0,150,300 and 450 days
			MIP	0 and 150 days
	Ordinary cement mortar	OCML	ESEM-BSE	0,150 and 450 days
Ordinary-cement-mortar-lined ductile iron pipe	Cement paste layer sample	OCML-C	Saturation-drying weighing method	0,150,300 and 450 days
			MIP, XRD	0 and 150 days
	Mortar layer sample	OCML-M	Saturation-drying weighing method	0,150,300 and 450 days
			MIP	0 and 150 days

Fig. 4 Preparation steps of measured samples from the cement-mortar-lined ductile iron pipe specimen

Fig. 5 Pictures of samples from cement-mortar-lined ductile iron pipe specimen

2.3.3 Test methods

Saturation-drying weighing method [13, 29]: The mass of the saturated and dried cement paste and mortar samples were measured by the high-precision electronic weighing balance (220V, 50Hz) with maximum range of 200g and accuracy of 0.1mg. All samples were dried using the vacuum drying oven. After each immersion, the samples were removed from the container, and washed under flowing water. The mass of each saturated surface-dried sample (m_s) was recorded, while the mass of samples suspended in distilled water (m_x) was also measured by the balance with a built-in type. Finally, the samples were kept in a vacuum drying oven to dry to a constant weight at temperature of 60 °C, and the dried mass was obtained. The average porosity of sample (ϕ) was calculated by the expression $\phi = (m_s - m_d) / (m_s - m_x) \times 100\%$.

MIP: The pore size distribution of the sample was measured by an Autopore IV 9500 automatic mercury intrusion porosimetry (MIP), which can generate a maximum pressure of 414MPa (60000psi) to evaluate a theoretical pore diameter of 0.006 μ m. The MIP test was executed in two steps: the low pressure step first evacuates gases, fills the sample holder with mercury and performs porosimetry from about 3.5 (0.5psi) to 207kPa (30psi); the high pressure reaches pressures between 207 kPa (30psi) and 241.5 MPa (35000psi). Low and high pressure steps were always performed within a period of 3 hours. The contact angle and surface tension assumed for all tests were 130 degrees and 485 dynes/cm respectively. All tests were performed to achieve the manufacturer recommendation of a mercury stem volume between 25% and 85%.

XRD: The phase compositions in the powder sample from the leached specimen were analyzed by using Brucker X-ray diffractometer, while a LynxEye array detector with high efficiency was applied for X-ray diffractometer. The diffraction pattern was obtained with Cu-K α radiation operating at 40kV and 30mA. Scans were collected at 0.15 s per step and at a step size of 0.02° over the range of 7° to 80° 2 θ . The Rietveld refinements of the measured XRD patterns [30-32] were performed to quantitatively analyze the phase composition of powder samples. The crystallographic information required for Rietveld refinement was taken from Crystallographic Information Files of Inorganic Crystal Structure Database [31].

ESEM-BSE: The prepared samples in Fig.5(c) were investigated using a Philips XL30 environmental scanning electron microscope (ESEM) with an energy spectrometer. The instrument was operated at 15 kV accelerating voltage, beam current 20 mA, 0.3 Torr pressure and at approximately 10 mm working distance for image acquisition. The electronic image of selected area with a resolution of 512 $\times$ 400 pixels and a total number of 32 frames was obtained by the back-scattered electron imaging, and in order to obtain the average Calcium-Silicon ratio of the selected area, the surface-scan mode of Energy Disperse Spectroscopy (EDS) was used to scan the electronic image.

3. Results and discussion

3.1. Porosity

Porosity is an important parameter characterizing the microstructure evolution of cement-based materials caused by calcium leaching in water environment, and it can reflect the leaching behavior of cement-based materials [33, 34]. Fig. 6 presents the porosity changes of the cement-mortar lining without and with slag with the leaching time. It can be obtained from the figure that, as a whole, the porosity of each sample increases with the leaching time, and its increase in cement paste layer samples OCML-C and SCML-C is significantly higher than that in mortar layer samples OCML-M and SCML-M. As shown in Fig.6 (a), at 0-150 days of the leaching experiment, the porosities of OCML-C and SCML-C increases respectively from 9.57% and 8.80% to 31.94% and 25.59%. But, at 150-300 days of the leaching experiment, the

porosity increments of OCML-C and SCML-C are 11.23% and 8.8% respectively, and at 300-450 days, there are respectively 9.14% and 6.75% porosity increments of OCML-C and SCML-C. Thus, for the cement paste layer, the porosity increment at every 150-days interval decreases with the leaching time, while the porosity increment of SCML-C with 40% slag is less than that of OCML-C without slag, especially from 0 to 150 days of the leaching experiment.

