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Effects of Sodium Silicate and Citrate on Magnesium Oxysulfate Cement

[Yingying Yang, Mingfang Ba, Jiefei Wang, Simin Zhao, Zheyu Tang]

***Abstract*—In order to improve the properties of Magnesium Oxysulfate (MOS) Cement, the effects of Citrate and Sodium Silicate with single or double-doped way on water resistance and mechanical strength of MOS cement were investigated. Also scanning electron microscope (SEM) technique was adopted to explain the morphology of phase composition. The experimental results showed that under the condition of 15±3°C, RH=70±5% single Citrate increasing improve the compressive and flexural strength of MOS cement while exert less effect on water resistance of MOS cement. The double-doped Citrate and Sodium Silicate by the mass ratio of 1:2 could both increased 7d flexural strength by twice and compressive strength by 50% and simultaneously largely improve water resistance of MOS cement. SEM results showed that a large number of connected wheat-like-needle hydration products were formed in hardened MOS cement paste with double-doped Citrate and Sodium Silicate.**

***Keywords*—Magnisium Oxysulfate Cement; Sodium Silicate; Citrate; Water Resistance; Mechanical Properties**

I. Introduction

Compared to Magnesium Oxychloride cementitious material, Magnesium Oxysulfate Cemented material has its own specialties in water resistance, environmental protection, no corrosion to steel, effective inhibition of the frost etc[1-3]. But its low strength restricts its popularization and utilization in the field of civil Engineering. Nowadays the research concerning improving the performance of MOS cemented material is very limited. Demediuk T et al.[4] pointed out that four kinds of basic MOS crystals consist in the hardening body of MOs cemented material, among which only $3Mg(OH)_2MgSO_4•8H_2O$ crystal stably exists in the room temperature; According to phase transformation process of MOs cemented material Ladawan [5] put forward that in normal temperature, the stable phase in hardened MOs is 5Mg(OH)2MgSO4•3H2O; Wu Chengyou et al [6] studied the phase composition of MOs cemented material by adding Citrate; Zhu Huirong [7- 10]considered the effects of Borate, Citrate, Sucrose and H3PO4 modifier towards the performance of MOs cemented material; Deng Dehua [11] proposed the formation mechanism of MOS cemented system.

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Based on the best mixture ratio of MOS in literature[12], the effects of double-doped Citrate and Sodium Silicate on properties of MOS cement were investigated in this research.

II. Experiments

A. *Raw materials*

Industrial grade of magnesium sulfate crystals from Tianjing and the light-burned magnesia powder from Yingkou were used. Their chemical compositions are shown in Table 1 and Table 2. The XRD pattern and particle size distribution of light-burned MgO was shown in Fig.1. Also Citrate and Sodium Silicate used in the experiment are all analytical pure reagents.

TABLE I CHEMICAL COPOSITION OF MGSO4·7H2O

Component	$MgSO_4$	$MgCl_2$	NaCl	Na_2SO_4	H_2O	others
Weight%	47.85	0.50	0.50	0.50	50.24	0.41

TABLE II CHEMICAL COPOSITION OF LIGHT-BURNED MgO

Component	SiO_2	MgO	CaO	Al_2O_3	Fe_2O_3	LOI
Weight%	0.40	96.50	0.85	0.19	0.21	1.85

