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THE EFFECT OF ALUMINATE MINERALS ON THE PHASES IN MAGNESIUM OXYCHLORIDE CEMENT

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ABSTRACT

The effects of aluminate minerals on the phases and strengths of magnesium oxychloride cement (MOC) have been studied. The X-ray diffraction examination results showed that the addition of small quantities of the hydraulic aluminate minerals can cause the conversion of the reaction products in MOC paste, but the addition of the inert aluminate minerals can not. The product formed in plain MOC paste, which the molar ratio of $MgO/MgCl_2$ is more than 5, is $5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (5·1·8 phase), but the product formed in the MOC pastes with the same molar ratio containing CA or C_4AF is $3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (3·1·8 phase). It is considered that the phase conversion could be related to the hydration products of the hydraulic aluminate minerals in the MOC paste. The results of the compressive strength measurement indicate that the addition of small quantities of the hydraulic aluminate minerals would not influence the strengths of the hardened MOC paste.

Introduction

The main reaction products of magnesium oxychloride cement (MgO-$MgCl_2$-H_2O system) had long been revealed to be four crystal phases : $5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_20$ (5·1·8 phase); $3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (3·1·8 phase); $2Mg(OH)_2{\cdot}MgCl_2{\cdot}4H_2O$ (2·1·4 phase) and $9Mg(OH)_2{\cdot}MgCl_2{\cdot}5H_2O$ (9·1·5 phase). Cole and co-worker (1,2) defined the temperature ranges over which the phases are stable. The stable phases observed below 100°C are the 5·1·8. phase and 3·1·8 phase. The stable phases above 100°C were reported to be 2·1·4 and 9·1·5 phase. Moreover, the phase assemblages in equilibria below 100°C are dependent on the MgO reactivity, $MgO/MgCl_2$ molar ratio, and the concentration of $MgCl_2$ solution. The phases equilibria in the system MgO-$MgCl_2$-H_2O at 25+3°C were determined and the importance of MgO reactivity to the formation of magnesium oxychloride cement(MOC) were described by Sorrell and Armstrong (3) on the basis of X-ray analysis of samples. They established the phase diagram of the ternary system at room temperature. In 1980, L. Urwongse and C.A. Scorrell (4) again constructed an equilibrium phase diagram for the system MgO-$MgCl_2$-H_2O from the measures of the solubility of MgO in aqueous HCl solution at 23°C and analyses of neat MOC pastes cured in sealed containers. According to the phrase diagram, it can be obtained that if $MgO/MgCl_2$ molar ratios are 5 and over, then, the reaction products will be 5·1·8 phase; if $MgO/MgCl_2$ molar ratios are below 5, the reaction products will be 3·1·8 phase or its mixtures with 5·1·8 phase and the reaction will proceed by the rapid formation of

5·1·8 phase which reaches a maximum in about 25 hours. The 3·1·8 phase forms more slowly at the expense of 5·1·8 phase and becomes the major phase after a period of time. H. Bilinski and co-worker (5) discussed the effect of initial composition, the activity of MgO on the MOC pastes. The investigation had revealed that the activity of MgO inlfuenced both the reaction speed and reaction products, the present of excess water in the initial composition also influenced the reaction products. For example, according to the phase diagram, at molar ratio $MgO/MgCl_2$ over 5 and some excess of water, the reaction products in MOC paste should be the mixtures of 5.1.8 phase and $Mg(OH)_2$. However, in the MOC paste prepared with the very active MgO, the reaction products were the large quantities of $Mg(OH)_2$ and the small quantities of 3.1.8 phase formed at later stages.

The effect of some additives or other sales on the reaction products in MOC pastes seems to have not been reported. This paper will deal with the influence of some aluminate minerals on the crystalline phase formed in MOC pastes and the strengths of hardened MOC pastes.

Experimental Procedure

Materials. MgO used for this work was the calcined magnesite powder at about 800°C. Typical chemical analysis is listed in TABLE 1.

$MgCl_2$ used was a halogenide $MgCl_2 \cdot 6H_2O$ obtained after KCl is refined form $KMgCl_2.6H_2O$ in Qinghai potash Fertilizer Plant. Typical chemical analysis is listed in TABLE 2.

High alumina cement used was commercial refractory cement (525#) supplied by Zheng Zhou Cement Plant. Its chemical analysis is given in TABLE 3.

