Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 33 (2003) 1311–1317

CEMENT AND CONCRETE RESEARCH

The mechanism for soluble phosphates to improve the water resistance of magnesium oxychloride cement

Dehua Deng*

School of Civil Engineering and Architecture, Central South University, Shao Shan Nan Road No. 22, Changsha, 410075 Hunan, People's Republic of China

Received 21 December 1999; accepted 17 January 2003

Abstract

This paper discusses the reasons why the addition of some soluble phosphates to magnesium oxychloride cement (MOC) can greatly improve its water resistance. With the XRD analysis and the determination of the strength retention coefficients (a judging index for the water resistance), it has been shown that the addition of small quantity of the soluble phosphates, such as H_3PO_4, $NaH_2PO_4 \cdot 2H_2O$, and $NH_4H_2PO_4$, to MOC pastes does not influence the phases formed in the MOC pastes, but can result in the great increases of the strength retention coefficients of hardened MOC pastes, i.e., the great improvement of the water resistance of MOC. It was considered that the key components being responsible for the improvement of the water resistance could be the anions $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} yielded by the ionization of these phosphates in the solution of MOC pastes. These anions can decrease the lowest concentration of Mg^{2+} ions in the solution required by the formation of $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (5-phase) or $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (3-phase) in the MOC pastes and increase the stability of these phases in water. Thus, when the hardened MOC pastes with small quantity of the soluble phosphates are immersed in water, the 5-phase or 3-phase in them will not be decomposed by water, which makes the strength of the hardened MOC pastes remain unchanged in water.

Keywords: Magnesium oxychloride cement; Durability; Water resistance; Phosphate; Mechanism

1. Introduction

Magnesium oxychloride cement (MOC) has many good engineering and mechanical properties, but it has the poor water resistance, i.e., the strengths of hardened MOC pastes in water are sharply decreased, which makes it be limited in engineering applications. For many years, many investigations on the water resistance of MOC have been carried out. There are a variety of literature, citations, and patents published, which, in our previous work, were reviewed in detail [1]. It was considered that a simple but efficient method to improve the water resistance of MOC would be additives. Additives that can greatly improve the water resistance of MOC are phosphoric acid and soluble phosphates, including the phosphates of alkali metals, the phosphates of alkali earth metals, iron, aluminum, and the phosphates of ammonia. Even small amount of these compounds can improve the water resistance of MOC very much. It is interesting to mention that the addition of soluble phosphates to MOCs improves the water resistance by the formation of insoluble phosphate complexes [2], and the phosphates is absorbed onto the surface of the grains of $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (5-phase), which results in a layer of insoluble complexes to protect 5-phase. However, as indicated by our earlier study [1], it is impossible for the great improvement of the water resistance to result from the formation of insoluble phosphates. The facts showed that the quantity of the soluble phosphates that can successfully improve the water resistance is very small, below 1% of the mass of a MOC paste. Even if the formation of insoluble phosphates occurs in MOC pastes, the quantity of the insoluble phosphates formed is certainly very small which is not enough to produce a layer of the insoluble phosphates to protect all of the 5-phase grains. Then, how can small amount of some soluble phosphates improve the water resistance of MOC very much? The present paper discusses the mechanism for soluble phosphates to improve the water resistance of MOC. For comparison, the soluble phosphates used in this work are H_3PO_4, $NaH_2PO_4 \cdot 2H_2O$, and $NH_4H_2PO_4$. The results reported include the XRD data, compressive strengths, and the strength retention coefficients.

---

* Tel.: +86-731-564-0257; fax: +86-731-222-2401.
E-mail address: dehua_deng@21cn.com (D. Deng).

0008-8846/03/$ – see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00043-7

2. Experimental procedure

2.1. Materials

MgO used for this work was magnesite powder calcined at about 900 °C. Typical chemical analysis is listed in Table 1.

$MgCl_2$ used for this work was a halogenide $MgCl_2 \cdot 6H_2O$ obtained after KCl is refined from $KMgCl_3 \cdot 6H_2O$ in Qinghai Potash Fertilizer Plant, China. Typical chemical analysis is listed in Table 2.

