

Recent Advances in Concrete Technology and Sustainability Issues

Proceedings
Fourteenth International Conference
Beijing, China

October-November 2018

**Tongbo Sui
Terence C. Holland
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American Concrete Institute

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Editors:

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Preface

The Canada Centre for Mineral and Energy Technology (CANMET) of Natural Resources of Canada, Ottawa, has played a significant role for more than 40 years in the broad area of concrete technology in Canada. In recent years CANMET has become increasingly involved in research and development dealing with the supplementary cementing materials, high-performance normal weight and lightweight concretes, and alkali-aggregate reactions. As part of CANMET's technology transfer program, an international symposium on Advances in Concrete Technology was sponsored jointly with the American Concrete Institute (ACI) and other organizations in Athens, Greece in May 1992. In June 1995, CANMET, in association with the ACI and other organizations in Canada and the U.S.A., sponsored the Second CANMET/ACI International Symposium on Advances in Concrete Technology in Las Vegas, Nevada. For the Athens symposium, the CANMET publication "Advances in Concrete Technology," constituted the proceedings of the symposium. The proceedings from the Las Vegas symposium were published by the ACI as SP-154.

In August 1997, CANMET in association with the ACI and other organizations in Canada and New Zealand, sponsored the Third CANMET/ACI International Symposium on Advance in Concrete Technology in Auckland, New Zealand. The main purpose of the symposium was to bring together representatives from industry, universities, and government agencies to present the latest information on concrete technology, and to explore new areas of research and development. Thirty-three refereed papers from 15 countries were presented and distributed at the symposium. The proceedings were published as ACI SP-171.

In June 1998, CANMET, in association with ACI, Japan Concrete Institute (JCI), and several other organizations in Canada and Japan, sponsored the Fourth CANMET/ACI International Conference on Recent Advances in Concrete Technology in Tokoshima, Japan. More than 80 papers from 20 countries were received and reviewed in accordance with the policies of the ACI. Sixty-one referred papers were accepted for presentation at the conference and for publication as ACI SP-179. In addition to the referred papers, more than 30 papers were presented and distributed at the conference.

In July-August 2001, CANMET, in association with the ACI and several organizations in Singapore, sponsored the Fifth CANMET/ACI International Conference on Recent Advances in Concrete Technology in Singapore. More than 100 papers from 25 countries were received and reviewed in accordance with the policies of the ACI. Forty-six refereed and more than 25 additional papers were accepted for presentation at the conference. The proceedings of the conference were published as ACI SP-200. In JUNE 2003 CANMET, in association with the ACI and several organizations in Romania, sponsored the Sixth CANMET/ACI International Conference on Recent Advances in Concrete Technology in Bucharest, Romania. More than 40 papers presented at the conference were distributed "as received," and no formal ACI special publication was published.

In May 2004, CANMET, in association with the ACI and several other organizations in the U.S.A., sponsored the Seventh CANMET /ACI International Conference on Recent Advances in Concrete Technology in Las Vegas, Nevada. Seventeen refereed papers from more than 10 countries were presented and distributed at the conference. The proceedings, consisting of the refereed papers, were published as ACI SP-222. In addition to the refereed papers, 20 additional papers were presented and distributed at the conference.

In May 2006, CANMET, in association with the ACI and several other organizations in Canada and the U.S.A., sponsored the Eighth CANMET/ACI International Conference on Recent Advances in Concrete Technology in Montreal, Canada. The proceedings of the conference consisting of 17 refereed papers, were published as ACI SP-235. In addition to the refereed papers, more than 30 additional papers were presented and distributed at the conference.

In May 2007, CANMET, In association with the ACI and several other organizations in Canada, Europe, and the U.S.A., sponsored the Ninth CANMET/ACI International Conference on Recent Advances in Concrete Technology in Warsaw, Poland. The proceedings of the conference consisted of 10 refereed papers were published as ACI SP-243. More than 20 additional papers were presented and distributed at the conference.

In October 2009, ACI, in association with several organizations in Canada, Europe and the U.S.A., sponsored the Tenth ACI International Conference on Advances in Concrete Technology in Seville, Spain. The proceedings of the conference consisting of 20 refereed papers were published as ACI SP-261. In addition to the refereed papers, more than 20 additional papers were presented at the conference and published in a supplementary papers volume.

In May 2010, the Committee for the Organization of International Conferences (COIC) (formerly CANMET/ACI Conferences), in association with the Chinese Ceramics Society(CCS) and several other organizations in China, sponsored the Eleventh International Conference on Advances in Concrete Technology and Sustainability Issues in Jinan, China. More than 40 papers were presented at the conference. The proceedings of the conference were published by the CCS, Beijing, China.

In October 2012, the COIC, in association with the ACI, sponsored the Twelfth International Conference on Advances in Concrete Technology and Sustainability Issues in Prague, Czech Republic. The proceedings of the conference consisted of more than 30 refereed papers and were published as ACI SP-288. In addition to the refereed papers, more than 40 other papers were presented at the conference, and were published in a supplementary papers volume.

In July 2015, the COIC, in association with the ACI sponsored the Thirteenth International Conference on Advances in Concrete Technology and Sustainability Issues in Ottawa, Canada. The proceedings of the conference consisting of 28 refereed papers were published by the ACI as SP-303. In addition to the refereed papers, more than 40 other papers were presented at the conference, and were published in a supplementary papers volume.

In October 30 to November 2, 2018, the CCS and the China Academy of Building Research (CABR), Beijing China, in association with the COIC sponsored the Fourteenth International Conference on Recent Advances in Concrete Technology and Sustainable Issues in Beijing, China. The proceedings of the Conference consisting of 19 refereed papers were published by the ACI as SP 330. In addition to the refereed papers, more than 52 papers were presented at the conference, and these were published in the supplementary papers volume.

Thanks are extended to the members of the technical papers review panel that met in March 2018 in Hainan Island, China. The members of the review panel were selected from Canada, China, Italy, Norway Switzerland, the U.K, and the U.S.A. Without their dedicated efforts, it would not have been possible to have the proceedings ready for distribution

at the conference. The co-operation of the authors in accepting the reviewers' suggestions, and in revising the draft manuscripts accordingly is greatly appreciated.

The guidance and great support for organization of the conference from Dr. V.M. Malhotra, Prof. Changwen Miao, the Honorary Chairpersons of the conference, are sincerely appreciated.

The support of CABR for the administrative work associated with the review of the papers, and the conference is gratefully acknowledged. Also, acknowledged is their support for the publication of the proceedings (ACI SP 330).

Dr. Tongbo Sui, Chairperson, Scientific Committee of the Conference

Dr. Terence C. Holland, Chairperson, Paper Review Panel

Prof. Ziming Wang, Secretary General of the Conference

Dr. Xiaolong Zhao, Vice Director of the Organizing Committee

Editors

Fourteenth International Conference on Advances in Concrete Technology and Sustainability Issues

October 30 to November 2, 2018,

Beijing, China

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Degradation Process of Cementitious Materials with Copper Slag Subjected to Sodium Sulfate Attack under Drying-Wetting Cycles

by Huashan Yang and Yujun Che

This paper presents an experimental study on the degradation process of cementitious materials with copper slag subjected to sodium sulfate attack under drying-wetting cycles. The cement pastes with 30% of copper slag (CS) were prepared by using water to binder ratio of 0.4. The degradation process of cementitious materials with copper slag immersed in 5% sodium sulfate solution under drying-wetting cycles were studied. X-ray diffraction (XRD) and backscattered electron image (BSE) were used to investigate microstructure changing. The research results indicate that the newly formed hydration products of partially reacted clinker increase the compactness of the hardened cementitious materials and increase the concentration of calcium hydroxide in the pore solution, thereby retarding the decomposition of C-S-H.

Keywords: cementitious materials; copper slag; sodium sulfate; hydration products; pore structure.

INTRODUCTION

Sulfate attack on cementitious materials has been a key durability issue and a subject of extensive investigation. It was established that sulfate attack on cementitious materials is generally attributed to the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum and ettringite,¹⁻⁴ which can cause expansion, cracking, and deterioration of concrete exposed to sulfate environment. Mehta⁵ pointed out that the decomposition of hydration products such as calcium hydroxide and C-S-H gel, should also be considered an integral part of the sulfate attack. For cementitious materials in splash and tidal zone, drying-wetting cycles tend to severely accelerate the sulfate attack, because drying-wetting cycle could make the sulfate accumulation and crystallization in concrete through cycled moisture gradient and capillarity absorption.⁶⁻⁸ For example, the conversion of anhydrous sodium sulfate (Na_2SO_4) to the hydrous ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) form is associated with 314% volumetric expansion.⁹ Thus, the degradation of concrete due to sulfate attack

is considered to be a complicated phenomenon of physical and chemical process. Therefore, it is necessary to deeply investigate and reasonably evaluate the degradation process of cementitious materials subjected to sulfate attack.

It was found that the incorporation of mineral additions such as fly ash, blast furnace slag, and silica fume as a partial replacement of ordinary Portland cement had good durability in sulfate environment.¹⁰⁻¹² The enhanced resistance of cementitious materials with mineral additions to sulfate attack is attributed to the reduced calcium hydroxide.¹¹

Recently, there has been a growing interest in the use of copper slag (CS) as a mineral addition in cementitious materials.^{13,14} Also, the effects of copper slag waste utilization as a mineral addition on durability performance of concrete in sulfate solution were investigated.^{15,16} However, these literatures did not consider other parameters such as partially reacted clinker and mineral additions in hardened cementitious materials, which can affect the mechanisms and kinetics of sulfate attack.

In this paper, the degradation process of cementitious materials with copper slag subjected to sodium sulfate attack under drying-wetting cycles are reported. The roles of partially reacted clinker and copper slag in hardened cementitious materials were analyzed using XRD and BSE.

RESEARCH SIGNIFICANCE

Most of the published research did not consider the important effect of partially reacted clinker and mineral additions in hardened cementitious materials on the process of sulfate attack. The present study deals with degradation process of cementitious materials with copper slag subjected to sodium sulfate attack under drying-wetting cycles. The newly formed hydration products of partially reacted clinker and copper slag are of great importance to the sulfate resistance of cementitious materials. Therefore, the results presented in this paper are useful to improve the resistance of sulfate attack.

EXPERIMENTAL INVESTIGATION

Materials

The main raw materials for experimental research are moderate heat Portland cement (MHC), copper slag, sodium sulfate and deionized water. The chemical compositions of the clinker and copper slag are shown in Table 1. Sodium sulfate is a commercial product. It can be observed from Fig. 1(a) that the XRD pattern of copper slag shows a broad and diffuse protuberance in the vicinity of 2θ of about 30° , indicating that copper slag is dominated by the glassy state. Angular copper slag particles with a broad particle size range can be observed from Fig. 1 (b).

Methods

MHC pastes with 30% of copper slag were prepared with deionized water using a water to binder ratio of 0.4. Six 0.78 in. (20 mm) cube paste specimens were cast and demolded after 24 hours. The specimens (C/CS-Unattacked) were test to obtain degradation process of cementitious materials subjected to sodium sulfate attack after 28 days of water curing at about 68°F (20°C). Control specimens (C/CS-Attacked) were cured in water continually until test. The test procedure is as follows:

- ① Specimens were placed in 5% sodium sulfate solution.

Table 1—Chemical compositions of clinker and copper slag

	Clinker	Copper slag
Loss of ignition, %	0.3	—
SiO ₂ , %	20.9	36.7
Al ₂ O ₃ , %	5.1	3.8
CaO, %	62.2	5.6
MgO, %	4.3	5.3
SO ₃ , %	0.6	—
Fe ₂ O ₃ , %	5.7	47.1
f-CaO, %	0.5	—
Others, %	0.4	1.5

— = not measured items.

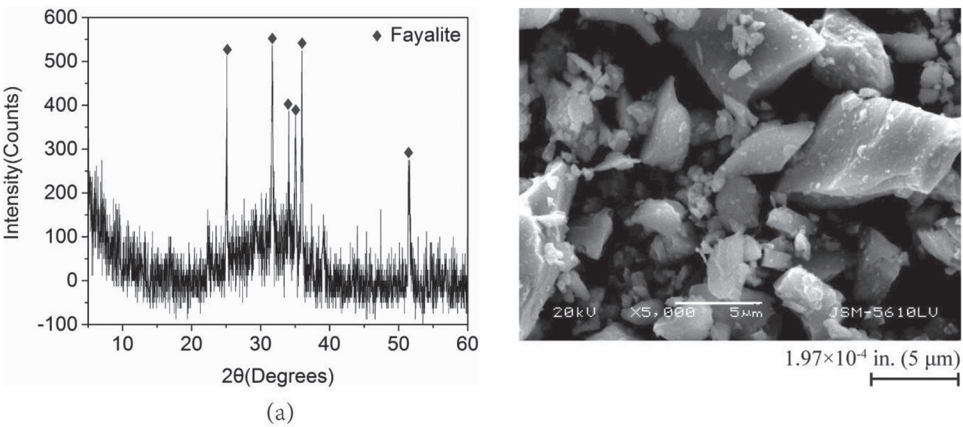


Fig. 1—(a) X-ray diffractogram and (b) SEM image of copper slag

② After 48 hours, the specimens were taken from the sodium sulfate solution and placed in a desiccator for 24 hours. This is the first cycle.