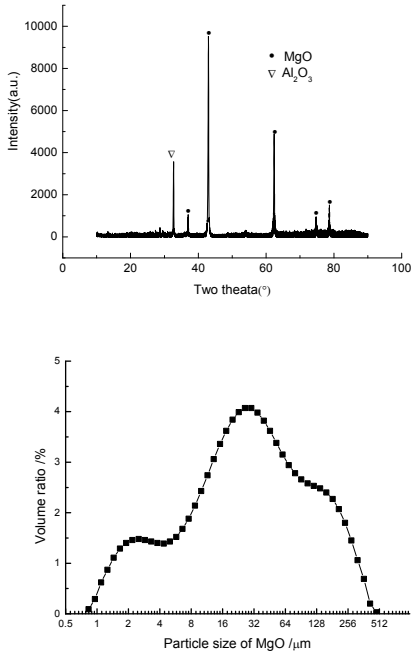


Fig.1 XRD Pattern and Particle size distribution of Light-burned MgO

B. Experimental program

a) MgO, $MgSO_4 \cdot 7H_2O$ and water were mixed by Molar ratio of 14:1:9 and the single-doped Citrate or double-doped Sodium Silicate and Citrate (mixing by mass ratio of 1:1, 1:2 and 2:1) was added by 0.5% MgO mass. And 40mm × 40mm × 160mm specimens were prepared. After 24 hours curing, the specimens were demolded and placed in room at 15 ± 3°C, with 70 ± 5% of relative humidity. By the age of 3d, 7d, 14d and 28d, compressive and flexural strength of specimens were tested.

b) By age of 14d, one set of specimens for each group were immersed in water in the same curing room. And by age of 28d, its compressive strength was tested to calculate the softening coefficient of specimens.

III. Results and Discussions

A. Effects of Single-doped Sodium Silicate and Citrate on MOS cement

a) Effects on Mechanical properties of MOS

The effects of single-doped Sodium Silicate on compressive and flexural strength of MOS cement were illustrated in Fig.2. It could be seen that with the increase of mixing mass ratio of Sodium Silicate, the compressive and flexural strength of MOS cement barely improved. It indicated that single adding Sodium Silicate is invalid.

The effects of single Citrate on mechanical strength of MOS cement were shown in Fig.3. it could seen that certain mass ratio of Citrate largely improved the flexural and compressive strength of MOS cement, and especially at the mass ratio of 0.5% the flexural and compressive strength of MOS cement increased by nearly 50% and twice respectively.