Because the mortar layer is located at the interior of the cement paste layer in the cement-mortar-lined ductile iron pipe, as illustrated in Fig.1(c), its calcium leaching is later than that of the cement paste layer under the flowing solution, and the porosity changes of mortar layer is different from that of cement paste layer, as presented in Fig.6(b). It can be obtained from Fig.6(b) that, at 0-150, 150-300 and 300-450 days of the leaching experiment, the porosity increments of OCML-M without slag are respectively 6.04%, 5.54% and 3.48%, and the porosity increments of SCML-M with 40% slag are respectively 2.98%, 4.94% and 2.91%. Thus, the porosity change of SCML-M with 40% slag is less than that of OCML-M without slag with the leaching times. It can be seen from these results that slag can slow down the calcium leaching process and effectively improve the leaching resistance of cement-mortar lining in ductile iron pipe. This is because, the slag improves the microstructure of the cement mortar, and in the hydration process of slag-cement-mortar system, the slag can consume calcium hydroxide generated by cement hydration and absorb calcium ions to cause the pozzolanic reaction, which can change the chemical compositions in the cement-mortar lining to generate C-S-H gel with more impact and stable microstructures in the alkaline environment [35, 36]. The generated C-S-H gel can fill the capillary pore and the space originally occupied by water, and it can reduce the porosity and calcium hydroxide content in the cement-mortar lining and slow down the calcium leaching process [37, 38].

Fig.6. Average porosity of cement-mortar lining

3.2. Pore size distribution

In order to obtain the pore size distribution in the cement-mortar lining at different leaching times, the mercury intrusion porosimetry (MIP) measurement was carried out to analyze the pore parameters of the unleached and 150-days-leached cement-mortar lining samples, such as the most probable pore diameter, pore size distribution, porosity, average diameter and critical pore size, as listed in Table 5. Fig.7 and Fig. 8 present the curves of cumulative pore size distribution (CPSD) and differential pore size distribution (DPSD) of the ordinary- and slag- cement-mortar lining at different leaching times. It can be obtained from Table 5 that, the porosities of the unleached SCML-C and SCML-M decrease from 9.57% and 13.58% to 8.80% and 9.31% respectively, and their most probable pore sizes (diameter) decrease from 17.11nm and 32.39nm to 12.25nm and 11.05nm, while their critical pore sizes (diameter) decrease from 120.82nm and 62.49nm to 62.51nm and 32.40nm, respectively. It can also be seen from Fig.8 that the unleached OCML-C

and OCML-M have higher systematic CPSD than the samples SCML-C and SCML-M. And this result can also be observed on the DPSD curves in the figures. Thus, the mixture of slag can not only decrease the porosity, most probable pore size and critical pore size, but also improve the pore size distribution of the cement-mortar lining, and it can slow down the diffusion process of calcium ion.

After leaching for 150 days, the total porosity, most probable pore size (diameter) and critical pore size (diameter) of each sample have obvious increases, as shown in Table 5, and the pore volume in the pore size range of 0.01-0.5 μ m have the most significant change, as illustrated in Fig.8. However, the degradation of pore structure in the slag-cement mortar lining is less than that in the ordinary-cement mortar lining. For example, the most probable pore size diameters of OCML-C without slag and SCML-C with 40% slag increased by 60.02nm and 28.08nm, while the critical pore size diameters of OCML-C without slag and SCML-C with 40% slag increased by 106.19nm and 88.53nm, respectively.

Based on the viewpoints of Wu[39, 40] on the classifications of pore structures in cement-based materials, there are the harmless pores (<20 nm), less-harmful pores (20–50 nm), harmful pores (50–200 nm) and much-harmful pores (>200 nm). On this basis, the pore size classification of the unleached and 150-days-leached cement-mortar lining samples are presented in Fig.9. It can be seen from the figure that, mixed with 40% slag in cement-mortar lining, its pore structure has a significant improvement, for example, the volume fraction of harmless pores in the cement paste layer increases from 23.77% to 42.45%, and the volume fractions of harmful and much-harmful pores reduce from 20.84% and 39.49% to 10.85% and 31.20%, respectively. In addition, after leaching for 150 days, the volume fraction of harmless pores decreases, while the volume fraction of less-harmful and harmful pores has a significant increase, so the pore structure of each sample degrades with the leaching time.