The phosphoric acid (H_3PO_4 85% solution), sodium dihydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$), and ammonia dihydrogen phosphate ($NH_4H_2PO_4$) used were all chemical grade compounds. Chemical grade MgO and $MgCl_2$ were also used for the neat MOC paste specimens in Fig. 2.

2.2. Preparation of specimens

To prepare the specimens of the neat MOC paste, $MgCl_2 \cdot 6H_2O$ was first dissolved in water to form the $MgCl_2$ solution with the desired concentration (°Be). Secondly, a small quantity of an additive (such as: H_3PO_4 or $NaH_2PO_4 \cdot 2H_2O$ or $NH_4H_2PO_4$) was mixed with the appropriate weight of the $MgCl_2$ solution in a bowl by hand to form the clear mix solutions. Then, the weighted magnesite powder calcined was mixed with the mix solutions mechanically to form homogenous MOC pastes. The MOC pastes were cast in $40 \times 40 \times 40$ or $40 \times 40 \times 160$ mm^3 steel moulds, and sealed and cured for 1 day at room temperature, then unmoulded and cured at air for 14 days.

The specimens used for XRD analysis are the neat MOC paste specimens. The specimens used for the determinations of the water resistance were not only the neat MOC paste specimens but also the MOC mortar specimens. The aggregate used in the mortar specimens was the standard silica sand. To prepare the MOC mortar specimens, at first, a neat MOC paste was formed, then the silica sand was mixed with the neat MOC paste to form the MOC mortar mixes. The MOC mortar mixes were cast in the $40 \times 40 \times 160$-mm^3 prisms and cured for 1 day at room temperature, then unmoulded and cured again at air for 14 days.

2.3. Measurements

The reaction products in the neat MOC paste specimens were identified by D/Max-3A X-ray powder diffractometry made in Japan, using (Cu, Ka) radiation at 30 kV and 25 mA.

Table 1
Chemical analysis of the magnesite powder calcined

Components	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	Others
Mass fraction (%)	85.0	1.3	3.09	0.16	0.33	10.03

Table 2
Chemical analysis of halogenide

Components	$MgCl_2 \cdot 6H_2O$	KCl	NaCl	$CaSO_4$	SiO_2
Mass fraction (%)	92.35	0.16	0.66	0.27	0.57

The poor water resistance of MOC means the great loss of the strengths of hardened MOC pastes in water. Thus, the strength retention coefficient, which indicates the relative variation of the strengths of hardened MOC paste specimens with time in water, is used as the judging index of the water resistance. The larger the strength retention coefficients, the better the water resistance. In this work, the strength retention coefficient is defined as the ratio calculated by the following formula:

$$W_n = \mathrm{Rc}_n / \mathrm{Rc} \quad (1)$$

where W_n—strength retention coefficient, in which n is the days of specimen immersing in water; Rc_n—the strength of the wet specimens after immersion in water for n days; Rc—the strength of the dry specimens cured for 15 days before immersion in water.

Here, the W_ns of all specimens were determined by the method proposed in our earlier study [3]. For example, for a set of same specimens cured for 15 days, three specimens were used to measure the compressive strength Rc (MPa) of the dry specimens, the other specimens were immersed in the flowing water with 1 l/min average flow, respectively. After n days, each time, three wet specimens were taken out of the flowing water, and the compressive strength of the wet specimen Rc_n (MPa) were measured at once. Thus, the strength retention coefficient Wn can be calculated by Eq. (1).