③ Repeat steps 1 and 2 until the end of the 5th cycle.

Hydration products and partially reacted clinker were analyzed by XRD. Partially reacted clinker, copper slag, porosity, and pore size distribution of specimens were analyzed by BSE.

The content of partially reacted clinker, copper slag, hydration products and pores in cementitious materials are particularly variable, but average features can be measured, which help to understand the degradation process of cementitious materials subjected to sodium sulfate attack. A JSM-IT300 scanning electron microscope was used to analyze the microstructure of the specimens based on backscattered electron imaging. A magnification of 500× was used for all images. At 500× the resolution of the 640×480 digital image, width of a single pixel is about 1.56×10^{-5} in. (0.397 μm). Fig. 2 (a) shows a typical BSE image of control specimen (C/CS-Unattacked). According to the working principles of

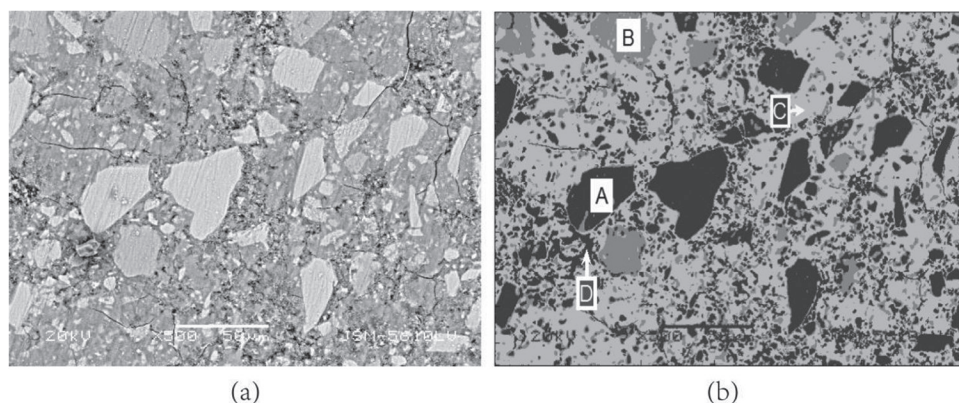


Fig. 2—(a) BSE image of C/CS-Unattacked, (b) cluster analysis, A: copper slag, B: clinker, C: hydration products, D: pores.

backscattered electron imaging in scanning electron microscope, areas with high average atomic numbers generate strong signals, resulting in a bright contrast in BSE images. Therefore, the relative atomic number of different areas can be determined based on BSE images contrasts.¹⁷ As can be seen from Fig. 2 (a), copper slag is brightly white due to its high content of Fe_2O_3 (47.1%); brighter areas correspond to partially reacted clinker; less bright areas correspond to hydration products; least-bright areas correspond to pores. Cluster analysis was conducted on BSE images to separate copper slag, partially reacted clinker, hydration products and pores, as shown in Fig. 2 (b). The degradation process of cementitious materials with copper slag subjected to sodium sulfate attack can be further investigated by calculating respective areas of copper slag, partially reacted clinker, hydration products, pores, and pore size distribution.

EXPERIMENTAL RESULTS AND DISCUSSION

XRD analysis

Fig. 3 (a) shows the XRD pattern of specimen C/CS-attacked subjected to sodium sulfate attack for 5 cycles. Control specimen C/CS-Unattacked cured in water, which has the same age as that of the C/CS-Attacked. It can be observed from the figure that the main phase of the C/CS-Unattacked and C/CS-Attacked are calcium hydroxide and partially reacted clinker. The diffraction peak of calcium hydroxide and partially reacted clinker in C/CS-Attacked is lower than that of C/CS-Unattacked. This is mainly because sodium sulfate reacts with calcium hydroxide in the pore solution to produce gypsum, which results in the dissolution of calcium hydroxide in hardened cementitious materials. The reduction of the calcium hydroxide concentration in the pore solution of hydrated cementitious materials promotes the further hydration of clinker. The hydration reaction can continuously generate calcium hydroxide to maintain its concentration in the pore solution.

BSE analysis

Based on the BSE images, the contents of copper slag, partially reacted clinker, hydration products, and porosities of specimens were calculated and shown in Table 2. After 5 cycles

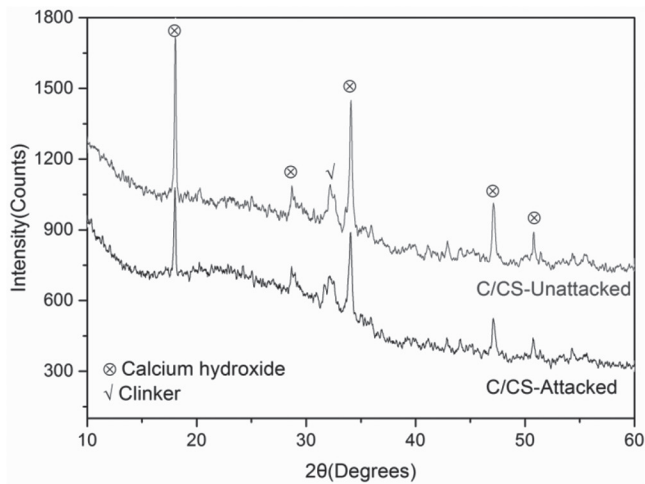


Fig. 3—X-ray diffractogram of specimens

Table 2—Copper slag, clinker and porosity of specimens

Specimens	Copper slag, %	Clinker, %	Porosity, %
C/CS-Unattacked	17.6	24.7	8.4
C/CS-Attacked	11.1	16.6	13.4

of sulfate attack, specimen C/CS-Attacked had lower contents of copper slag and partially reacted clinker than that in specimen C/CS-Unattacked. However, the porosity of specimen C/CS-Attacked was higher than that of specimen C/CS-Unattacked. In other words, specimen C/CS-Attacked had lower structure compactness than that of control specimen. It can be observed from Fig. 4 that the larger pores of C/CS-Attacked are increased, while the smaller pores are decreased.

The reaction between sodium sulfate and calcium hydroxide in the pore solution produces gypsum, which caused the hardened cementitious materials to undergo a crystalline expansion under drying-wetting cycles. Also, sodium sulphate in the pores will generate sodium sulfate decahydrate under drying-wetting cycle conditions, which will also cause crystallization pressure, leading to cracking of the hardened cementitious materials. This is the main reason for the increase in porosity and larger pores of the specimen. On the other hand, the reaction of sodium sulfate and calcium hydroxide, in turn, reduces the concentration of calcium hydroxide in the pore solution as discussed in the XRD analysis. Thus, the calcium hydroxide in the hardened cementitious materials dissolves to maintain its saturated concentration, which will drive the continued hydration of the partially reacted clinker. This is why the clinker in the C/CS-Attacked is lower than that of control specimen. The increase of porosity also provides a larger space for the growth of hydration products, thereby promoting the further hydration of copper slag to form C-S-H. This process leads to an increase in the resistance of the material to sodium sulfate attack.

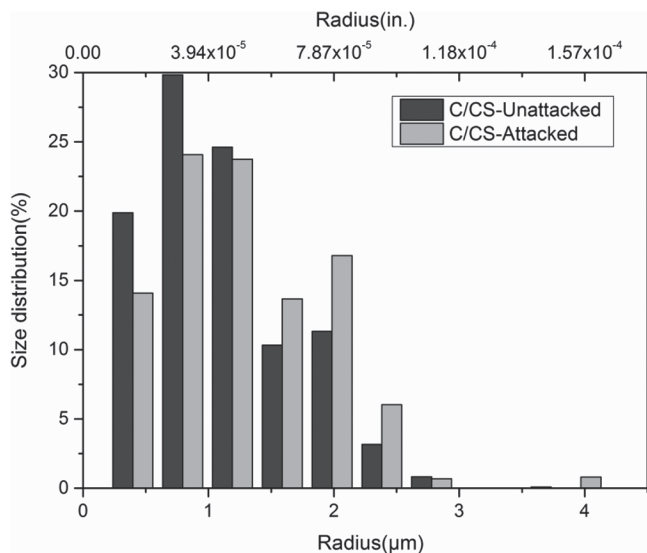


Fig. 4—Pore size distribution of specimens

Degradation process

Based on the test results of XRD and BSE, Fig. 5 shows the degradation process of hardened cementitious materials with copper slag in sodium sulfate solution. Point A is on the surface of hydrated cementitious materials, points B, C and D are inside the hardened cementitious materials.

Degradation processes include the cracking of hardened cementitious materials and the dissolution of calcium hydroxide. Calcium hydroxide in the pore solution near point A reacts with sodium sulfate to form gypsum. Formation of gypsum plays an important role in the damage of material(2). Dihydrate gypsum and sodium sulfate decahydrate in the pores will cause crystallization pressure, leading to cracking of the hardened cementitious materials under drying-wetting cycles. Drying-wetting cycles coarsened the pores of concrete specimens so that the sulfate was more prone to enter the interior of concrete.⁸ Also, cracking gives easier access to further penetration of sulfates.¹⁸ On the other hand, decreasing the concentration of calcium ions in the pore solution will result in the dissolution of calcium hydroxide from the hardened cementitious materials. The hydration products, such as C-S-H, may be decomposed when the concentration of calcium hydroxide reduced to the ultimate lime concentration of hydration products, resulting in an increase in porosity. This process leads to loss of C-S-H gel stiffness and overall degradation of the hardened cementitious materials.⁵ Wang also proposed that the removal of calcium hydroxide and the ensuing decomposition of C-S-H gel should be a part of the mechanism for the material damage.² However, the decrease of concentration of calcium hydroxide in the pore solution and the increase of porosity drive the hydration of clinker continuously, resulting in the increase of concentration of calcium hydroxide in the pore solution again. Furthermore, the pozzolanic reaction of copper slag also produces lower C/S ratio C-S-H. Berner suggested that C-S-H is stable when the calcium concentration in the pore solution

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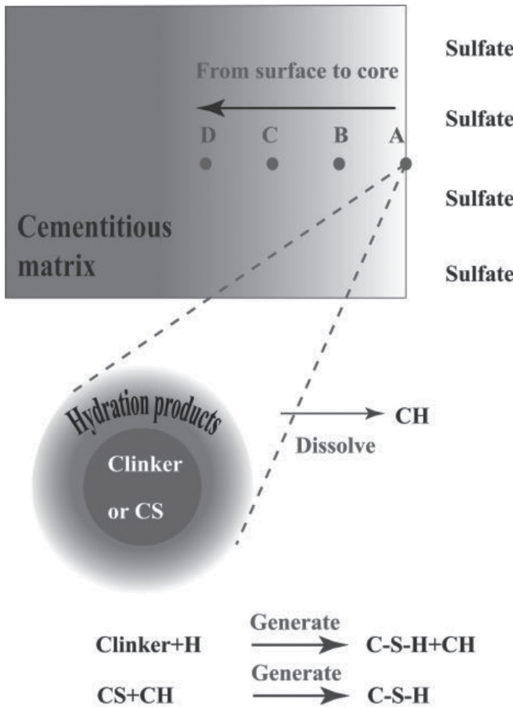


Fig. 5—Degradation process of cementitious materials with copper slag in sodium sulfate solution. CH: calcium hydroxide, H:H₂O, C-S-H: calcium silicate hydrate, CS: copper slag, sulfate: sodium sulfate solution.

is 1.53 to 15.3 mol/yd³ (2 to 20 mol/m³), such equilibrium depends on its C/S ratio (the lower the C/S ratio of the gel the lower the equilibrium).¹⁹ Mineral additions decrease calcium hydroxide content and form denser and more stable C-S-H than Portland C-S-H by pozzolanic effect. Mineral additions to cement play a significant role in the improvement of mechanical behavior and resistance to leaching.²⁰ Therefore, the hydration products of copper slag in the sodium sulfate solution are more stable.