Table 5

Most probable pore size and critical pore size of samples

Leaching time (days)	Series	Porosity (%)	Most probable pore size, diameter, (nm)	Critical pore size, diameter (nm)
0	SCML-C	8.80	12.25	62.51
	OCML-C	9.57	17.11	120.82
	SCML-M	9.31	11.05	32.40
	OCML-M	13.58	32.39	62.49
150	SCML-C	25.59	40.33	151.04
	OCML-C	31.94	77.13	227.01
	SCML-M	12.29	50.34	120.77
	OCML-M	19.62	95.33	151.04

(a) Differential pore size distribution of cement layer

(b) Differential pore size distribution of mortar layer

(c) Cumulative pore size distribution of cement layer

(d) Cumulative pore size distribution of mortar layer

Fig.7. Pore size distributions of unleached samples with/without slag

(a) Differential pore size distribution of cement layer

(b) Differential pore size distribution of mortar layer

(c) Cumulative pore size distribution of cement layer

(d) Cumulative pore size distribution of mortar layer

Fig.8. Differential and Cumulative pore size distributions of 150 days leached samples

(a) Cement paste layer

(b) Mortar layer
Fig.9. Pore volume distribution of cement-mortar lining

3.3. Phase composition

Fig.10 presents the XRD patterns of the unleached and 150-days-leached samples OCML-C and SCML-C, which are from the cement paste layers in ordinary- and slag- cement-mortar linings. It can be seen from the figure that, there are the obvious diffraction peaks of portlandite, ettringite and some unhydrated clinker minerals in the unleached samples OCML-C and SCML-C, and the intensity of diffraction peaks of portlandite in the OCML-C without slag is slightly higher than that in the SCML-C with 40% slag. Additionally, the traces of calcites, probably produced by the carbonation when the samples were prepared [41], can also be observed. After leaching for 150 days, the intense diffraction peaks at $2\theta = 17.9^\circ$ and 34.2° of portlandite disappear, and the diffraction peaks of belite and alite are also difficult to be observed in the OCML-C and SCML-C. In order to further analyze the influence of slag on the leaching behavior of cement-mortar lining, the full profile Rietveld method [32, 42] was used to obtain the content of each phase in the samples OCML-C and SCML-C, and the quantitative results are listed in Table 6. It can be seen from the table that, after adding the slag in the cement-mortar lining, the content of portlandite decrease from 6.94% to 5.16%, while the content of ettringite increase from 0.10% to 0.17%. After leaching for 150 days, there is no traces of portlandite in OCML-C without slag, but a little of portlandite is measured in SCML-C with 40% slag. However, ettringite has a slight increase from 0.10% and 0.17% to 0.14% and 0.22% in OCML-C and SCML-C respectively, and this result is also reported by Faucon [43]. Thus, the addition of slag results in the increase of the ettringite content and the reduction of the calcium hydroxide content [38, 44], and consequently slow down the calcium leaching process of cement-mortar lining.

Additionally, as seen from Table 6, after leaching for 150 days in 6M ammonium chloride solution, the main phase compositions in the samples OCML-C and SCML-C are calcite, ettringite, belite, tricalcium aluminate and brownmillerite, and they are similar to the results from the leaching experiment on 3-mm-thick cement paste specimen immersed into deionized water for more than 10 years [45-47]. It shows that the change of phase composition of the cement paste in 6M ammonium chloride solution is consistent with that of the cement paste in deionized water, and there are no new crystal phases in the leaching process of cement paste immersed into ammonium chloride solution. Thus, the calcium leaching behavior of cement-mortar lining in ammonium chloride solution can be used to simulate that in deionized water, but its leaching rate in ammonium chloride solution is far more than that in deionized water.