3. Experimental results

3.1. The effect of phosphoric acid (H_3PO_4) on the water resistance of MOC

For the neat MOC paste specimens cured at air for 15 days and followed by immersing in the flowing water for 28 and 60 days, respectively, we measured their strengths Rc; Rc_{28} and Rc_{60} and calculated strength retention coefficients W_{28} and W_{60} are shown in Table 3. These specimens were prepared by adding the different mass fractions (%) of H_3PO_4 (85% solution) to the neat MOC pastes, in which the mass ratio between the magnesite powder

Table 3
The strengths and the strength retention coefficients of the specimens of the neat MOC pastes added by H_3PO_4

Samples		13 ∼ 0	13 ∼ 1	13 ∼ 2	13 ∼ 3	13 ∼ 4	13 ∼ 5
Fractions of H_3PO_4	mass (%)	0	0.2	0.37	0.57	0.74	1.28
	moles (/kg)	0	0.017	0.032	0.05	0.064	0.111
Rc (MPa)		70.4	70.3	69.4	63.1	55.0	53.1
In water for 28 days	Rc_{15} (MPa)	6.90	52.2	53.9	53.1	50.0	39.1
	W_{28}	0.1	0.74	0.78	0.84	0.91	0.74
In water for 60 days	Rc_{60} (MPa)	4.50	31.2	36.0	52.2	52.8	41.9
	W_{60}	0.06	0.44	0.52	0.83	0.96	0.78

Table 4
The strengths and the strength retention coefficients of the specimens of the MOC sand mortar mixes added by H_3PO_4

Samples		$22\sim 1$	$22\sim 2$	$22\sim 3$	$22\sim 4$	$22\sim 5$
Mass fractions of H_3PO_4(%)		0	0.11	0.22	0.33	1.00
Rc (MPa)		68.9	57.4	54.3	56.6	55.2
In water for	Rc_{15} (MPa)	37.4	50.0	43.2	50.17	47.16
15 days	W_{15}	0.54	0.87	0.80	0.88	0.85
In water for	Rc_{30} (MPa)	31.17	50.9	46.4	47.1	50.27
30 days	W_{30}	0.45	0.88	0.85	0.83	0.91
In water for	Rc_{45} (MPa)	27.5	46.0	46.4	45.8	46.3
45 days	W_{45}	0.40	0.80	0.85	0.80	0.83

calcined (MgO) and $MgCl_2$ solution with 25°Be concentration is 1:0.7.

The MOC sand mortar specimens were prepared by the mixes in which the mass ratio of the magnesite powder calcined/28°Be $MgCl_2$ solution/the silica sand was 1:0.7:3.0, and to which the different mass fraction of H_3PO_4 were added. After these, specimens were cured at air for 15 days and followed by immersing in the flowing water for 15 days; 30 and 45 days, respectively, their strengths Rc, Rc_{15}, Rc_{30}, and Rc_{45} were measured, and the strength retention coefficients W_{15}, W_{30}, and W_{45} were calculated, respectively. The results are given in Table 4.

From the test data in these two tables, the following could be concluded:

(1) Regardless of whether the specimens are neat MOC paste specimens or MOC sand mortar specimens, the strengths of the specimens without H_3PO_4 are sharply decreased with days in water. However, the strengths of the specimens with H_3PO_4 are only minimally decreased with days in water; thus, their strength retention coefficients are greater than the ones of the specimens without H_3PO_4. Consequently, the phosphoric acid is able to greatly improve the water resistance of MOC.

(2) When the days *n* of the specimens immersed in water are the same, their strength retention coefficients are increased as the mass fractions of phosphoric acid added to MOC pastes is increased up to a certain value, beyond which the excessive H_3PO_4 has little influence on the strength retention coefficients.

Table 5
The strengths and the strength retention coefficients of the specimens of the neat MOC pastes added by $NaH_2PO_4{\cdot}2H_2O$

Samples		$12\sim 1$	$12\sim 2$	$12\sim 3$	$12\sim 4$	$12\sim 5$
Fractions of	mass (%)	0.28	0.50	0.78	1.00	1.73
NaH_2PO_4	moles (/kg)	0.018	0.032	0.050	0.064	0.111
Rc (MPa)		64.4	63.1	60.0	54.0	50.8
In water for	Rc_{28} (MPa)	42.8	46.2	46.6	50.9	49.4
28 days	W_{28}	0.66	0.73	0.77	0.94	0.97
In water for	Rc_{60} (MPa)	24.4	36.9	47.5	50.0	45.0
2 months	W_{60}	0.38	0.58	0.78	0.93	0.88