When the clinker at point A is fully hydrated, the surface of the hardened cementitious materials is degraded. Then sodium sulfate solution penetrates through the surface of hardened cementitious materials. As sodium sulfate diffuses to point B, at which point the hardened cementitious materials begin to degrade. In the same way, the sodium sulfate continuously penetrates into the hardened cementitious materials until it is completely destroyed.

CONCLUSIONS

According to the XRD analysis and BSE analysis of hardened cementitious materials subjected to sodium sulfate attack, the following conclusions can be drawn:

(1) Hydration of partially reacted clinker produces hydration products such as calcium hydroxide and C-S-H. The newly formed hydration products are of great importance to the sulfate resistance of cementitious materials. On the one hand, these hydration products increase the compactness of the hardened cementitious materials and therefore prevent the further penetration of sulfates. On the other hand, These hydration products increase the concentration of calcium hydroxide in the pore solution, thereby retarding the decomposition of C-S-H.

(2) Copper slag decreases portlandite content and form more hydration products by pozzolanic effect. Thus the newly formed hydration products of copper slag also play a significant role in the improvement of resistance to leaching.

AUTHOR BIOS

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REFERENCES

1. Gollop, R. S., and Taylor, H. F. W., "Microstructural and Microanalytical Studies of Sulfate Attack: I. Ordinary Portland Cement Paste," *Cement and Concrete Research*, V. 22, No. 6, 1992, pp. 1027-1038. doi: 10.1016/0008-8846(92)90033-R
2. Wang, J. G., "Sulfate Attack on Hardened Cement Paste," *Cement and Concrete Research*, V. 24, No. 4, 1994, pp. 735-742. doi: 10.1016/0008-8846(94)90199-6
3. Al-Akhras, N. M., "Durability of Metakaolin Concrete to Sulfate Attack," *Cement and Concrete Research*, V. 36, No. 9, 2006, pp. 1727-1734. doi: 10.1016/j.cemconres.2006.03.026
4. Tang, S. W.; Yao, Y.; Andrade, C.; and Li, Z., "Recent Durability Studies on Concrete Structure," *Cement and Concrete Research*, V. 78, 2015, pp. 143-154. doi: 10.1016/j.cemconres.2015.05.021
5. Mehta, P. K., "Mechanism of Sulfate Attack on Portland Cement Concrete - Another Look," *Cement and Concrete Research*, V. 13, No. 3, 1983, pp. 401-406. doi: 10.1016/0008-8846(83)90040-6
6. Bassuoni, M. T., and Nehdi, M. L., "Durability of Self-consolidating Concrete to Sulfate Attack Under Combined Cyclic Environments and Flexural Loading," *Cement and Concrete Research*, V. 39, No. 3, 2009, pp. 206-226. doi: 10.1016/j.cemconres.2008.12.003

7. Gao, J. M.; Yu, Z. X.; Song, L. G.; Wang, T. X.; and Wei, S., "Durability of Concrete Exposed to Sulfate Attack Under Flexural Loading and Drying-wetting Cycles," *Construction & Building Materials*, V. 39, 2013, pp. 33-38. doi: 10.1016/j.conbuildmat.2012.05.033
8. Yuan, J.; Liu, Y.; Tan, Z. C.; and Zhang, B. K., "Investigating the Failure Process of Concrete Under the Coupled Actions Between Sulfate Attack and Drying-wetting Cycles by Using X-ray CT," *Construction & Building Materials*, V. 108, 2016, pp. 129-138. doi: 10.1016/j.conbuildmat.2016.01.040
9. Chen, F.; Gao, J. M.; Qi, B.; and Shen, D. M., "Deterioration Mechanism of Plain and Blended Cement Mortars Partially Exposed to Sulfate Attack," *Construction & Building Materials*, V. 154, 2017, pp. 849-856. doi: 10.1016/j.conbuildmat.2017.08.017
10. Hooton, R., "Influence of Silica Fume Replacement of Cement on Physical Properties and Resistance to Sulfate Attack, Freezing and Thawing, and Alkali-silica Reactivity," *ACI Materials Journal*, V. 90, No. 2, 1993, pp. 143-151.
11. Al-Amoudi, O. S. B.; Maslehuddin, M.; and Saadi, M. M., "Effect of Magnesium Sulfate and Sodium Sulfate on the Durability Performance of Plain and Blended Cements," *ACI Materials Journal*, V. 92, No. 1, 1995, pp. 15-24.
12. Al-Dulaijan, S. U.; Maslehuddin, M.; Al-Zahrani, M.; Sharif, A.; Shameem, M.; and Ibrahim, M., "Sulfate Resistance of Plain and Blended Cements Exposed to Varying Concentrations of Sodium Sulfate," *Cement and Concrete Research*, V. 25, No. 4-5, 2003, pp. 429-437. doi: 10.1016/S0958-9465(02)00083-5
13. Shi, C.; Meyer, C.; and Behnood, A., "Utilization of Copper Slag in Cement and Concrete," *Resources, Conservation and Recycling*, V. 52, No. 10, 2008, pp. 1115-1120. doi: 10.1016/j.resconrec.2008.06.008
14. Yang, H.; Fang, K.; and Tu, S., "Copper Slag with High MgO as Pozzolanic Material: Soundness, Pozzolanic Activity and Microstructure Development," *Wuhan Ligong Daxue Xuebao*, V. 32, No. 17, 2010, pp. 94-98. (Journal of Wuhan University of Technology)
15. Goñi, S.; Lorenzo, M. P.; and Sagrera, J., "Durability of Hydrated Portland Cement with Copper Slag Addition in NaCl+ Na₂SO₄ Medium," *Cement and Concrete Research*, V. 24, No. 8, 1994, pp. 1403-1412. doi: 10.1016/0008-8846(94)90153-8
16. Najimi, M.; Sobhani, J.; and Pourkhorshidi, A. R., "Durability of Copper Slag Contained Concrete Exposed to Sulfate Attack," *Construction & Building Materials*, V. 25, No. 4, 2011, pp. 1895-1905. doi: 10.1016/j.conbuildmat.2010.11.067
17. Scrivener, K. L., "Backscattered Electron Imaging of Cementitious Microstructures: Understanding and Quantification," *Cement and Concrete Composites*, V. 26, No. 8, 2004, pp. 935-945. doi: 10.1016/j.cemconcomp.2004.02.029
18. Bakharev, T.; Sanjayan, J. G.; and Cheng, Y. B., "Sulfate Attack on Alkali-activated Slag Concrete," *Cement and Concrete Research*, V. 32, No. 2, 2002, pp. 211-216. doi: 10.1016/S0008-8846(01)00659-7
19. Berner, U. R., "Modeling the Incongruent Dissolution of Hydrated Cement Minerals," *Radiochimica Acta*, V. 44-5, 1988, pp. 387-393.
20. Matte, V., and Moranville, M., "Durability of Reactive Powder Composites: Influence of Silica Fume on the Leaching Properties of Very Low Water/binder Pastes," *Cement and Concrete Composites*, V. 21, No. 1, 1999, pp. 1-9. doi: 10.1016/S0958-9465(98)00025-0

The Influence of Alkalinity on the Properties of the Accelerated Cement Pastes

by Zhenping Sun, Chao Chen, Yanliang Ji, Xu Yang,
Yuansong Sun, and Lelin Wu

The objective of this study was to evaluate the influence of alkalinity on the properties and acceleration mechanism of the accelerated cement pastes. Properties of cement pastes relating to its setting time and the strength development as well as its hydration behavior were experimentally tested. XRD and SEM analysis were also performed on the cement pastes to identify the hydration products and their structures.

Results showed that with the increase of alkalinity, the hydration rate and the early compressive strength of cement paste with both alkaline and alkali-free accelerators were accelerated and the setting time was shortened. However, it is harmful for the long-term compressive strength. XRD analysis disclosed the existence of more ettringite with the increase of the alkalinity. However, it appeared no difference between the formation of the ettringite in the cement paste with different alkalinity.

Keywords: alkalinity; properties; acceleration mechanism; cement paste; set accelerator; shotcrete.

INTRODUCTION

Sprayed concrete is a widely used construction material which can form integral structure with proper thickness, with both sufficient rigidity and strength in a short time. Therefore, it has been used in many engineering cases with requirements of fast setting and rapid hardening, such as shotcrete preparation for underground mining, tunnel construction, or other emergency repairing works.¹ In order to prevent dangerous and costly fallouts of large masses of fresh material from walls and overhead areas, sprayed concrete must present a rapid setting and a high early strength development.^{2,3} These properties can be mainly attributed to the corporation of the set accelerators.⁴

Set accelerators are composed of different organic and inorganic chemicals, which will shorten the setting time and increase the early strength development of the sprayed concrete. The manufacturing and application of cement set accelerators date back to the thirties of the last century. The first-generation products were almost powder state and composed of

Table 1—Mineral and chemical compositions of the cement

Mineral composition		Chemical composition	
Compound	Content (%)	Compound	Content (%)
C ₃ S	56.07	CaO	64.90
C ₂ S	21.08	SiO ₂	22.10
C ₃ A	6.21	Al ₂ O ₃	4.53
C ₄ AF	10.43	Fe ₂ O ₃	3.43
Others	6.21	MgO	3.35
		SO ₃	0.40
		Na ₂ O _{eq}	0.50

alkaline substances.⁵ However, these powder-alkaline accelerators will cause severe compressive strength reduction of the cement. Besides, it could pose a threat to the workers' health. Tremendous efforts have been made to prepare liquid and alkaline-free accelerators.

However, sometimes the adaptability of the accelerator to different types of cement was poor and the 28-day strengths of different types of cement varied significantly. Several parameters could affect this phenomenon such as: accelerator type,⁶ type and chemical composition of cement,⁷ setting regulator, curing conditions.⁸ Maltese et al.⁸ and Salvador⁹ showed that the instantaneous dissolution rate of the setting regulators will affect hydration kinetics and strength development of accelerated cement paste. Zhang L et al.¹⁰ showed that supplementary cementitious materials such as silica fume and fly ash will affect the 1-day compressive strength and workability of concrete added with alkaline accelerators. Only few studies have been published to evaluate the influence of cement properties on accelerator reactivity.

RESEARCH SIGNIFICANCE

Cement alkalinity is an important characteristic of the cement. The main objective of this study is to elucidate the influence of cement alkalinity on the properties and acceleration mechanism of the accelerated cement pastes, focusing on hydration mechanisms and kinetics. These results would help engineers in preliminary design studies to properly select cement without numerous and extensive field spray trials.

EXPERIMENTAL INVESTIGATION

Materials

The cement used is the reference cement for testing the performance of concrete admixture, which has a strength level exceeding 42.5. No composite material is added. **Table 1** presents the cement mineral and chemical compositions determined by XRD and XRF, respectively.

To prepare accelerated cement pastes, two types of set accelerators were used. One of them is an alkaline solution based on sodium aluminate, while the other is an alkaline-free solution composed of aluminate sulfate. Their composition and properties are listed on **Table 2**.

Cement pastes compositions

Cement paste compositions used in this experiment and their abbreviations are shown in **Table 3**. In order to achieve the cement with different alkalinity, mixing water with different amount of NaOH was used. The alkaline and the alkali-free accelerators were added in the dosages of 3.0% and 7.0% by mass of cementitious materials, respectively.

Table 2—Compositions and properties of accelerators

Characteristic	Alkali-free (AF)	Alkaline (AK)
Solid content (%)	46.0	42.0
Al ₂ O ₃ content (%)	12.8	23.0
SO ₄ ²⁻ content (%)	20.8	—
Na ₂ O content (%)	—	16.0
Formic acid content (%)	3.6	0
pH at 20°C (68°F)	3.2	11.8

Table 3—Compositions of cement pastes

Nomenclature	Cement, g (lb)	Deionized water, g (lb)	NaOH, g (lb×10 ⁻³)	Equivalent N ₂ O, g (lb×10 ⁻³)	Set accelerators type
P0.50	100 (0.22)	35.0 (0.077)	0 (0)	0.50 (1.1)	—
PAF0.50	100 (0.22)	31.2 (0.0688)	0 (0)	0.50 (1.1)	AF
PAF0.87	100 (0.22)	31.2 (0.0688)	0.48 (1.058)	0.87 (1.9)	AF
PAF1.18	100 (0.22)	31.2 (0.0688)	0.88 (1.940)	1.18 (2.6)	AF
PAK0.98	100 (0.22)	33.2 (0.0732)	0 (0)	0.98 (2.2)	AK
PAK1.35	100 (0.22)	33.2 (0.0732)	0.48 (1.058)	1.35 (3.0)	AK
PAK1.66	100 (0.22)	33.2 (0.0732)	0.88 (1.940)	1.66 (3.7)	AK

* For the cement paste with alkali-accelerators, the alkalinity includes the alkali added from the alkaline accelerators.