The aluminate minerals synthesized in the laboratory are three kinds of the fine powder, that are named as No. 1, No. 2 and No. 3 powder respectively, prepared by the calcination of the paste mixtures of alumina ore or/and iron ore and limestone at 1,250-1,350°C. Their XRD analyses are given in FIG. 2 to FIG. 4.

Preparation of Specimens. To prepare the specimens of neat MOC paste, $MgCl_2.6H_2O$ was dissolved in water to form the $MgCl_2$ solution with 28° Be concentration, then small quantities of high alumina cement or the synthetic aluminate powder was mixed with the appropriate weight of the $MgCl_2$ solution in a bowl by hand, the weighted calcined magnesite powder (all experiments used a $MgO/MgCl_2$ molar ratio of 8.0) was added in the mixes and were mixed again by hand to form homogeneous MOC paste. The pastes were cast in cyclindrial PVC plastic cups (20 mm in diameter, 40 mm high) and sealed and cured for 28 days at room temperature, then, unmolded. These neat MOC paste specimens were used for XRD analysis.

TABLE 1
Chemical Analysis of Calcined Magnesite Powder

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 specimens used for the measurements of strengths were the mortar specimens. The aggregate employed was the standard silica sand. The cement paste/aggregate mass ratio was 1:2.5. The test specimens were 40 X 40 X 160 mm^3 prisms which were cured for 28 days at room temperature.

Measurement. The reaction products in the MOC paste specimens were identified by D/Max -3A X-ray powder diffractometer made in Japan, using (Cu, Ka) radiation at 40 kV and 30 mA.

Experimental Results

The Effect of High Alumina Cement (HAC) on the Reaction Products in MOC Pastes. The XRD pattern of the MOC paste specimen with the molar ratio of $MgO:MgCl_2:H_2O$ at 8:1:14 is shown in FIG. 1 (a), the reaction product in the specimen is 5·1·8 phase. This result is in keeping with the ternary phase diagram established by L. Urwongse and his co-worker for the system $MgO\text{-}MgCl_2\text{-}H_2O$.

However, as shown in FIG. 1 (b), the reaction product in the specimen of the MOC paste with the same molar ratio but added by 5.6% mass fraction of high alumina cement is 3·1·8 phase. This case is out of accordance with the ternary phase diagram. The fact indicates clearly that the addition of small quantities of high alumina cement causes the change of the reaction products in the MOC pastes.

In general, the major mineral phases in high alumina cement are some calcium aluminates with the hydraulity and the calcium silicoaluminate without the hydraulity. For this reason, the comparison of the influence of the three kinds of the synthesized powder on the reaction products has been made.

The Effect of the Hydraulic Calcium Aluminate (CA) on the Reaction Products in MOC Pastes. As shown in FIG. 2, the curve (a) indicates that the mineral phase in No.1 powder synthesized in the laboratory are mainly CA and C_2AS, but CA is a principal phase and C_2AS is a secondary phase. The curve (b) indicates that the reaction product in the MOC paste specimen added by 5.6% mass fraction of No.1 powder also is 3·1·8 phase rather than

TABLE 3
Chemical Analysis of High Alumina Cement

component	Al_2O_3	CaO	MgO	SiO_2	Fe_2O_3	Other
mass fraction (%)	44.5	39.3	0.1	2.0	12.9	1.2