Table 6
The strengths and the strength retention coefficients of the specimens of the neat MOC pastes added by $NH_4H_2PO_4$

Samples		$10\sim 1$	$10\sim 2$	$10\sim 3$	$10\sim 4$	$10\sim 5$
Fractions of	mass (%)	0.20	0.37	0.57	0.74	1.28
$NH_4H_2PO_4$	moles (/kg)	0.017	0.032	0.050	0.064	0.111
Rc (MPa)		70.5	65.0	62.8	59.4	38.8
In water for	Rc_{28} (MPa)	44.4	51.6	52.8	55.6	30.9
28 days	W_{28}	0.63	0.79	0.84	0.94	0.80
In water for	Rc_{60} (MPa)	21.9	28.8	49.4	51.9	25.0
2 months	W_{60}	0.31	0.44	0.79	0.87	0.64

(3) In general, the addition of phosphoric acid causes the compressive strength of dry specimens cured for 15 days to be decreased, the larger the mass fraction of phosphoric acid added to MOC paste, the lower the compressive strength of the MOC paste specimens cured for 15 days.

3.2. The effect of the soluble phosphates on the water resistance of MOC

When either $NaH_2PO_4{\cdot}2H_2O$ or $NH_4H_2PO_4$ was used as the additive to prepared the MOC paste specimens, in which the mass ratio between the magnesite powder calcined and 25°Be $MgCl_2$ solution was also 1: 0.7, the results were shown in Table 5 and Table 6, respectively. It can be seen that the two soluble phosphates have the same effects on MOC paste as phosphoric acid. In other words, the addition of the soluble phosphates to MOC pastes also results in little variations in the strengths of the specimens with time in water and in much more increase in their strength retention coefficients. Hence, it is concluded that the soluble phosphates, like phosphoric acid, are able to greatly improve the water resistance of MOC as well.

4. Analysis and discussion

4.1. The reason why the soluble phosphates can improve the water resistance of MOC

As shown in Table 3, the strength retention coefficients W_{28}s of the sample $13\sim 0^{\#}$ without any additives and the sample $13\sim 4^{\#}$ with 0.74% (mass) of H_3PO_4 are 0.1 and 0.91, respectively; correspondingly, the losses of their compressive strength are 90.2% and 9.1%, respectively. The results shown in Tables 5 and 6 also indicate that the strength retention coefficients W_{28}s of both the sample $12\sim 4^{\#}$ with 0.78% of $NaH_2PO_4{\cdot}2H_2O$ and the sample $10\sim 4^{\#}$ with 0.74% of $NH_4H_2PO_4$ are 0.94; correspondingly, the losses of their compressive strength are 5.7% and 6.4%, respectively. On the other hand, the XRD analysis results given in Table 7 illustrate that before these samples are immersed in water, the main phases formed in them are all $5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (5-phase), but after these sam-

Table 7
Composition of the phases observed by XRD and weight loss in four typical specimens before and after their immersion in water for 28 days

Sample number	Kind of additives	Before immersion in water			After immersion in water 28 days			
		Five phase	MgO	$Mg(OH)_2$	Five phase	MgO	$Mg(OH)_2$	Weight loss (%)
$13\sim0$	–	+++	+	–	–	–	+++	37
$13\sim4$	H_3PO_4	+++	+	–	+++	–	+	2.3
$12\sim4$	NaH_2PO_4	+++	+	–	+++	–	+	2.5
$10\sim4$	$NH_4H_2PO_4$	+++	+	–	+++	–	+	1.9

ples are immersed in water for 28 days, 5-phase in the sample $13\sim0^{\#}$ without any additives has totally disappeared; only $Mg(OH)_2$ is observable, and its weight losses is 37%, and 5-phase in the samples with either H_3PO_4 or $NaH_2PO_4{\cdot}2H_2O$ or $NH_4H_2PO_4$ remains almost unchanged, and the weight losses of these samples are very small. These results clearly indicate that the phase compositions in $13\sim0^{\#}$ sample are totally changed by water; thus, its strength retention coefficients W_{28} is very small. However, the phase compositions in $13\sim4^{\#}$; $12\sim4^{\#}$, and $10\sim4^{\#}$ samples remain unchanged in water; thus, their strength retention coefficients W_{28}s are very large. So, the water resistance of hardened MOC pastes are related to the change of the phase compositions in them caused by water.