These dosages were also corresponding to those general used in sprayed concrete construction. Water contents present in the accelerators were deducted from the mixing water, in order to keep water-cement ratio (w/c).

The pastes produced with the compositions presented in Table 3 were used for all the test methods according to China standard JC477-2005.¹¹

Methods

The determination of setting time of the cement paste incorporating set accelerators was conducted according to China standard JC477-2005, under the test conditions of water to cement ration of 0.40, environmental temperature 20°C (68°F) and relative humidity(RH) not less than 90%.

Mortar prisms of the size 160×40×40mm(6.30×1.57×1.57 in) were casted according to China standard JC477-2005 for the determination of compressive strength.

The isothermal calorimetry was performed to determine how accelerators influence the kinetics of hydration of cement pastes. The hydration temperature profiles were measured on 50.0g(0.11lb) of cement paste using a home-made isothermal calorimeter based on GB12959-2008.¹²

X-ray diffraction analysis was carried out by using the X-ray diffractometer with D/max 2550 VB 3+/PC, and 0.02° per step was conducted in 2θ range of 5°-75°.

The concentrations of calcium ions were determined by ion chromatography (Dionex ICS3000). The tests were carried out in diluted cement suspensions (w/c equals to 9). During the test, the suspensions were kept under constant stirring at the room temperature of 20°C (68°F).

For microstructural investigations, hardened cement paste specimens with fresh fractured surface without any polishing treatment were prepared and used for SEM observation.

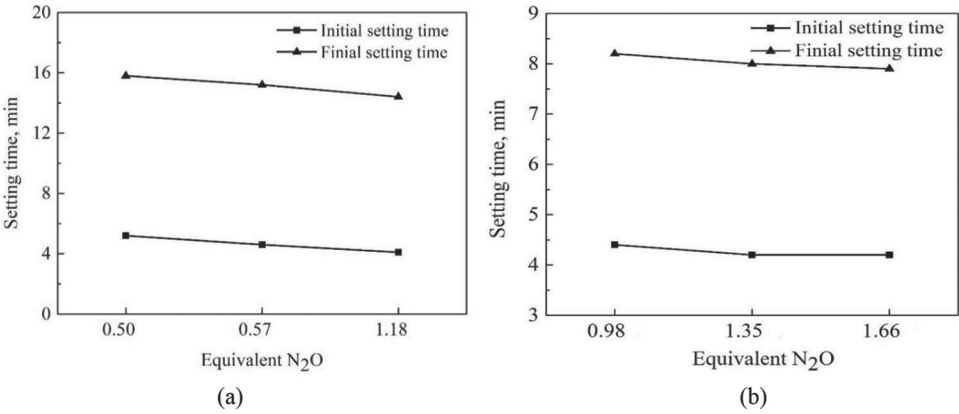


Fig. 1—Setting time of the cement pastes: (a) cement pastes with alkali-free accelerators; (b) cement pastes with alkaline accelerators.

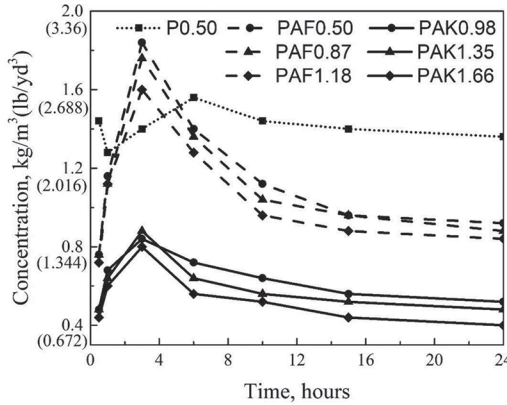


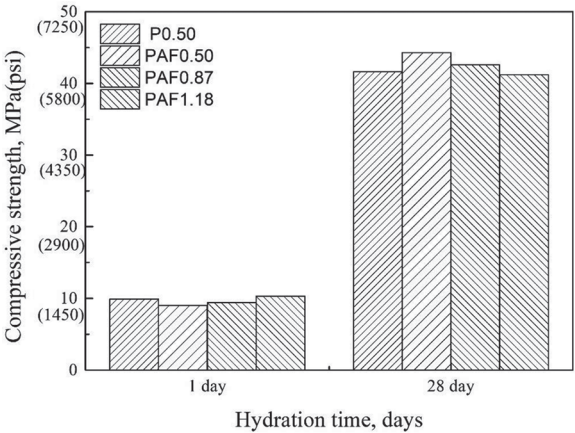
Fig 2— Ca^{2+} concentration of cement suspensions ($1 \text{ kg/m}^3 = 1.68 \text{ lb/yd}^3$).

EXPERIMENTAL RESULTS AND DISCUSSION

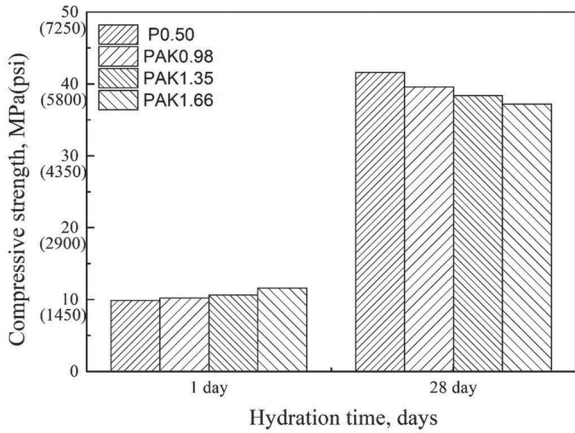
The effect of alkalinity on the setting time

Figure 1 shows the effect of alkalinity on the setting time of the accelerated cement pastes. It can be seen from the test results that, with the increase of the alkalinity, the setting time decreased gradually, which was caused by the increase in reaction speed of hydration between cement, accelerator and water. Moreover, compared to the cement pastes with alkaline accelerators, the cement pastes with alkali-free accelerators is more sensitive to the cement alkalinity.

The setting time of the accelerated cement paste is closely related to the hydration products. **Figure 2** shows the $[Ca^{2+}]$ concentration of the cement suspensions. It can be seen from the test results that after 3 hours, with the formation of Aft, the concentration of the $[Ca^{2+}]$ decreased rapidly. The higher the alkalinity of the cement, the more rapidly the $[Ca^{2+}]$ is depleted, both in the cement paste with alkali-free accelerators and alkaline



(a)



(b)

Fig 3—Compressive strength of the cement pastes:(a) cement pastes with alkali-free accelerators; (b) cement pastes with alkaline accelerators. (1 MPa = 145 psi).

accelerators. This result is in good accordance with the literature.^{9,13} Richartz¹³ found that the hydration degree of the C₃A with high alkalinity is higher than that with low alkalinity. The reactivity of the cement clinker is improved with the increase of the alkalinity in the cement, thus decrease the concentration of the [Ca²⁺] in the solution and promote the generation of the Aft, which will shorten the setting time of the accelerated cement paste.

The effect of alkalinity on the compressive strength

Figure 3 shows the effect of the alkalinity on the compressive strength of the cement pastes with alkaline and alkali-free accelerators. It can be seen from the test results that, in the cement pastes with alkali-free accelerators, the early compressive strength (1 day)

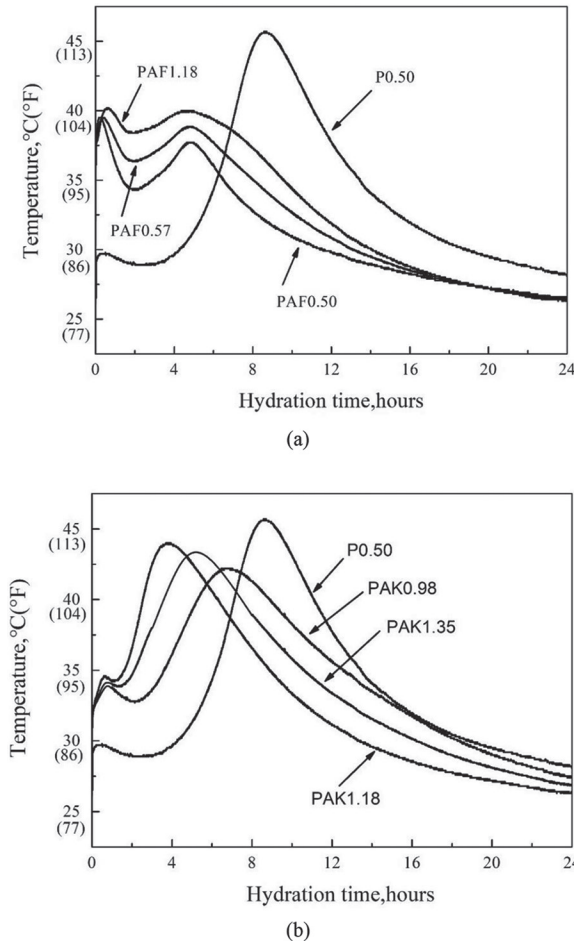


Fig. 4—Hydration temperature profile of the cement pastes with accelerators.

decreased with the addition of the alkali-free accelerators compared with the cement pastes without accelerators. With the increase of the alkalinity of the cement, the compressive strength increased slowly. However, when it comes to the 28-day compressive strength, the higher the alkalinity of the cement, the lower the 28-day compressive strength.

In the cement pastes with alkaline accelerators, the early compressive strength is higher than that of the cement paste without accelerators. Moreover, with the increase of the alkalinity of the cement, the compressive strength decreased, especially the 28-day compressive strength.

Isothermal calorimetry

The hydration temperature profiles of the cement pastes with alkaline and alkali-free accelerators during 24h are shown in **Fig. 4**.

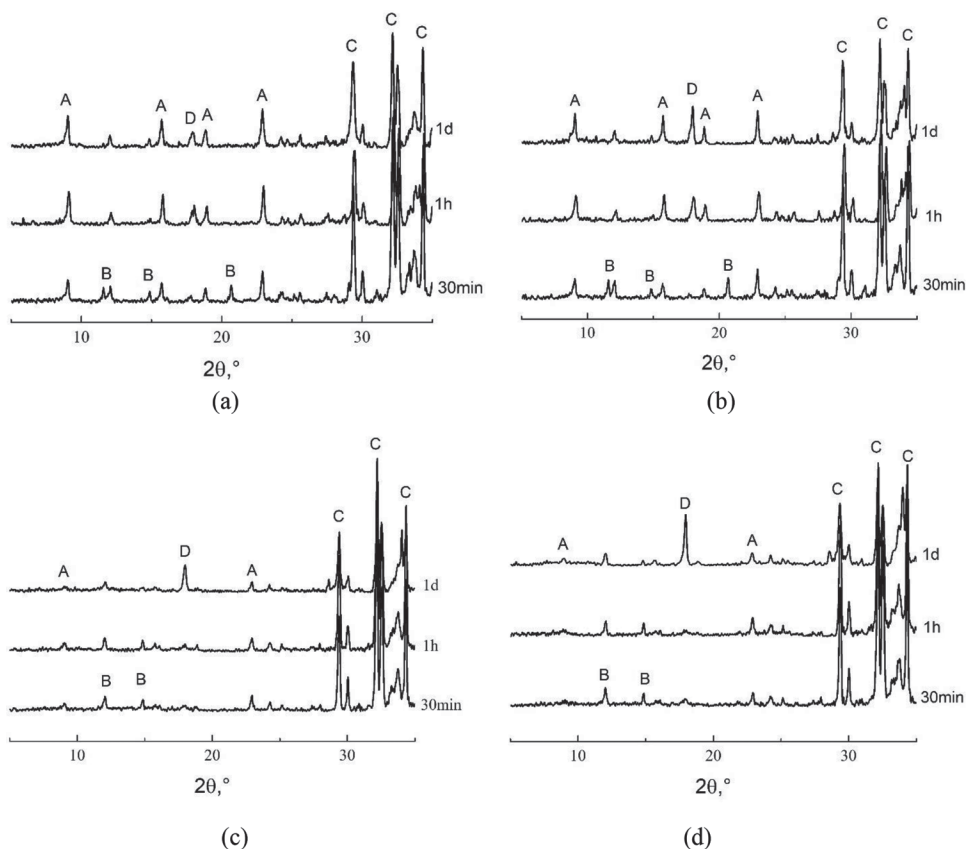


Fig. 5—XRD patterns of cement pastes with alkaline and alkali-free accelerators at different hydration times (A: AFt; B: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; C: C_3S ; D: $\text{Ca}(\text{OH})_2$): (a) cement paste (PAF0.50) with alkali-free accelerator; (b) cement paste (PAF1.18) with alkaline accelerator; (c) cement paste (PAK0.98) with alkaline accelerator; (d) cement paste (PAK1.66) with alkaline accelerator.