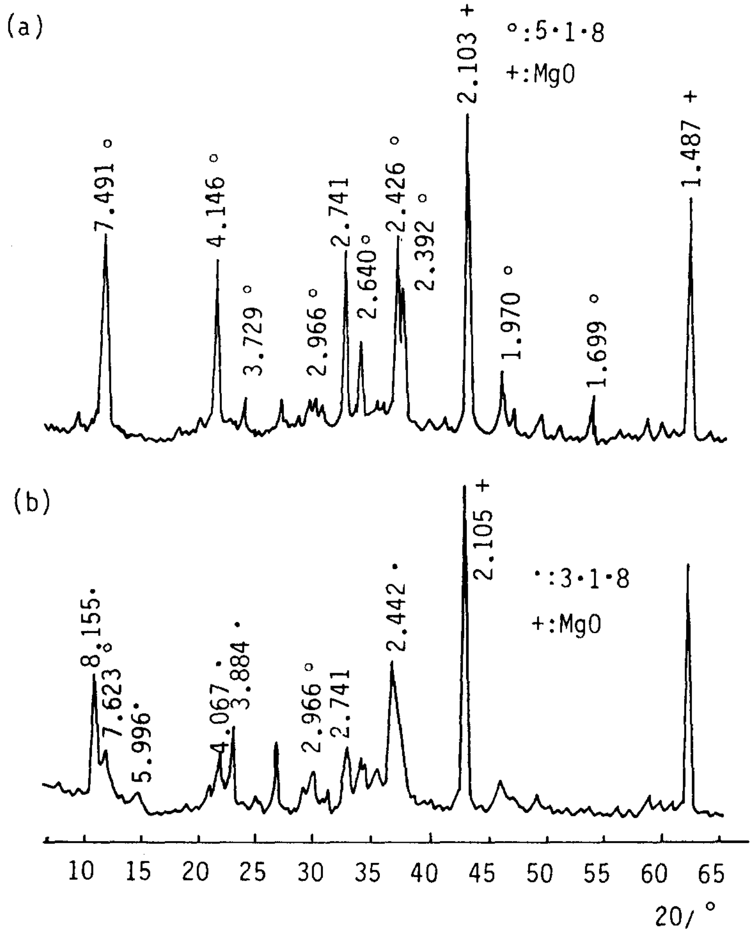

FIG. 1.
X-ray diffraction patterns of the plain MOC pastes without high alumina cement (curve a) and with 5.6% (mass) high alumina cement (curve b).

5·1·8 phase. This result shows that No.1 powder with the dominant phase of CA has the same effect as high alumina cement.

The Effect of Calcium Silicoaluminate (C_2AS) on The Reaction Products in MOC Paste. As shown in FIG. 3, when 5.6% of mass fraction of No. 2 powder in which the dominant phase is C_2AS, evidenced by the curve (a), is added into the MOC paste, the reaction product is not 3·1·8 phase but 5·1·8 phase. This is to say that the No. 2 powder with the dominant phase of C_2AS can not cause the conversion of reaction products in MOC paste.

The Effect of Calcium Ferroaluminate (C_4AF) on the Reaction Products in MOC Paste. The XRD patterns of No. 3 synthesized powder and the MOC paste specimen added by 5.6% mass fraction of No. 3 powder are given in FIG. 4. It can be seen that the dominant phase in No. 3 powder is C4AF shown in curve (a) and the reaction product in the MOC paste added

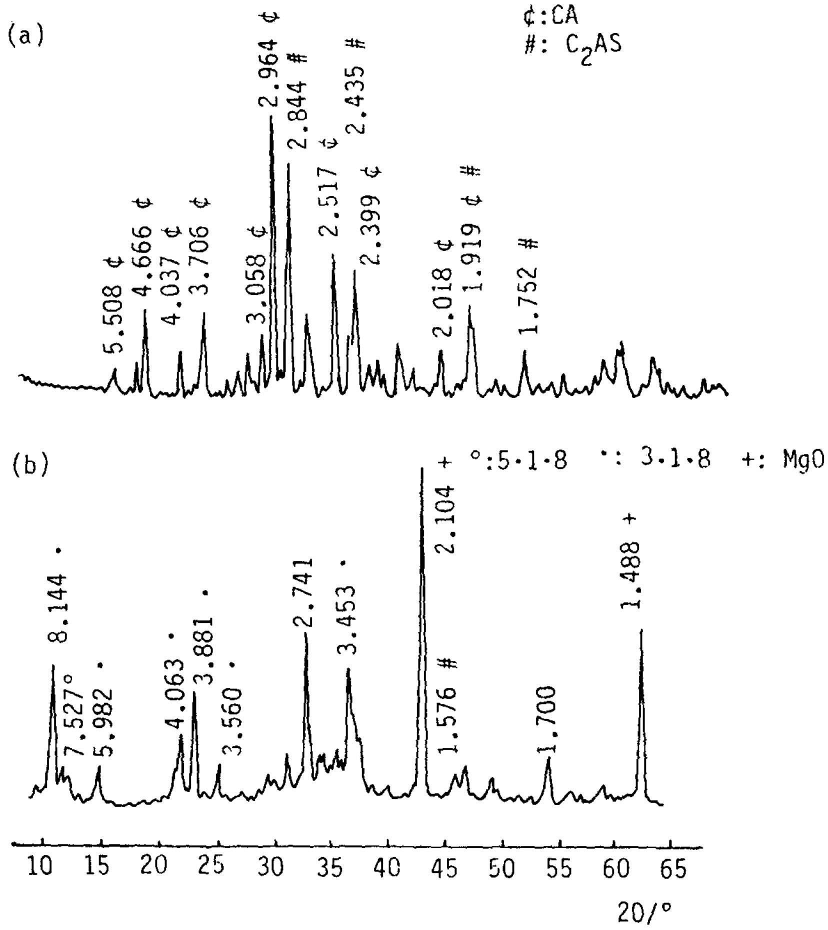

FIG. 2.
X-ray diffraction patterns of No. 1 powder (curve a) and the MOC paste added by 5.6% (mass) No. 1 powder.