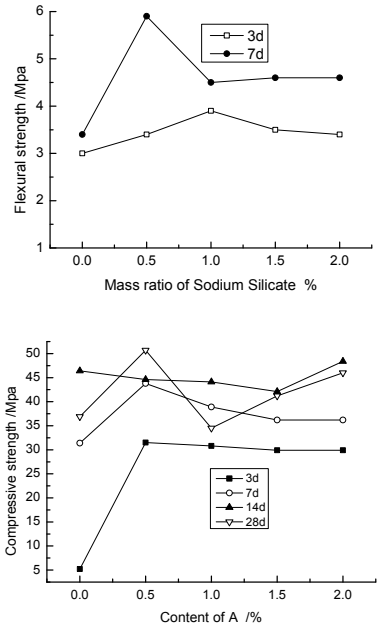


Fig.2 Effects of single Sodium Silicate on strengths of MOS cement

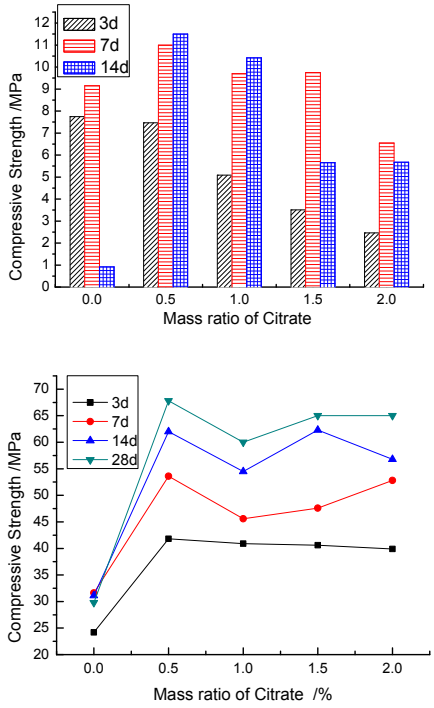


Fig.3 Effects of Citrate on mechanical properties of MOS cement

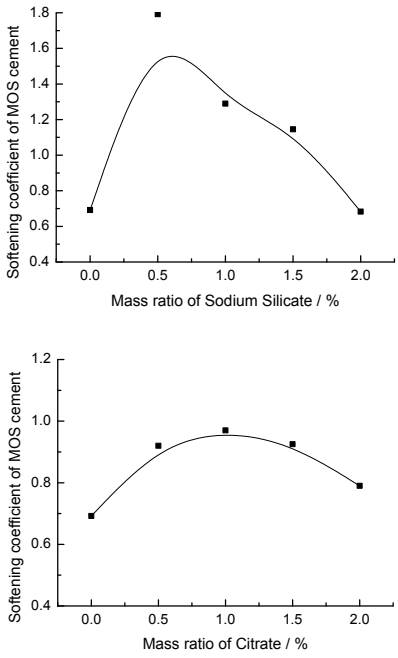


Fig.4 Effects of single-doped Sodium Silicate and Citrate on water-resistance of MOS cement

b) Effects on water-resistance of MOS cement

The softening coefficients of MOS cement with single-doped Sodium Silicate and Citrate was calculated and shown in Fig.4. From Fig.4 it could be found that both single Sodium Silicate and Citrate could improve the water-resistance property of MOS cement. While it is obvious that the adding

mass ratio of Sodium Silicate is 0.5% - 1%, the best effects on water-resistance properties of MOS cement was attained.

B. Effects of compound Sodium Silicate with Citrate on MOS cement

a) Effects on mechanical properties

From Fig.5 it could be seen that dual-doped Citrate and Sodium Silicate can improve the early flexural strength of MOS cement, and when mixing Citrate and Sodium Silicate are mixed by mass ratio of 1:2, the corresponding 7d flexural strength of MOS cement improved by twice as much compared to that of the blank test specimen, and the compressive strength at early 3d and 7d age increased by 50%.

b) Effects on water resistance

From Fig.6 it can be seen that the best effects on improving water resistance of MOS cement has been obtained when mixing Citrate with Sodium Silicate by mass ratio of 1:2. And the corresponding softening coefficient of modified MOS cement is greater than 1 and reaches 1.14. It can be attributed to the new-formed insoluble hydration phases.

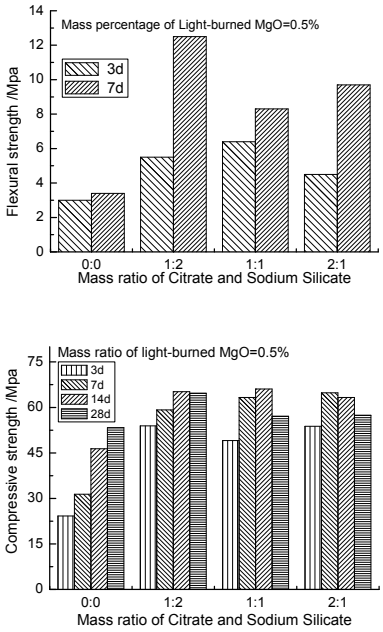


Fig.5 Effects of mass ratio of Citrate and Sodium Silicate on mechanical properties of MOS

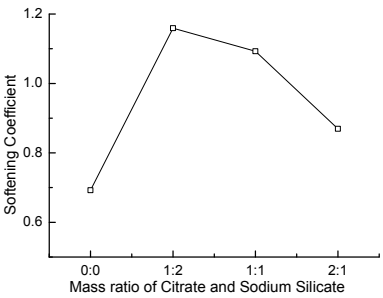


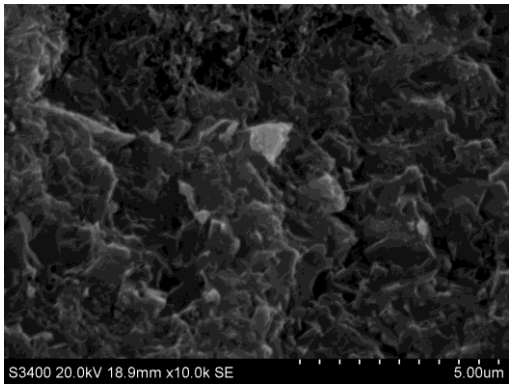
Fig.6 Effects of mass ratio of Citrate /A on mechanical property of MOs