However, the change of the phase compositions is due to the instability of the main phase in MOC pastes in water. As indicated by our earlier work [4], main phases formed in MOC pastes, 5-phase and 3-phase ($3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$), are unstable in water and will decompose as follows:

$$5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \rightarrow 5Mg(OH)_2 + 2Cl^- + Mg^{2+} + 8H_2O \quad (2)$$

$$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \rightarrow 3Mg(OH)_2 + 2Cl^- + Mg^{2+} + 8H_2O \quad (3)$$

Thus, when hardened MOC paste specimens are immersed in water, 5-phase or 3-phase in them will progressively decompose to $Mg(OH)_2$ phase and some soluble ions and H_2O molecules that can be dissolved out of the specimens by water, which causes the strengths and weight of the specimens to lose much.

Therefore, the key reason why the water resistance of MOC is very poor, i.e., the strengths of MOC is greatly lost in water, is that the main phases in MOC pastes are unstable in water. If only the main phases are stable in water, the water resistance of MOC will become very good. It is by a greater increase in the stability of 5-phase in water that the addition of the phosphoric acid or the soluble phosphates to MOC pastes can greatly improve the water resistance.

4.2. How do the soluble phosphates greatly enhance the stability of 5-phase in water

It is interesting to mention that the phosphates can be absorbed onto the surface of the grains of 5-phase, which results in a layer of insoluble complexes to protect 5-phase [2]. However, the results of XRD analysis in this work do not support this idea. XRD patterns of the sample $13\sim4^{\#}$ with 0.74% (mass) H_3PO_4, the sample $12\sim4^{\#}$ with 0.78% of $NaH_2PO_4{\cdot}2H_2O$, and the sample $10\sim4^{\#}$ with 0.74% of $NH_4H_2PO_4$, after their immersion in water for 28 days, are shown in Fig. 1. Obviously, besides the main peak lines of 5-phase, $Mg(OH)_2$ and MgO, any characteristic peak lines of insoluble phosphates or phosphate complexes, such as $Mg_3(PO_4)_2$, $MgNH_4PO_4{\cdot}6H_2O$, etc. cannot be observed in these XRD curves in Fig. 1. This result explains that there are no insoluble phosphates or phosphate complexes in the samples with either H_3PO_4 or $NaH_2PO_4{\cdot}2H_2O$ or $NH_4H_2PO_4$. In addition, the results in Tables 3, 5, and 6 also show that when the mass fractions of these soluble phosphates to MOC pastes are over 0.74% ~ 1.0%, the strength retention coefficients of the samples are no longer increased with the mass fractions. However, the values of 0.74–1.0% is too small to produce a layer of insoluble phosphates to protect all of 5-phase grains in the samples from the decomposition caused by water. Hence, it is hard to say that the enhancement of the stability of 5-phases in the MOC pastes with either the phosphoric acid or the soluble phosphates is due to the protection of any insoluble phosphates.

On the other hand, H_3PO_4, $NaH_2PO_4{\cdot}2H_2O$, and $NH_4H_2PO_4$ are all soluble and can be ionized in water to form such phosphate radical anions as $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. From the data in Tables 3, 5, and 6, it can be seen that no matter what the additive is either H_3PO_4 or $NaH_2PO_42H_2O$ or $NH_4H_2PO_4$, the strength retention coefficients of these samples with much the same moles of the additive per kilogram MOC pastes are almost same. These results show that the effect of the soluble phosphates on the stability of 5-phases in water is related to no such cations as H^+, Na^+, and NH_4^+, but the moles of such phosphate radical anions as $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} yielded by the ionization of the soluble phosphates. Thus, it can be concluded that the key components being responsible for the improvement of the stability of 5-phase in water are these phosphate radical anions, and the amount of the phosphate radical anions required by the great improvement of the stability of 5-phase in water is about 0.06 mol/kg of MOC pastes. This is a very important fact.