From Fig. 4(a) and Fig. 4(b), the hydration temperature profile of the cement pastes with alkaline and alkali-free accelerators both have two exothermic peaks. From Fig. 4(a) we can see that in the cement pastes with alkali-free accelerators, the first exothermic peak occurs in the first few minutes of hydration, which is closely related to the early rapid formation of AFt. The first exothermic peak in the cement paste with accelerators is more intense than that of the reference paste. With the increase of the cement alkalinity, the first exothermic peak is higher. The second exothermic peak corresponding to the dissolution of alite, occurs at about 5h is fairly early than the main peak in the reference cement paste, which occurs at about 9h.

From Fig. 5(b) we can see, in the cement pastes with alkaline accelerators, the first exothermic peak is fairly small, while the second exothermic peak observed at approximately 5h is far more intense than the first exothermic peak. With the increase of the cement alkalinity, both the first exothermic peak and the second exothermic peak are higher.

XRD analysis

Hardened cement paste specimens (PAF0.50, PAF1.18, PAK0.98 and PAK1.66) with alkaline and alkali-free accelerators, hydrated for different time duration (30min, 1h, 1d) were prepared for XRD analysis in order to understand the mechanism of setting acceleration with the aid of accelerator.

Figure 5 shows the result of XRD analysis. It can be seen from the test result that in the cement paste with accelerators, XRD peaks corresponding to ettringite were detected at early hydration times. The XRD peaks corresponding to ettringite at 1-day is more intense than that of 30min or 1h, while the XRD peaks corresponding to the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is lower than that of 30min or 1h. In **Fig. 5(a)** and **Fig. 5(b)** or **Fig. 5(c)** and **Fig. 5(d)**, we can see that, with the increase of alkalinity of the cement, more Aft and $\text{Ca}(\text{OH})_2$ is detected.

SEM Observation

Hardened cement paste specimens with alkaline and alkali-free accelerators at very early age of 30 min were respectively prepared. Specimens with fresh fractured surface were then observed under SEM in order to confirm the formation of the ettringite.

Results obtained in the SEM analysis are presented from **Fig. 6(a)-(c)**. SEM images obtained with the paste with alkaline-free accelerator at 30min of hydration are presented in **Fig. 6(a)**. SEM images obtained with the paste with alkaline accelerator at 30min of hydration are presented in **Fig. 6(b)**. It can be observed that the ettringite in needle shapes has formed in the hardened cement specimen both with alkaline and alkali-free accelerators and is randomly distributed among the hardened cement paste matrix, which is in a good agreement with the accelerated setting behavior of the cement pastes with accelerators. **Fig. 6(c)** shows the SEM images obtained in the paste with alkaline accelerator at 30min of hydration, besides ettringite, we can also find $\text{Ca}(\text{OH})_2$.

However, due to the limitations of the equipment, we can hardly find the difference of the formation of the ettringite in the cement paste with different alkalinity. In our future work, some more advanced quantitative methods may be used.

CONCLUSIONS

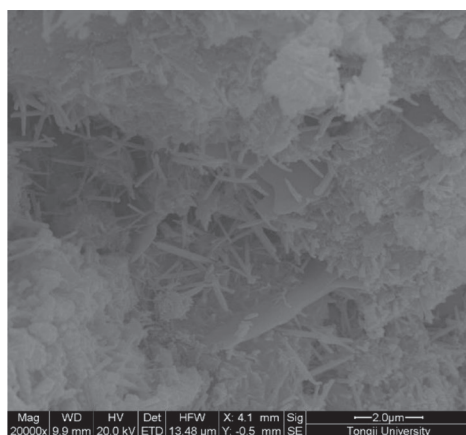
1) The alkalinity has an impact on the setting time and compressive strength both in the cement paste with alkali-free and alkaline accelerators. With the increase of the cement alkalinity, the setting times of the cement pastes both with alkali-free and alkaline accelerators are shortened and the early compressive strength is raised. However, the 28-day compressive strength will decrease with the increase of the cement alkalinity. Therefore, the cement alkalinity must be controlled for the sprayed concrete.

2) With the increase of the cement alkalinity, more Aft and $\text{Ca}(\text{OH})_2$ is detected. Therefore, the early hydration rate is accelerated.

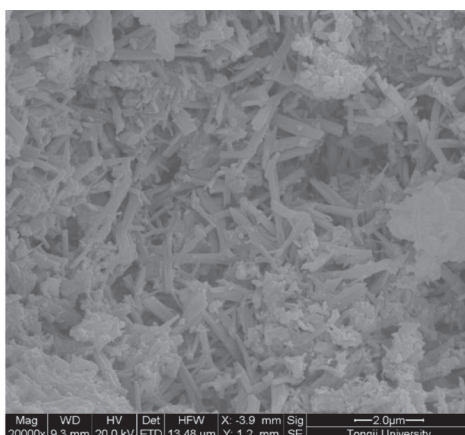
3) Ettringite has formed in the first few minutes of hydration both in the cement paste with alkali-free and alkaline accelerators. However, more advanced methods should be used to clarify the formation of the ettringite in the cement paste with different alkalinity.

AUTHOR BIOS

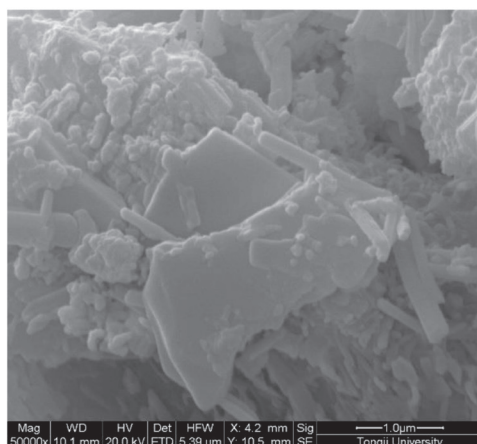
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(a)



(b)



(c)

Fig. 6—SEM images of cement pastes with alkaline and alkali-free accelerators at different hydration times: (a) cement paste (PAF0.50) hydrate for 30 min; (b) cement paste (PAF1.18) hydrate for 30 min; (c) cement paste (PAK0.98) hydrate for 30 min.

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REFERENCES

1. Galobardes, I., "Characterization and Control of Wet Mix Sprayed Concrete with Accelerators," *Reviews in Environmental Science and Biotechnology*, V. 11, No. 4, 2013, pp. 353-363.
2. Prudêncio, L. R. Jr., "Accelerating Admixtures for Shotcrete," *Cement and Concrete Composites*, V. 20, No. 2-3, 1998, pp. 213-219. doi: 10.1016/S0958-9465(98)80007-3
3. Figueiredo, D., and Antonio, D., "Early Strength and Physical Properties in Accelerated Shotcrete," *Shotcrete for Underground Support VIII*, 2010, pp. 108-124.
4. Salvador, R. P.; Cavalaro, S. H. P.; Segura, I.; Figueiredo, A. D.; and Pérez, J., "Early Age Hydration of Cement Pastes with Alkaline and Alkali-Free Accelerators for Sprayed Concrete," *Construction & Building Materials*, V. 111, 2016, pp. 386-398. doi: 10.1016/j.conbuildmat.2016.02.101
5. Pan, Z.; Wang, X.; and Liu, W., "Properties and Acceleration Mechanism of Cement Mortar Added with Low Alkaline Liquid State Setting Accelerator," *Journal of Wuhan University of Technology*, V. 29, No. 6, 2014, pp. 1196-1200. doi: 10.1007/s11595-014-1067-4
6. Maltese, C.; Pistolesi, C.; Bravo, A.; Cerulli, T.; Salvioni, D.; and Squinzi, M., "Formation of nanocrystals of Aft phase during the reaction between alkali-free accelerators and hydrating cement: a key factor for sprayed concretes setting and hardening," *Materials and Structures*, V. 45, 2005, pp. 329-338.
7. De Belie, N.; Grosse, C. U.; Kurz, J.; and Reinhardt, H.-W., "Ultrasound monitoring of the influence of different accelerating admixtures and cement types for shotcrete on setting and hardening behaviour," *Cement and Concrete Research*, V. 35, No. 11, 2005, pp. 2087-2094. doi: 10.1016/j.cemconres.2005.03.011

8. Maltese, C.; Pistolesi, C.; Bravo, A.; Cella, F.; Cerulli, T.; and Salvioni, D., "Effects of setting regulators on the efficiency of an inorganic acid based alkali-free accelerator reacting with a Portland cement," *Cement and Concrete Research*, V. 37, No. 4, 2007, pp. 528-536. doi: 10.1016/j.cemconres.2007.01.002
9. Salvador, R. P.; Cavalaro, S. H. P.; Cincotto, M. A.; and Figueiredo, D., "Parameters controlling early age hydration of cement pastes containing accelerators for sprayed concrete," *Cement and Concrete Research*, V. 89, 2016, pp. 230-248. doi: 10.1016/j.cemconres.2016.09.002
10. Zhang, L.; Li, S.; Li, S.; and Liao, Q., "Effect on the performance of shotcrete mixed with silica fume and fly ash," *Journal of Shandong University*, V. 46, No. 4, 2016, pp. 102-109.
11. JC477-2005, "Flash setting admixture for shotcrete," China Standard, 2005.
12. GB12959-2008, "Test methods for heat of hydration of cement," China Standard, 2008.
13. Richartz, W., "Einfluß des K₂O-Gehalt und des Sulfatisierungsgarts auf Erstarren und Erhärten des Zements," *Zement-Kalk-Gip*, No. 12, 1996, 678 pp.

Absolute Volume Change of Portland Cement Studied by Helium Pycnometry

by Zhenping Sun, Xu Yang, Juntao Tian, Haijing Yang,
Yanliang Ji, and Kuangyi Hu

Based on detection technology of helium pycnometry, the study developed a novel approach for studying absolute volume change of Portland cement in early-age hydration process. Traditional methods, such as heat evolution, chemical shrinkage test (ASTM C 1608) and X-ray diffraction (XRD), were also adopted for comparison and analyzation. Results indicated that helium pycnometry is quite suitable in the study of the absolute volume change of Portland cement. Compared with chemical shrinkage test, the data captured by helium pycnometry is more accurate and efficient for analyzing the absolute volume change of Portland cement. Meanwhile, helium pycnometry is found to have a good correspondence with the traditional methods, the trends of which are almost the same. According to the trends of the absolute volume change and heat flow, hydration process of Portland cement can be divided into five stages, which are dissolution stage, induction stage, acceleration stage, deceleration stage and stable stage.

Keywords: Helium pycnometry; Hydration process; Absolute volume change.

INTRODUCTION

The early volume change of concrete is generally considered as the main driving mechanism leading to early age cracking and, consequently, to the loss of durability of concrete structures.¹ And the key to solve this problem is measuring the volume change accurately, making sense of the mechanism of shrinkage and preventing the formation of cracks. In recent years, with the rapid development of high-strength concrete, the proportion occupied by chemical shrinkage of the whole volume change increased apparently, and more attention are needed on chemical shrinkage.

The total absolute volume of cement hydration product is smaller than the combined initial volume of the anhydrous cement and water. This reduction in volume during hydration is known as chemical shrinkage. Since chemical shrinkage was found for the first time by Le Chatelier in 1900, lots of research on chemical shrinkage have been done. There are two main methods utilized in the study on chemical shrinkage nowadays, which are the volumetric method represented by Japan Concrete Institution(JCI)² and American Society for Testing and Materials(ASTM)³ and density method represented by Boivin, Geiker,

Table 1—Chemical compositions of Portland cement/%

Cement type	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Other
P.I 42.5	3.9	3.9	19.6	0.4	2.2	0.4	61.9	0.3	5.2	2.2

Paulini, Holt and Sant^{4,5} However, human records in a certain time interval is required for the former, and complex operations are needed for the latter, both of which would cause human errors. Moreover, limited by the permeability of water, all the voids are not occupied by water entirely, and chemical shrinkage tested by these means is smaller than the real one. Therefore, a method for accurately and conveniently measuring chemical shrinkage of cement-based material is imperative and necessary, and helium pycnometry might be an ideal choice.

Helium pycnometry, as a method capable of doing in-situ, continuous and non-destructive investigation, is designed to measure the absolute volume of solid or liquid materials by applying Achimedes’ principle of fluid (gas) displacement and Boyle’s law of gas expansion. It has been widely used in many subject areas, such as food,⁶ phytoogy,⁷ materials,⁸ and so on, and has been proved to be accurate and reliable.