5.6% mass fraction by No. 3 powder also is 3·1·8 phase, not 5·1·8 phase. It is evidenced that the effect of No. 3 powder with the dominant phase of C_4AF is just the same as the No. 1 powder.

Discussion

Above XRD analysis results firstly reveal that the reaction products in MOC paste can be changed by the addition of small quantities of high alumina cement or the hydraulic aluminate minerals. When the molar ratio $MgO:MgCl_2:H_2O$ is 8:1:14 in the initial composition, the reaction product in MOC paste should be 5·1·8 phase. But, if small quantities of high alumina cement or the hydraulic aluminate minerals are added, the reaction product in the MOC paste with the same molar ratio is not 5·1·8 phase but 3·1·8 phase that can be formed only in the MOC pastes with MgO/$MgCl_2$ below 5, predicted by the ternary phase diagram. This phenomenon can be named as "phase conversion effect".

Although the mechanism of the phase conversion effect has not been made clear, it can be certain that the effect should be related to the hydraulicity of the aluminate minerals. As shown in FIG. 2 to FIG. 4, high alumina cement and the two kinds of powder with dominant phase of CA or C_4AF have the phase conversion effect, but the No. 2 powder with the dominant phase of inert C_2AS has not. In addition, the main peak line 2.964 Å of CA and 2.649 Å of C_4AF can not be observed in the curves (b) in FIG. 2 and FIG. 4, but the main peak line 2.850 Å of inert C_2AS can still be observed in the curve (b) in FIG. 3. This seems to confirm that the hydraulic CA and C_4AF are disappeared due to the hydration reaction in the liquid phase of MOC paste, but the inert C_2AS is still present in the hardened MOC paste. So it can be considered that the phase conversion effect can be related with the hydration of the hydraulic aluminate minerals in MOC paste.

The past studies showed: the composition of the reaction products formed depends upon the relative ratio between Mg^{2+} and Cl^- ions and pH value in the liquid phase of MOC paste.

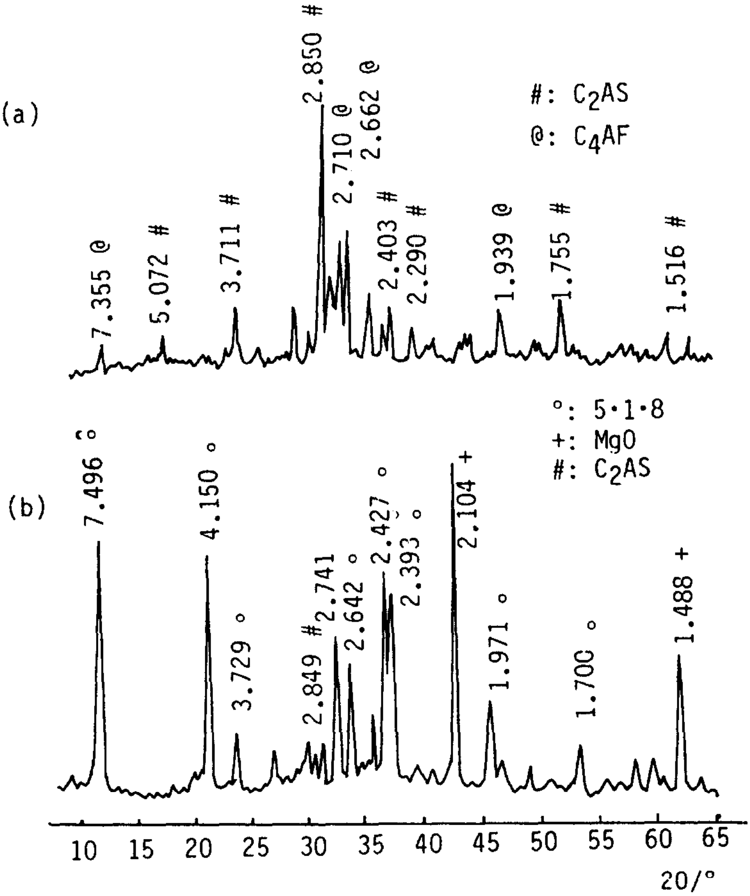

FIG. 3.