There had been evidences [5,6] which indicate that the formation of 5-phase or 3-phase is dependent on the concentration of Mg^{2+} ions in the solutions of MOC pastes. There is the lowest concentration of Mg^{2+} ions in the solutions needed by the formation of these main phases in MOC pastes. When the concentration of Mg^{2+} ions is lower than the lowest concentration, the reaction product formed in MOC pastes is only $Mg(OH)_2$, not 5-phase or 3-phase.

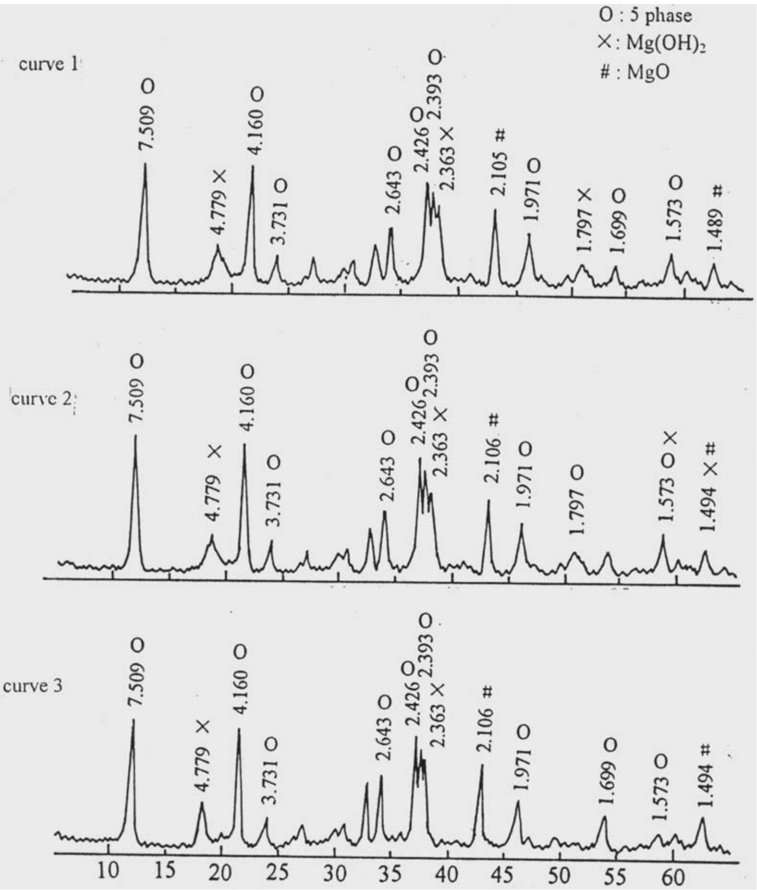

Fig. 1. XRD patterns of the MOC paste specimens by 0.74% (mass) H_3PO_4 (curve 1) and with 0.78% of $MaH_2PO_4 \cdot 2H_2O$ (curve 2) and with 0.74% of $NH_4H_2PO_4$ (curve 3) after their immersion in water for 28 days.

For example, when the molar ratio of $MgO/MgCl_2/H_2O$ in the MOC paste is 10:1:29, in which the concentration (15°Be) of the $MgCl_2$ solution is much lower, neither 5-phase nor 3-phase are produced, and the only phase formed is $Mg(OH)_2$. As shown in Fig. 2, all of the main peak lines observed in the curve 1 belong to $Mg(OH)_2$.

Also, according to the solubility theory of a ionic crystalline, when a hardened MOC paste sample is immersed in water in which the concentration of Mg^{2+} ions is very much lower, 5-phase or 3-phase in the sample is unstable and will decompose into $Mg(OH)_2$ and some soluble ions by Eq. (2). The result of the sample 13 ~ 0 in Table 7 has explained this idea.