In this study, absolute volume change of Portland cement in early-age hydration process was investigated using helium pycnometry, heat evolution, chemical shrinkage test and X-ray diffraction (XRD). Besides, hydration process of Portland cement was divided into five stages, which were dissolution stage, induction stage, acceleration stage, deceleration stage and stable stage.

RESEARCH SIGNIFICANCE

Many methods were developed to study the chemical shrinkage of Portland cement at an early age in the last couple of decades. Most of the studies were carried out by improving the testing device mentioned in the standard test method for chemical shrinkage of hydraulic cement paste (ASTM C 1608-2007). However, the limitation of water environment still existed. Water can’t penetrate into pores which are much too small limited by its penetration capacity, leading to an inaccurate testing result. The authors believe that this novel study of chemical shrinkage by helium pycnometry will be very useful to cement technology.

EXPERIMENTAL INVESTIGATION

Materials

Portland cement (P·I 42.5) provided by China Building Materials Academy and de-air water were used in this study. The chemical compositions of Portland cement determined by X-ray fluorescence analysis are shown in **Table 1**, and the calculated Bogue phase compositions and some other parameters of the cement are shown in **Table 2**.

Specimens

Cement pastes were prepared by using a low-speed mixer with a water/cement (w/c) ratio of 0.267, which equals to its water demand for normal consistency. The stirring time is 1 min.

The prepared cement pastes were then separated into two parts. The fresh part (in 3 min) was used for continuous testing, and the other part was cast in a polyethylene bottle and cured at 20±1 °C (68±1.8 °F) and RH 100%. After the desired periods of storage (21,

Table 2—Bogue phase compositions and some other parameters of Portland cement

Bogue phase compositions/%					Density kg/m ³ (lb/yd ³)	Blaine fineness m ² /kg	Setting time/min	
C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Gypsum			Initial	Final
58.9	11.8	1.6	15.8	3.8	3205 (5384)	370	130	165

5h, 12h and 24h), the standby cement paste was sawed into slices and crushed in an agate mortar. The hydration of the cement was stopped by immersing the crushed samples in blocks into ethyl alcohol for 3 days.⁹ Afterwards, the samples were dried at 40 °C (104 °F) in an oven with the protection of nitrogen until constant weights were reached.

Items of investigation

The fresh cement pastes were tested continuously with helium pycnometry, chemical shrinkage test and heat evolution test, which were conducted based on our previous study,¹⁰ ASTM C 1608-2008 and GB/T 12959-2008, respectively.

Besides, X-ray diffraction analysis was performed on the dried cement pastes by using the X-ray diffractometer of D/max 2550 VB 3+/PC at a scanning step of 0.02° and with a scanning range of 5°-75°.

ANALYTICAL INVESTIGATION

Helium pycnometer (Ultrapyc 1200e, Quantachrome, The U.S) was used in this study for measuring the absolute volume of Portland cement pastes in early-age hydration process at ambient temperature and atmospheric pressure. However, just like most of the gas detection methods, water loss is inevitable for helium pycnometry. Based on our trial tests and prior study,¹⁰ the weight loss of water during each running cycle is limited, which is no more than 0.0020 g (4.41×10⁻⁶ lb) per 100 g (0.22 lb) cement paste and remains almost constant as the hydration goes on. However, considering hundreds of cycles are needed for monitoring the early-age hydration process of Portland cement, the total water loss during measurement has to be taken into account. Therefore, the sample weights before and after the test should be recorded utilizing a high-precision analytical balance (Sartorius AG, Germany). Then, the theoretical absolute volume of cement paste without water loss (V_t) can be calculated with Equation (1):

$$V_t = V_p + \frac{(m_1 - m_2)N_t}{N} \quad (1)$$

where V_t = theoretical absolute volume of cement paste without water loss at time t; m₁ = sample weight before the test; m₂ = sample weight after the test; N_t = cycle number at time t; N = maximum cycle number of the test.

In addition, the theoretical absolute volume of the cement and water before mixing obtained with Equation (2):

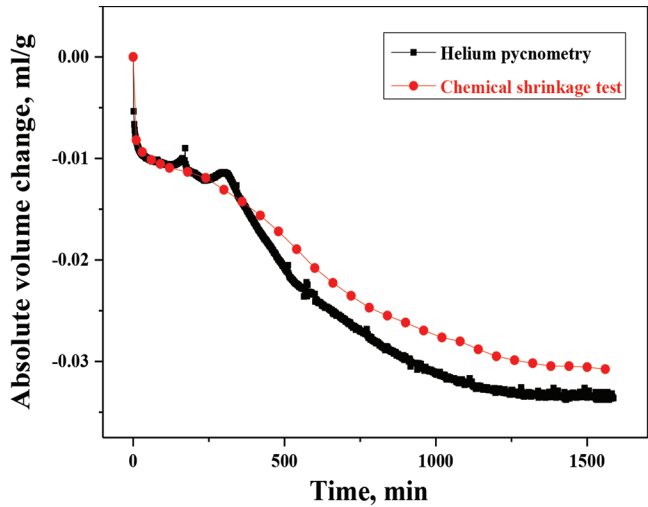


Fig. 1—Absolute volume change of cement paste (1 ml = 3.53×10^{-5} cu ft; 1 g = 0.0022 lb).

$$V_0 = \frac{m_1}{\rho_c (1 + \mu)} + \frac{\mu m_1}{\rho_w (1 + \mu)} \tag{2}$$

where V_0 = theoretical absolute volume of Portland cement and water before mixing; μ = water/cement ratio; ρ_c = true density of Portland cement; ρ_w = true density of water.

Thus, the absolute volume change of cement pastes at time t can be obtained with Equation (3).

$$S_t = \frac{V_t - V_0}{m_1} = \frac{\left(V_p + \frac{(m_1 - m_2) N_t}{N} \right) - \left(\frac{m_1}{\rho_c (1 + \mu)} + \frac{\mu m_1}{\rho_w (1 + \mu)} \right)}{m_1} \tag{3}$$

where, S_t is the absolute volume change of Portland cement paste at time t .

EXPERIMENTAL RESULTS AND DISCUSSION

Absolute volume change of Portland cement

Both of the chemical shrinkage test and helium pycnometry can be employed to study the absolute volume change of Portland cement. **Fig. 1** illustrates the absolute volume change of cement paste, which was obtained by helium pycnometry and chemical shrinkage test, separately. It can be noted that trends of the two curves look the same, but the details of each curve are quite different. The data of chemical shrinkage test is obtained through eyesight, which is discontinuous and easy to introduce human errors. Thus, the trend

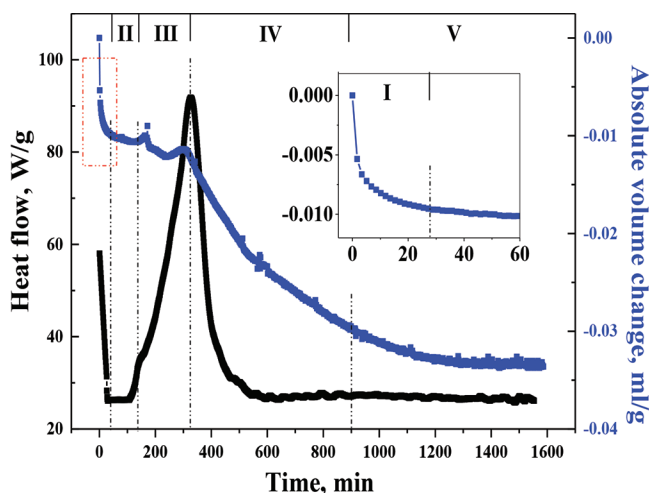


Fig. 2—Heat flow and absolute volume change of cement paste ($1 \text{ ml} = 3.53 \times 10^{-5} \text{ cu ft}$; $1 \text{ g} = 0.0022 \text{ lb}$).

is rough, and the volume change rate is gentle, both of which will cover up the volume change characteristics during hydration, especially the turning points between each hydration stage. While, helium pycnometry can solve this problem perfectly. The data of helium pycnometry is calculated out and recorded automatically by a built-in program of helium pycnometer, which is accurate and continuous. Consequently, the curve becomes detailed, and more information (such as the two hill like protuberance) can be observed.

Besides, it is noteworthy in **Fig. 1** that the absolute volume change obtained by the two methods at very early age (within about 120 min) are almost consistent. Since cement paste is in a plastic state in this period, which is not dense, both water and helium can penetrate into all the pores of cement paste, so the absolute volume change of cement paste can be obtained accurately by both methods. It also implies that helium pycnometry is reliable in studying the absolute volume change of Portland cement. Without regard to the two hill like protuberance temporarily, absolute volume change in later period obtained by helium pycnometry is found to be bigger than that by chemical shrinkage test at the same hydration time. And this is due to the different characteristics of the two methods. Limited by the penetrability of water molecules, chemical shrinkage test can't measure the real absolute volume change of the hardened cement paste that excludes all the voids in it¹¹ Conversely, thanks to the ideal penetrability of helium, absolute volume change of the hardened cement paste can be well captured accurately by helium pycnometry. Helium pycnometry is proved to be more suitable than chemical shrinkage test in this study.

Hydration stage identification of Portland cement

As was talked above, more information of cement hydration can be observed by helium pycnometry, which means that helium pycnometry can reflect the hydration process to a certain extent. **Fig. 2** illustrates the heat flow and absolute volume change of cement paste. According to the characteristics of heat flow, hydration process of Portland cement can

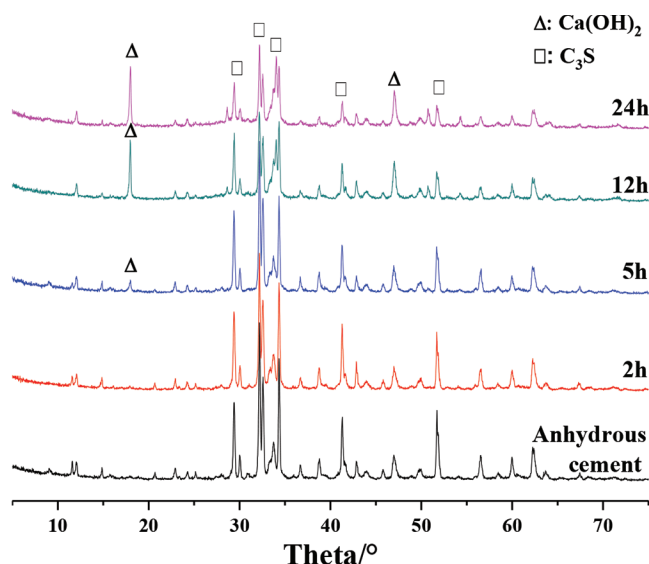


Fig. 3—XRD patterns of anhydrous cement and hydrated cement pastes at different hydration ages.

be divided into five stages,¹² which are dissolution stage (Stage I), induction stage (Stage II), acceleration stage (Stage III), deceleration stage (Stage IV) and stable stage (Stage V). Meanwhile, the trend of absolute volume change obtained by helium pycnometry can also be divided into five stages according to the volume change rate, which has a very good correspondence with that of heat flow. Though the turning point of stage I and stage II is not that clear, the first hill like protuberance appears as the turning point of stage II and stage III, and the second one appears as that of stage III and stage VI. And both heat flow and helium pycnometry can't distinguish stage IV and stage V definitely.

In order to make clear the hydration mechanisms of each hydration stage, mineral components of anhydrous cement and hydrated cement pastes at different hydration ages (2h, 5h, 12h and 24h) were analyzed by XRD, as shown in **Fig. 3**. XRD pattern of anhydrous cement mainly shows the presence of C_3S (32.1° , 32.5° and 34.3°), C_2S (31.0° , 32.1° and 32.5°) and C_4AF (12.0° , 33.4° and 33.7°), while C_3A (33.1° , 47.7° and 59.2°) is almost absent because of its low content as shown in **Table 2**. Afterwards, $Ca(OH)_2$ is found to generate as the hydration goes on, as shown in the XRD patterns of hydrated cement pastes.

Dissolution stage (Stage I) occurred within 30 min since cement was mixed with water. It has been reported that dissolution stage is attributed to a combination of dissolution and quick reactions.¹²⁻¹⁵ As soon as cement particles came into contact with water, mineral phases such as C_3S and C_3A will dissolve quite rapidly into water, and quick reactions will begin immediately upon wetting.^{16,17} And both of the two behaviors are accompanied by lots of heat evolution, characterized by a large exothermic signal in heat flow test.¹⁸ However, the dissolution rates decelerate very quickly while the solution is still undersaturated,^{19,20} just as the heat flow and absolute volume change trends shown in **Fig. 2**. The mechanism of this early deceleration has been a subject of considerable debate over the

years, and many hypotheses have been proposed, such as metastable barrier hypothesis,²¹⁻²⁶ slow dissolution step hypothesis,²⁷⁻³¹ and so on, but the exact mechanism is still unknown.