C. Effects of Citrate on morphology of hydration products in hardened MOS paste by SEM

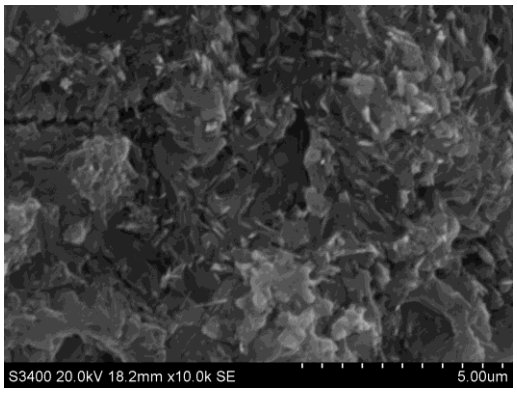
The morphology of hydration products inside 3d hardened MOS cement was examined by SEM technique and was exhibited in Fig.7. It can be seen from the figure that a large number of wheat-like products was new-formed after adding Citrate in MOS cement. The increased strength and water-resistance should be attributed the tightly connected newly formed phases inside the hardened MOS cement paste.

D. Conclusions

When Citrate mixed with Sodium Silicate by mass ratio of 1:2 are added at 0.5% percentage of mass light-burned MgO, the flexural strength of MOS cement paste at 7d could increase twice as much, and the corresponding softening coefficient of hardened MOS paste is larger than 1 indicating largely improved water resistance of MOS cement paste. Compare with morphology of hydration product in MOS without modifier, there are a large number of connected wheat-like hydration products are new formed in hardened MOS paste.



(a) Blank MOS cement paste



(b) Single-doped Citrae in MOS cement

Fig.7 Effects of Citrate on morphology of hydration products in MOS cement

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Reference

[1] Y Jin, X.L Guang, Y.D Zhao. Effects of additives on Magnesium Oxychloride cement water resistance [J]. Jilin Building Materials,2000,82 (2):11-13.(In Chinese)

[2] Z.Y Li, D.X Jin, and C Zhou etc. “Research for plugging wells and interior magnesia cement temporarily closed[J]”. Southwest Petroleum University (Natural Science), 2011,33(5):152-156.(In Chinese)

[3] H.F, Yu. “Oxygen’s new water-resistant magnesium cement grip[J]”. Ceramic Society,1992,20(4):374-380.(In Chinese)

[4] T Demediuk, W.F.A Cole. “Study of magnesium oxy-sulphates [J]”. Australian Journal of Chemistry, 1957, 10(2):287-294.

[5] L Urwongse, C.A Sorrell. “Phase relationships in Magnesium Oxysulfate cements[J]”. Joumal of the American Ceramic Society,1980, 63(9-10):523-526.

[6] C.Y Wu, H.F Yu, J Weng and J.M Dong. “Phase composition and performance of Magnesium Oxysulfate cements[J]”. New Building Materials,2013, 5:68-72.(In Chinese)

[7] H.R Zhu. “Research for Magnesium Oxysulfate performance[D]”. Jilin Architectural and Civil Engineering School of Engineering Master Thesis, 2010, 1- 4.(In Chinese)

[8] JZ Ruan, H.R Zhu, R Liang, etc. “Research for Magnesium Oxysulfate performance[J]”. Jilin Institute of Architectural Engineering, 2009, 26(4):17-25. (In Chinese)

[9] J.J Beaudoin, V.S Ramachandran. “Strength development in magnesium oxysulfate cement[J]”. Cement and Concrete Research, 1978, 8(1):103-112.

[10] C.Y Wu, H.F Yu, J.M Dong , et al. “Effects of Material Ratio, Fly Ash, and Citric Acid on Magnesium Oxysulfate Cement [J]”. ACI Material Journal, 2014,111(3):291-298

[11] D.H Deng. “A Study on the Theories and Techniques for improvimg Properties of MgO-Based Basic Salt Cements and Their Articles[D]”. Central South University PhD thesis, 2005: 10-15.(In Chinese)

[12] M.F Ba, J.F Wang, Y.Y Yang, and S.M Zhao,etc. “Preparation and Property for modified Magnesium Oxy-sulfate Materials[J]”. .Ningbo University Journal .2014,27(2):83-87.(In Chinese)