Now that 5-phase in the samples with the phosphate radical anions is very stable and can remain unchanged in water (see Table 7 and Fig. 1), then, 5-phases should be produced in the MOC pastes with much lower concentration of Mg^{2+} ions and the phosphate radical anions. This has just been clarified by the curve 2 in Fig. 2 that is the XRD pattern of the hardened MOC paste with the same molar ratio of $MgO/MgCl_2/H_2O$ as one in the curve 1 and 1% (mass) of H_3PO_4. Obviously, the main peak lines of 5-phases can be clearly observed in the curve 2; in other words, the main phase formed in this hardened MOC paste with H_3PO_4 is 5-phase, not $Mg(OH)_2$ phases. This shows that the addition of H_3PO_4 makes the formation of 5-phases in the MOC pastes with much lower concentration of Mg^{2+} ions possible. Thus, 5-phases in the hardened MOC pastes with H_3PO_4 should be stable in the solutions with the lower concentration of Mg^{2+} ions, even in water. Therefore, the phosphate radical anions in the soluble phosphates act the part of decreasing the lowest concentration of Mg^{2+} ions in the solutions required by the formation and stable existence of the main phases in MOC pastes. This action of the phosphate radical anions can be related to the effect of the anions on the formation reactions of 5-phase or 3-phase in MOC pastes.

From our earlier work [6], both 5-phase and 3-phase are ionic crystalline of basic salts $[Mg_x(OH)_y(H_2O)_z]^{2x-y} \cdot Cl^- \cdot nH_2O$ and are composed of the polynuclear aqueohydroxy magnesium complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ (abbr. polynuclear complex),Cl^-, OH^-, and H_2O molecules, while the polynulear complexes are to be yielded by the hydrolyzing–bridging reactions of Mg^{2+} ions in the solutions of MOC pastes:

$$x\,Mg^{2+}(aq) + (z-y)H_2O \Longleftrightarrow [Mg_x(OH)_y(H_2O)_z]^{2x-y} + yH^+ \qquad (4)$$

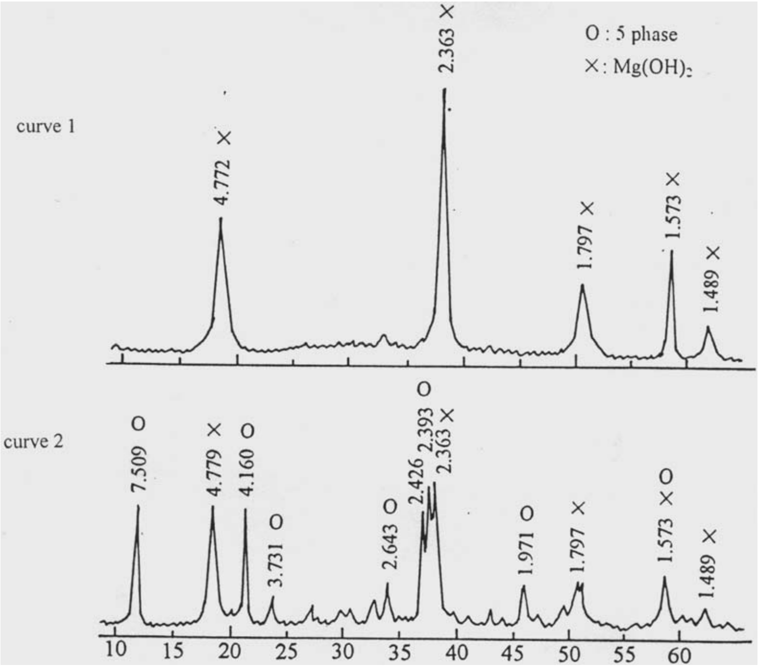

Fig. 2. XRD patterns of the MOC pastes with 10:1:29 (molar ratio) of MgO/$MgCl_2$/H_2O without any additives (curve 1) and with the addition of 1% (mass) of H_3PO_4 (curve 2).