Induction stage (Stage II) lasted from about 30 min to 130 min, as shown in **Fig. 2**. In this stage, the absolute volume change rate of cement paste decreased linearly but slowly, while heat flow remained almost constant. It has been reported^{30,32} that the primary mechanism controlling the kinetics until the end of induction stage is under-saturation. Thus, the slow decrease of the absolute volume change rate might result from the dissolution effect or some intermediate reactions before saturation rather than the hydration of C_3S . It can be noted in **Fig. 3** that the content of C_3S remains almost unchanged, which implies that C_3S contributed little to the absolute volume change in this stage. Similarly, it might be attributed to the same reason for the steady of heat flow in this stage.

Acceleration stage (Stage III) began right after induction stage, and lasted for no more than 3h, as shown in **Fig. 2**. Two hill like protuberance appeared in the absolute volume change curve, while heat flow kept increasing until reaching its peak in this stage. It has been reported³³ that initial setting time is usually close to the end of induction time, which corresponds very well in this study, as shown in **Table 2**. Meanwhile, the first hill like protuberance seems to be corresponding to the initial setting time, which implies the beginning of this stage, and it might result from the sudden heat evolution upon initial setting. However, the second hill like protuberance is not due to final setting, but might be attributed to the high heat flow. As the rapid increasing of heat flow, heat becomes difficult to be exhausted out of the chambers of helium pycnometry, which might result in the temporary expansion finally.

Deceleration stage (Stage IV) occurred from about 310 min since cement hydration began, as shown in **Fig. 2**. Compared with acceleration stage, a quite large absolute volume change occurred in this stage, while heat flow kept decreasing from its peak to a quite low level. It has been reported¹⁵ that a switch to diffusion control might be the onset of deceleration stage. Thus, this process can't be as fast as that of reaction control represented by acceleration stage. Therefore, the hydration rate will stay at a quite high speed for a long time in this stage, which will lead to a much larger absolute volume change than that of acceleration stage. Meanwhile, it can be seen in **Fig. 3** that content of $Ca(OH)_2$ generated in this stage (5h-12h) is much more than that of acceleration stage (2h-5h). However, it's difficult for us to identify the ending point of deceleration stage exactly, because hydration rate has decreased a lot at the end of this stage, and the absolute volume change trend was almost smooth.

Stable stage (Stage V) came into being following deceleration stage with no stop, as shown in **Fig. 2**. It is found that the absolute volume of cement paste didn't change much and heat flow stayed almost constant in this stage. And the content of $Ca(OH)_2$ and C_3S stayed almost unchanged in this stage, as shown in **Fig. 3**. Diffusion might dominate in this stage, supported by Youyuan Lu,³⁴ Karen L. Scrivener,¹⁵ etc in their articles.

FURTHER RESEARCH

It is desirable to test specimens made of different kinds of cements, and efforts should be made to find out the major factor that play a decisive role in the hydration process of cement. The results of such studies would directly benefit the construction industry.

CONCLUSIONS

Based on the results of this experimental investigation under normal environment, the following conclusions are drawn:

1. Helium pycnometry is found especially suitable for monitoring the absolute volume change of cement pastes in early-age hydration process. Compared with the “chemical shrinkage” test, the result tested by helium pycnometry is more accurate and efficient. Besides, it is also found to have a good correspondence with the traditional methods, the trends of which are almost the same.

2. According to the trends of the absolute volume change and heat flow, hydration process of Portland cement can be divided into five stages, which are dissolution stage, induction stage, acceleration stage, deceleration stage and stable stage. Combined with the XRD patterns, the hydration stage identification of Portland cement by helium pycnometry proved to have a good correspondence with that of heat flow.

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REFERENCES

1. Zhang, J.; Weissinger, E. A.; Peethamparan, S.; and Scherer, G. W., "Early hydration and setting of oil well cement," *Cement and Concrete Research*, V. 40, No. 7, 2010, pp. 1023-1033. doi: 10.1016/j.cemconres.2010.03.014
2. Tazawa, E. I., and Miyazawa, S., "Autogenous Shrinkage of Concrete," *Cement and Concrete Research*, V. 25, No. 8, 1999, pp. 1633-1638. doi: 10.1016/0008-8846(95)00159-X
3. Standard Test Method for Chemical Shrinkage of Hydraulic Cement Paste. Astm.
4. Geiker, M., and Knudsen, T., "Chemical shrinkage of portland cement pastes," *Cement and Concrete Research*, V. 12, No. 5, 1982, pp. 603-610. doi: 10.1016/0008-8846(82)90021-7
5. Paulini, P., "A weighing method for cement hydration," V., No., 1992, pp.
6. Mateus, M. L.; Rouvet, M.; Gumy, J. C.; and Liardon, R., "Investigations by S.E.M. and helium pycnometry of the effect of water on the physical properties of roast and ground coffee," 2007. 620-4 p.
7. Hill, C. A. S., and Ormondroyd, G. A., "Dimensional changes in Corsican pine (*Pinus nigra* Arnold) modified with acetic anhydride measured using a helium pycnometer," *Holz-forschung*, V. 51, No. 1, 2004, pp. 493-547.
8. Ayral, A.; Phalippou, J.; and Woignier, T., "Skeletal density of silica aerogels determined by helium pycnometry," *Journal of Materials Science*, V. 27, No. 5, 1992, pp. 1166-1170. doi: 10.1007/BF01142014
9. Chaunsali, P; and Mondal, P, "Physico-chemical interaction between mineral admixtures and OPC-calcium sulfoaluminate (CSA) cements and its influence on early-age expansion," *Cement and Concrete Research*, V. 80, No., 2016, pp. 10-20.
10. Yang, X; Sun, Z; Shui, L; and Ji, Y, "Characterization of the absolute volume change of cement pastes in early-age hydration process based on helium pycnometry," *Construction and Building Materials*, V. 142, No., 2017, pp. 490-8.
11. Pang, X; Bentz, DP; Meyer, C; Funkhouser, GP; and Darbe, R, "A comparison study of Portland cement hydration kinetics as measured by chemical shrinkage and isothermal calorimetry," *Cement and Concrete Composites*, V. 39, No., 2013, pp. 23-32.
12. Taylor, H. F. W., "Cement chemistry," *Academic*, 1997.
13. Ma, S; Li, W; Zhang, S; Ge, D; Yu, J; and Shen, X, "Influence of sodium gluconate on the performance and hydration of Portland cement," *Construction and Building Materials*, V. 91, No., 2015, pp. 138-44.
14. Bullard, J. W.; Jennings, H. M.; Livingston, R. A.; Nonat, A.; Scherer, G. W.; Schweitzer, J. S.; Scrivener, K. L.; and Thomas, J. J., "Mechanisms of cement hydration," *Cement and Concrete Research*, V. 41, No. 12, 2011, pp. 1208-1223. doi: 10.1016/j.cemconres.2010.09.011
15. Scrivener, K. L., and Nonat, A., "Hydration of cementitious materials, present and future," *Cement and Concrete Research*, V. 41, No. 7, 2011, pp. 651-665. doi: 10.1016/j.cemconres.2011.03.026
16. Damidot, D.; Bellmann, F.; Möser, B.; and Sovoidnich, T., "Calculation of the dissolution rate of tricalcium silicate in several electrolyte compositions," *Cement, Wapno, Beton*, V. 12/74, No. 2, 2007, pp. 57-67.
17. Barret, P.; Ménétrier, D.; and Bertrandie, D., "Mechanism of C_3S dissolution and problem of the congruency in the very initial period and later on," *Cement and Concrete Research*, V. 13, No. 5, 1983, pp. 728-738. doi: 10.1016/0008-8846(83)90064-9

18. Fernández, MMC, "Effect of Particle Size on the Hydration Kinetics and Microstructural Development of Tricalcium Silicate," V., No., 2008, pp.

19. Stein, H. N., "Thermodynamic considerations on the hydration mechanisms of Ca_3SiO_5 and $\text{Ca}_3\text{Al}_2\text{O}_6$," *Cement and Concrete Research*, V. 2, No. 2, 1972, pp. 167-177. doi: 10.1016/0008-8846(72)90039-7

20. Gartner, E. M., and Jennings, H. M., "Thermodynamics of Calcium Silicate Hydrates and Their Solutions," *Journal of the American Ceramic Society*, V. 70, No. 10, 2010, pp. 743-749. doi: 10.1111/j.1151-2916.1987.tb04874.x

21. Stein, H. N., and Stevels, J. M., "Influence of silica on the hydration of $3\text{CaO}\cdot\text{SiO}_2$," *Journal of Applied Chemistry*, V. 14, No. 8, 2010, pp. 338-346. doi: 10.1002/jctb.5010140805

22. Jennings, H. M., and Pratt, P. L., "An experimental argument for the existence of a protective membrane surrounding portland cement during the induction period," *Cement and Concrete Research*, V. 9, No. 4, 1979, pp. 501-506. doi: 10.1016/0008-8846(79)90048-6

23. Jennings, H. M., "Aqueous Solubility Relationships for Two Types of Calcium Silicate Hydrate," *Journal of the American Ceramic Society*, V. 71, No. 2, 2010, pp. C-113-C-5.

24. Livingston, R. A.; Schweitzer, J. S.; Rolfs, C.; Becker, H. W.; and Kubsy, S., "Characterization of the induction period in tricalcium silicate hydration by nuclear resonance reaction analysis," *Journal of Materials Research*, V. 16, No. 3, 2001, pp. 687-693. doi: 10.1557/JMR.2001.0108

25. Garrault, S.; Finot, E.; Lesniewska, E.; and Nonat, A., "Study of C-S-H growth on C_3S surface during its early hydration," *Materials and Structures*, V. 38, No. 4, 2005, pp. 435-442. doi: 10.1007/BF02482139

26. Bellmann, F.; Damidot, D.; Möser, B.; and Skibsted, J., "Improved evidence for the existence of an intermediate phase during hydration of tricalcium silicate," *Cement and Concrete Research*, V. 40, No. 6, 2010, pp. 875-884. doi: 10.1016/j.cemconres.2010.02.007

27. Thomas, J. J., "A New Approach to Modeling the Nucleation and Growth Kinetics of Tricalcium Silicate Hydration," *Journal of the American Ceramic Society*, V. 90, No. 10, 2007, pp. 3282-3288. doi: 10.1111/j.1551-2916.2007.01858.x

28. Odler, I., and Dörr, H., "Early Hydration of Tricalcium Silicate - II - The Induction Period," *Cement and Concrete Research*, V. 9, No. 3, 1979, pp. 277-284. doi: 10.1016/0008-8846(79)90119-4

29. Nonat, A., "Modeling Hydration and Setting of Cement," V., No., 2005, pp.

30. Juilland, P.; Gallucci, E.; Flatt, R.; and Scrivener, K., "Dissolution theory applied to the induction period in alite hydration," *Cement and Concrete Research*, V. 40, No. 6, 2010, pp. 831-844. doi: 10.1016/j.cemconres.2010.01.012

31. Damidot, D.; Nonat, A.; and Barret, P., "Kinetics of Tricalcium Silicate Hydration in Diluted Suspensions by Microcalorimetric Measurements," *Journal of the American Ceramic Society*, V. 73, No. 11, 2010, pp. 3319-3322. doi: 10.1111/j.1151-2916.1990.tb06455.x

32. Makar, J. M., and Chan, G. W., "End of the Induction Period in Ordinary Portland Cement as Examined by High-Resolution Scanning Electron Microscopy," *Journal of the American Ceramic Society*, V. 91, No. 4, 2008, pp. 1292-1299. doi: 10.1111/j.1551-2916.2008.02304.x

33. Yuan, R., "Cementitious Material Science," *Wuhan University of Technology*, 1996.

34. Lu, Y; Zhang, J; and Li, Z, "Study on hydration process of early-age concrete using embedded active acoustic and non-contact complex resistivity methods," *Construction and Building Materials*, V. 46, No., 2013, pp. 183-92.

Natural Rubber Latex as Admixture for Polymer Concrete

by My Linh Vo and Johann Plank

The applicability of Natural Rubber Latex (NRL) as film forming agent was tested in mortar.

Two NRL samples, a commercial concentrated and a laboratory-treated, deproteinized one, were compared with a commercial synthetic ethylene-vinylacetate (EVA) copolymer regarding their particle size distribution, surface charge and minimum film forming temperature (MFFT). Additionally, a potential retarding effect of the dispersions was investigated by heat flow calorimetric measurements. Cement mortars holding 2 percent by mass of the dispersions were tested for their strength development after 1, 3, 7 and 28 days.