X-ray diffraction patterns of No. 3 powder (curve a) and the MOC paste added by 5.6% (mass) No. 3 powder (curve b).

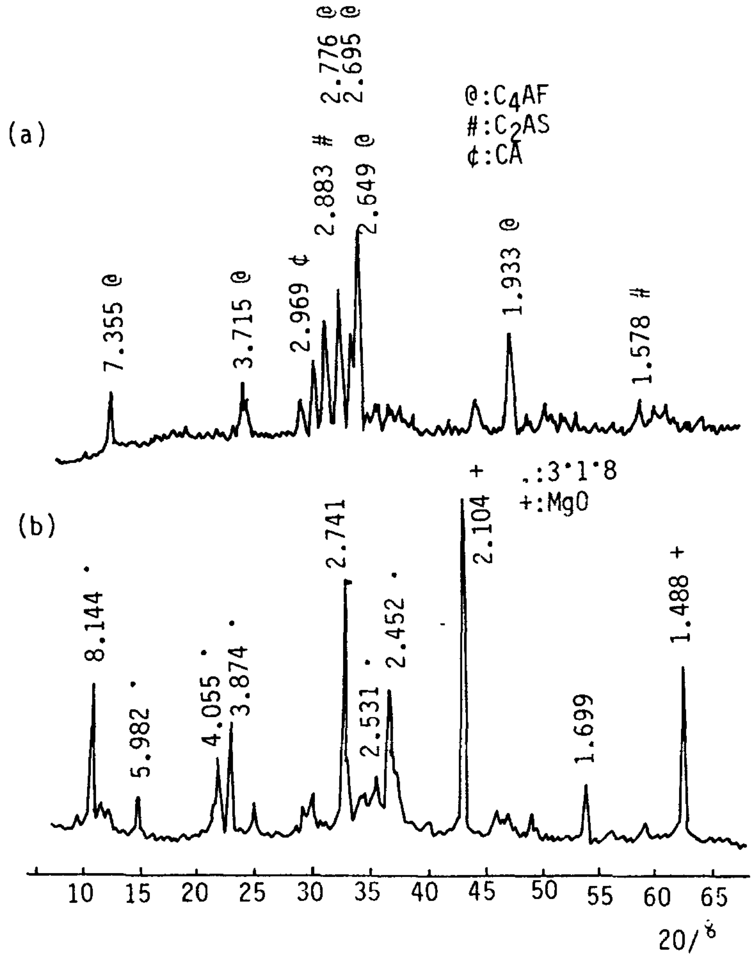

FIG. 4.
X-ray diffraction patterns of No. 3 powder (curve a) and the MOC paste added by 5.6% (mass) No. 3 powder (curve b).

The lower molar ratio Mg^{2+}/Cl^- and pH value are favorable to form 3·1·8 phase, but the higher molar ratio Mg^{2+}/Cl^- and pH value are favorable to form 5·1·8 phase.

B.R. Currell and co-workers (6) suggested that the following chemical changes take place during the initial hydration of high alumina cement:

$$CaO.Al_2O_3 + 10\,H_2O \longrightarrow Ca(OH)_2 + 2[Al(OH)_3(H_2O)] \qquad (1)$$

$$[Ca(H_2O)_2]^{2+} + 2[Al(OH)_4(H_2O)_2]^- \qquad (2)$$

Here, these chemical changes take place in the liquid phase that is the high concentration solution of $MgCl_2$, thus the OH^- ion in $[Al(OH)_3(H_2O)_3]$ or $[Al(OH)_4(H_2O)_2]^-$ would be exchanged with Cl^- ion in the solution to form some Al complexes with Cl^- ligand:

TABLE 4
Effect of High Alumina Cement (HAC) on the strengths of MOC cement Mortar

Sample	10-1	10-2	10-3	10-4
$MgO/MgCl_2$ (mole ratio)	7.0	7.0	7.0	7.0
HAC/MOC paste (mass ratio)	0.0	0.02	0.04	0.08
Sand/MOC paste (mass ratio)	2.5	2.5	2.5	2.5
Compressive strength (Mpa)	68.9	69.7	69.1	69.4
Flexure strength (Mpa)	14.6	14.3	14.8	14.1

$$[Al(OH)_3(H_2O)_3] + Cl^- \longrightarrow [Al(OH)_2Cl(H_2O)_3] + OH^- \qquad (3)$$

$$[Al(OH)_4(H_2O)_2]^- + Cl^- \longrightarrow [Al(OH)_3Cl(H_2O)_2]^- + OH^- \qquad (4)$$