Thus, the formation of these phases is dependent on the production of the stable polynuclear complexes in the solutions of MOC pastes. According to the hydrolysis theory of metal ions, whether polynuclear complexes can or cannot be produced by the hydrolysis of Mg^{2+} ions is related not only to the concentration of OH^- ions, but also to the concentration of Mg^{2+} ions in the solutions. There is the lowest concentration of Mg^{2+} ions for the production of the stable polynuclear complexes, which is decided by the properties of Mg^{2+} ions. When the concentration of Mg^{2+} ions in the solutions of an MOC paste is below the lowest concentration, there are no stable polynuclear complex in the solutions. Of course, neither 5-phases nor 3-phases can be formed in the MOC paste. Consequently, the lowest concentration of Mg^{2+} ions for the formation of the stable polynuclear complexes is exactly the lowest concentration of Mg^{2+} ions in the solutions required by the formation and stable existence of the main phases in MOC pastes.

When the phosphoric acid or soluble phosphates are added to a MOC paste, the phosphate radical anions yielded in the solutions of the MOC paste could influence the hydrolysis reactions of Mg^{2+} ions in the solutions. This effect contributes to the great decrease of the lowest concentration of Mg^{2+} ions required by the formation of the stable polynuclear complexes and the formation of the main phases in MOC pastes. This idea is to be further proven in the future.

In addition, just because of this effect, the formation reaction speed of the main phases in MOC pastes is low, which brings about the retardation of the setting of the MOC pastes. So, the earlier strengths of the hardened MOC pastes with a phosphate additive are much lower than one of the hardened MOC pastes without any additives.

Therefore, it can be concluded that the soluble phosphates act the part of decreasing the lowest concentration of Mg^{2+} ions in the solutions required by the formation and stable existence of the main phases in MOC pastes. This action makes the main phases formed in the MOC pastes and the strength of the hardened MOC pastes remain unchanged in water. That is the mechanism for the phosphoric acid or soluble phosphates to greatly improve the water resistance of MOC.

5. Conclusion

1. The soluble phosphates can greatly improve the water resistance of MOC; thus, the strength retention coefficients of hardened MOC pastes are increased with the increase of the mass fraction of the phosphates added into the MOC pastes. When the mass fraction reaches 0.5–1.0% of the MOC paste mass, the strength retention coefficients can be more than 0.8 which is enough to meet the requirement of engineering applications.
2. The water resistance of MOC is poor, i.e., the strength retention coefficients of hardened MOC pastes are very small due to their main phases such as 5-phase and 3-phase becoming unstable in water and the phase compositions in them totally changed by water. However, the addition of soluble phosphates to MOC pastes increases the stability of the main phases in water and prevents the phase compositions from changing, which

makes the strength retention coefficients of hardened MOC pastes to become very large.

3. The key components being responsible for the increase of the stability of the main phases in water are the phosphate radical anions yielded by the soluble phosphates. The phosphate radical anions act the part of decreasing the lowest concentration of Mg^{2+} ions in the solutions required by the formation and the stable existence of the main phases. The action makes the formation of the main phases in the MOC pastes with much lower concentration of Mg^{2+} ions possible and the main phases in hardened MOC pastes remain unchanged in water.

References

[1] Z. Chuanmei, D. Dehua, Research on the water resistance of magnesium oxychloride cement and its improvement (Chinese), Gui Suan Yan Xue Bao 23 (6) (1995) 673–679.

[2] W. Kurdowski, F. Sorrentino, Special cements, in: P. Barnes (Ed.), Structure and Performance of Cement, Appl. Sci. Pub., London, 1983, p. 539, Chapter 10.

[3] Z. Chuanmei, D. Dehua, Research on evaluation indexes of the water resistance of magnesium oxychloride cement (Chinese), Xin Xing Jian Zhu Cai Liao 22 (2) (1995) 11–14.

[4] Z. Chuanmei, D. Dehua, The stability of the reaction products of magnesium oxychloride cement in water, J. Wuhan Univ. Technol. 6 (3) (1994) 51–59.

[5] C. Mazuranic, H. Billinski, B. Matkovic, Reaction products in the system $MgCl_2$–NaOH–H_2O, J. Am. Ceram. Soc. 65 (1982) 523–525.

[6] D. Dehua, Z. Chuanmei, The formation mechanism of the hydrate phases in magnesium oxychloride cement, Cem. Concr. Res. 29 (9) (1999) 1365–1371.