(a) OCML-C sample

(b) SCML-C sample

Fig.10. XRD patterns of unleached and leached samples

Table 6

XRD- Rietveld results of samples—10% internal standard Al_2O_3 was added to the mixtures

Phases	unleached		150 days leaching	
	SCML-C	OCML-C	SCML-C	OCML-C
Portlandite	5.16%	6.94%	0.86%	-
Calcite	5.59%	6.99%	5.46%	6.40%
Ettringite	0.17%	0.10%	0.22%	0.14%
Belite	9.11%	6.99%	1.66%	1.03%
Alite	14.94%	12.01%	0.83%	0.80%
Tricalcium aluminate	0.55%	1.06%	0.25%	1.23%
Brownmillerite	8.92%	6.82%	3.39%	8.43%
Hydrogarnet	0.85%	0.24%	0.70%	1.46%
Gypsum	2.61%	0.59%	1.09%	0.33%
Bassanite Bezou	-	0.33%	0.33%	0.14%
Ca-langbeinite	0.47%	1.20%	-	-
Aphthitalite	2.01%	0.66%	0.55%	0.45%
Thenardite	1.76%	1.49%	0.57%	0.08%
Hydrocalumite	-	-	2.87%	1.91%

3.4. Ca/Si

Generally, the phases of calcium and silicon in cement-based materials can be dissolved to calcium ions and silicate ions in water environments, but the solubility of silicon phase is far less than that of calcium phase in the pore solution. Therefore, in order to conveniently characterize calcium leaching process, the influence of silicon dissolution on the calcium leaching behavior is not considered, so the change of Calcium-Silicon ratio (Ca/Si) can characterize the calcium leaching behavior of cement-mortar lining in the flowing solution [19]. Fig.11 presents the SEM microstructure, EDS spectrum, element content and Ca-Si ratio at 1.5mm depth of in the unleached samples OCML and SCML, which is located in cement paste layer, and the time-varying Ca/Si at the different depths of the OCML and SCML is presented in Fig. 12. it can be seen from the figures that, the Ca/Si in the unleached SCML is lower than that in the unleached OCML, and both of them have a gradual decrease with the leaching time. However, after accelerated leaching for 450 days, the Ca/Si of the OCML and SCML at 1.5mm depth decreases from 2.8 and 3.1 to an even value of 0.8, respectively, which indicates that the calcium leaching degree of the SCML is smaller than that of the OCML. This is because, after the partial replacement of cement by slag, the cement content in lining has a decrease, and the calcium oxide in slag is lower than that in cement, as shown in Tables 1 and 2, so the Ca/Si in the unleached SCML is smaller than that of the unleached OCML. The mixture of 40% slag results in the reduction of the Ca/Si and calcium hydroxide in cement-mortar lining, and causes the increase of its microstructure and compactness, as illustrated in Fig.6 and Fig.9. These can slow down the calcium leaching process and enhance the leaching resistance of the lining. In addition, the changes of Ca/Si with the leaching time at 3.0mm, 7.5mm and 11.0mm depths of the samples OCML and SCML are similar to that at 1.5mm depth, as shown in Fig.12(b), (c) and (d).

(a) OCML sample

(b) SCML sample

Fig.11. SEM photo, EDS spectrum and element content at 1.5mm depth of unleached OCML and SCML samples

Fig.12. Changes of Ca/Si at different depths of the SCML and OCML samples with leaching time

4. Conclusion

This paper designs two kinds of specimen of the ductile iron pipe, lined with ordinary- and 40% slag-cement mortar, and an accelerated leaching experiment on the specimens was carried out to investigate the influence of slag on the calcium leaching behavior of cement-mortar lining in the ductile iron pipe under 6M ammonium chloride solution with the flowing rate of 0.3m/s. By using the saturation-drying weighing method, MIP, XRD and ESEM-BSE, the changes of some parameters with the leaching time, such as porosity, pore size distribution, phase composition and Ca/Si, were measured to analyze the influence of slag on the calcium leaching process of cement-mortar lining. Some conclusions are obtained. Firstly, the porosity, calcium hydroxide content and Ca/Si of the unleached slag-cement-mortar lining are lower than that of ordinary cement-mortar lining. Secondly, in the calcium leaching process, the compactness, calcium hydroxide content and Ca/Si of ordinary- and slag- cement-mortar linings decrease with the leaching time, but the decrease rate of cement-mortar lining with 40% slag is lower than that without slag. Finally, the addition of slag in cement-mortar lining can reduce its microstructure deterioration in the leaching process, and improve its calcium leaching resistance in ductile iron pipes.

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