Thus, the hydration product with the structural formula of $[Ca_4Al_2(OH)_{12}]^{2-}\cdot X_2^-\cdot YH_2O$ could be formed, in which X is an anion Cl^- or OH^- (in fact, the ordinary hydration products CAH_{10}, C_2AH_8, or C_3AH_6 etc, are not detected in the MOC paste specimens by XRD analyses). These hydration products would deposite on the surface of MgO grain, which will slow down the process of the dissolve of MgO grain in the liquid phase of MOC paste. The consequence is that both the molar ratio Mg^{2+}/Cl^- and pH value in the liquid phase of the MOC paste with CA are the lower than in the liquid phase of the MOC paste without CA. Thus, although the molar ratio $MgO/MgCl_2$ is more than 5, 3·1·8 phase can be preferable to 5·1·8 phase in the former MOC paste. Because the similar hydration product of C_4AF can be formed in the MOC paste, C_4AF also has the phase conversion effect. But, C_2AS is inert and any chemical changes of it can not take place in the liquid phase of the MOC paste, so, C_2AS does not have the phase conversion effect.

It can be concluded that the phase conversion caused by the hydraulic aluminate minerals is due to the cover of their hydration products on the surface of MgO grain in the MOC paste, the cover slows down the dissolving process of MgO grain and creates the condition in the liquid phase being favorable to form 3·1·8 phase.

In addition, the phase conversion effect is probably related to the processes of nucleation and the formation of both the hydration products of the hydraulic aluminate minerals and the reaction products in the MOC pastes. At this point, there are many problems to be investigated in the future.

The compressive strengths of the MOC mortar specimens are shown in TABLE 4, it can be seen that the strength of MOC mortars is not decreased by the addition of high alumina cement. There is only little difference between the strength of the MOC mortar without high alumina cement, in which the reaction product is 5·1·8 phase, and the strengths of the MOC mortars with high alumina cement, in which the reaction product is 3.1.8 phase. This confirms that the contributions of 5·1·8 and 3·1·8 phases to the strength of hardened MOC paste are same. It is different from the previously reported opionion, that the contribution of 5·1·8 phase to the strengths is the larger. Under normal condition, when the molar ratio of $MgO/Mg(OH)_2$ is 8-10, the strengths of the hardened MOC paste are the highest (7), in which there are MgO or $Mg(OH)_2$ crystallines phases besides 5·1·8 phase. When the reaction product is mainly 3·1·8 phase, the $MgO/MgCl_2$ molar ratio must be less than 5 in the MOC pastes, in which MgO or $Mg(OH)_2$ crystalline phases are absent but some uncrystallized oxychlorides or chlorides with the larger solubility can be present in addition to 3·1·8 phase. Both the absence of MgO or $Mg(OH)_2$ and the presence of the uncrystallized oxychlorides or/and chlorides cause the hardened MOC pastes easily to get damp and have the lower strength (7). When high alumina cement is added into the MOC paste with the molar ratio $MgO/MgCl_2$ of 8-10, not only the reaction product is 3·1·8 phase, but also MgO or $Mg(OH)_2$ phases are present in the hardened MOC paste. Thus, the hardened MOC paste in which 3·1·8 phase and MgO or $Mg(OH)_2$ phases are co-present have the same strength as the hardened MOC pastes in which 5·1·8 phase and MgO or $Mg(OH)_2$ phases are co-present. So, the addition of small quantities of high alumina cement or the hydraulic aluminate minerals does not influence the strength of MOC pastes.

Conclusions

1. The addition of the hydraulic aluminate minerals to MOC paste can produce "the phase conversion effect", i.e. when the initial molar ratios $MgO/MgCl_2$ are 5 and over, the reaction product in the MOC pastes with the hydraulic aluminate minerals CA, C_4AF etc, is 3·1·8 phase rather than 5·1·8 phase predicted by the Sorrell's phase diagram. However, the addition of the inert aluminate C_2AS minerals can not produce "the phase conversion effect". Tis may be related to the hydration of the hydraulic aluminate minerals in the liquid phase of MOC paste.
2. The contribution of 3·1·8 phase being co-present with MgO or $Mg(OH)_2$ phase to the strength of hardened MOC pastes is similar to that of 5·1·8 phase. Converting the reaction products, the addition of small quantities of the hydraulic aluminate minerals or high alumina cement does not influence the strength of MOC phase.

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