NRL exhibits an average particle size of 350 nm, possesses a highly anionic charge and possesses a MFFT of ~ 1 °C (34 °F). Heat flow measurements show that the non-treated NRL retards cement hydration. Mortar tests revealed that both NRL samples showed slightly higher strength values than the industrial EVA latex. However, the NRL latexes require addition of a PCE superplasticizer to achieve workability and strong defoamers.

Keywords: natural rubber latex; ethylene vinylacetate; film forming polymer; latex; retardation; cement mortar; mortar tests; tensile strength.

INTRODUCTION

The use of latex dispersions in cement-based building materials has been very popular in the last decades. The latexes increase the cohesion and adhesion of fresh mortar on solid substrates and the tensile strength of hardened mortar due to the formation of elastic polymer films within the inorganic mortar matrix.^{1,2} So far, all latex dispersions applied in the construction industry are synthetic ones, most of them are based on ethylene/vinylacetate, styrene/butadiene or acrylate chemistry.³ The construction industry is interested in applying natural materials from renewable resources to guarantee an energy efficient and environmentally responsible construction practice. Natural rubber latex is such a natural polymer which is eco-friendly and sustainable. Furthermore, low cost and increasing production make natural rubber attractive for the use in cementitious materials.⁴

NRL is harvested from the rubber tree *Hevea brasiliensis* and is composed of the polymer poly(*cis*-1,4-isoprene) with a concentration of 25 to 40 percent by mass. The polymer particles are surrounded by a mixed layer of adsorbed proteins and phospholipids.^{5,6} The remaining part consists of water where several minor components such as proteins, lipids,

carbohydrates, organic solutes and inorganic substances are contained.^{7,8} NRL is generally treated with ammonia, so that the proteins and lipids on the surface of the rubber particles become negatively charged in the alkaline environment. Consequently, the latex particles are stabilized colloids.⁸ It is well-known that proteins may have a retarding effect on cement hydration. To avoid this, the proteins on the rubber particles can be replaced by surfactants such as e.g. sodium dodecyl sulfate (SDS).⁹

So far, no successful large-scale application of natural rubber in cementitious mixtures has been reported.

This study investigated whether it is generally possible to apply NRL as film-forming agent in standard cement-based mortars. Therefore, a commercial concentrated and a laboratory deproteinized NRL sample were compared with a commercial, industrially manufactured EVA sample. These three latex dispersions were characterized regarding their solids contents, pH values, zeta potential, particle size distribution and their minimum film-forming temperature (MFFT). Furthermore, their potential retarding effect on cement hydration was assessed in cement paste by heat flow calorimetry. Effectiveness of the three dispersions in a standard cementitious mortar formulation was investigated with respect to compressive and tensile strength development at comparable consistency and air content. Finally, a closer look at the micro structure of the mortar samples containing the non-treated or the deproteinized NRL was taken via scanning electron microscopy (SEM).

RESEARCH SIGNIFICANCE

Synthetic latexes, such as EVA, are already widely used in the construction field as they enhance the flexural and adhesive tensile strength of mortar. However, these synthetic latexes are petroleum-based and thus non-renewable. Therefore, natural polymers that show performance comparable to synthetic polymers, but are sustainable, are preferred. NRL is such a natural polymer which presents an eco-friendly, renewable and non-petroleum based material. Moreover, it is broadly available due to continuously rising production in Asia. In spite of its huge success in the tyre and rubber industry, successful applications of natural rubber in cementitious materials have not yet been published.

EXPERIMENTAL PROCEDURE

Materials

Latex dispersions—The natural rubber latex sample was a commercial, low ammonia treated latex from Thailand with a solids content of 62 percent by mass, while the commercial EVA sample possessed a solids content of 51 percent by mass.

Sodium dodecyl sulfate—Sodium dodecyl sulfate (SDS) was used to produce the deproteinized NRL sample.

Cement—A CEM I 52.5 R was used for the studies. Its phase composition as determined by X-ray diffraction employing *Rietveld* refinement is presented in **Table 1**. Its average particle size (d_{50} value) as obtained by laser granulometry was found at $3.21\ \mu\text{m}$ ($3.94 \cdot 10^{-5}$ in.). The specific density was $3.15\ \text{g/cm}^3$ ($1.821\ \text{oz/in}^3$) (Helium pycnometry).

Defoamer—Tributyl phosphate, Surfynol and Dowfax were used to decrease the air content of the mortars.

Superplasticizer—A superplasticizer based on a copolymer of methacrylic acid and ω -methoxy poly(ethylene glycol) methacrylate ester (MPEG type PCE) was self-synthesized.

Table 1—Phase composition of the CEM I 52.5 R sample as determined via Q-XRD using Rietveld refinement

Phase	Content [Percent by mass]
C ₃ S	53.14
C ₂ S	16.51
C ₃ A, cubic	6.89
C ₃ A, orthorhombic	1.92
C ₄ AF, orthorhombic	9.12
Free lime (Rietveld)	0.42
Free lime (Franke)	0.03
CaSO ₄	3.18
CaSO ₄ ·0.5 H ₂ O	2.01
CaSO ₄ ·2 H ₂ O	0.00
Calcite	4.63
Quartz	0.81
Dolomite	1.34
Total	100.00

sized and used in the mortar samples. The molar ratio of methacrylic acid to MPEG methacrylate ester was 6:1 and it contained a side chain comprising of 45 ethylene oxide units. Its synthesis is described in.¹⁰

Methods

Deproteinisation of NRL—

20 mL (0.676 fl oz) of commercial NRL (solids content 62 percent by mass) were diluted with 20 mL (0.676 fl oz) of DI water before adding 1 percent by mass sodium dodecyl sulfate (SDS). This mixture was treated for 10 min in an ultrasonic bath, followed by centrifugation at 8,500 rpm.^{9,11} The rubber fraction (upper part) was collected, re-dispersed in 20 mL (0.676 fl oz) of 1 percent by mass SDS solution, then again treated in an ultrasonic bath and centrifugated. This procedure was repeated four times to ensure that the protein content is minimized in the final product. The final rubber fraction was collected and dispersed in deionized water.

Charaterization of the dispersions—

Solids content of liquid latex—The solids content of the latex dispersions was determined on a MA-30 infrared drying balance.

pH value—The pH value was determined on a pH 11 instrument.

Particle size distribution and zeta potential—Particle size distribution and zeta potential of the dispersions were determined via dynamic light scattering (DLS) utilizing a Zetasizer Nano ZS apparatus. The calculation of the zeta potentials was made by converting the electrophoretic mobility data using the *Smoluchowski* relation.

Minimum film forming temperature (MFFT)—The MFFT of the latex polymers was determined by a MFT Thermostair Kofler bench.

Isothermal heat flow calorimetry—Hydration of CEM I 52.5 R in the presence of the latex dispersions was tracked via heat flow calorimetry using a TAM Air heat conduction calorimeter. There, 4 g (0.14 oz) of cement were mixed in a 20 mL (0.676 fl oz) volume

glass ampoule with the appropriate amount of aqueous latex solution at a water to cement ratio (w/c) of 0.45. The latex dosage varied from 1 to 15% by mass of cement (bmc). The glass ampoules were sealed with a metal lid, shaken for 2 minutes on a vortex mixer to homogenize the paste and transferred into the instrument. Heat flow curves were recorded at 20 °C (68 °F) until heat release ceased.

Mortar tests—

Mortar preparation—Mortars were prepared from 450 g (15.87 oz) of CEM I 52.5 R, 1350 g (47.62 oz) of CEN norm sand, 202.5 g (7.14 oz) of total water (w/c = 0.45) and 9 g (0.32 oz) of latex calculated as dry solids (polymer dosage 2% bmc). The mortars were mixed according to the DIN EN 196.¹²

Mortar flow values—The flow value (spread) of the mortars was determined according to DIN EN 1015-3¹³ standard. The Vicat cone was placed on a wet metal plate and the mortar was poured in two layers into it. Each layer was compacted 10 times with a tamping rod. Thereafter, the cone was removed vertically and the flow table was lifted and then dropped 15 times, causing the mortar to flow. After that, the resulting spread was measured twice, the second measurement being at a 90° angle to the first and averaged to give the spread value.

Air content in mortar—The air content was determined by an air content meter according to DIN EN 12350-7.¹⁴ The mortars were filled into the container of the air content tester and compacted for 30 s by vibration. After that, the vessel was closed and the remaining space was filled with water.

Preparation and storage of the mortar specimens—Three mortar specimens with the dimensions of 40 mm x 40 mm x 160 mm (1.58 in x 1.58 in x 6.30 in) were prepared for each mixture and stored for 24 h in a climate chamber at 20 °C (68 °F) and 60% relative humidity. Thereafter, the specimens were demoulded and stored under water at 20 °C (68 °F) until the end of the test period. Mortar samples from which the strengths were measured after one day were not stored under water.

Compressive and tensile strengths—Compressive and tensile strengths were measured according to DIN EN 196¹² standard after 1, 3, 7 and 28 days respectively. For the tensile strength, three specimens were measured for each sample. During the tensile strength measurements each specimen was broken into two pieces so that a total of six pieces resulted for each formulation for the compressive strength measurement. The average of the values was calculated.

SEM imaging of polymer films in mortar samples—SEM images were obtained from an XL-30 FEG microscope after the gold metallization of the samples. The accelerating voltage ranged between 4.0 kV and 7.5 kV, magnifications ranged between 2,500 and 10,000×

EXPERIMENTAL RESULTS AND DISCUSSION

Physico-chemical properties of the latex samples

Two natural rubber latex samples; a commercial, concentrated, low ammonia treated NRL sample (labelled as NRL) and a laboratory-treated, deproteinized NRL (designated as NRL-SDS) were studied and compared with a commercial EVA sample. The EVA sample was stabilized by PVOH. NRL-SDS was prepared to remove the proteins which may have a retarding effect on cement hydration. Furthermore, most of the ammonia was removed during the centrifugation steps which causes an unpleasant smell in mortar.

The main properties of the three liquid latex samples are summarized in Table 2.

Table 2—Physico-chemical properties of NRL, NRL-SDS and EVA polymer dispersions

Sample	Solid content [percent by mass]	pH	Zeta potential [mV]	MFFT, °C (°F)	d_{50} [nm]	d_{av} [nm]
NRL	62	11	- 60	0-1 (32-33.8)	150	350
NRL-SDS	49	9	- 40	0-1 (32-33.8)	850	1000
EVA	51	5	- 15	6-8 (42.8-46.4)	1050	1500

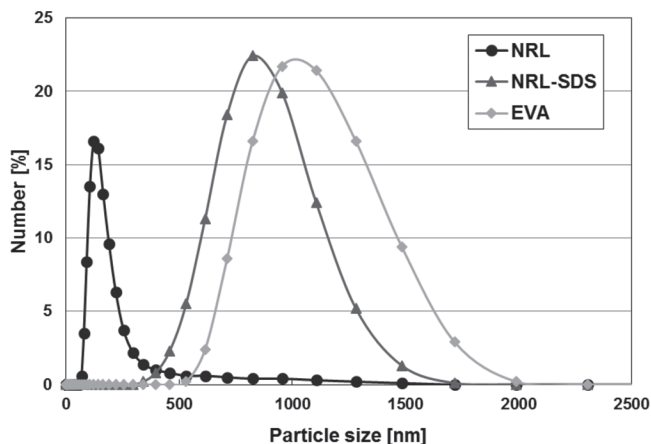


Fig. 1—Particle size distributions of the latex samples used in this study.

Due to stabilization of the commercial NRL sample with ammonia, this dispersion attained a pH value of ~11. The pH value of the deproteinized NRL sample (NRL-SDS) was lower at ~9 as the majority of ammonia was removed during the washing steps performed in the preparation. In comparison, the reference dispersion EVA had an acidic pH of ~5.

A common way to evaluate the stability of colloidal dispersions is by determining its zeta potential. The particles in dispersions tend to repel each other if the zeta potential value of the dispersion is > 30 mV (absolute value). Consequently, no agglomeration occurs and the dispersions are electrostatically stable.¹⁵ Thus, both NRL dispersions; the commercial one with a zeta potential value of -60 mV and the deproteinized one with a value of -40 mV are electrostatically stable. In comparison, the EVA dispersion generated a zeta potential value of -15 mV only, hence it is sterically stabilized by a layer of PVOH on the surface of the particles.

The minimum film forming temperature (MFFT) were found at $0 - 1^{\circ}\text{C}$ ($32 - 33.8^{\circ}\text{F}$) for the NRL-based samples and $6 - 8^{\circ}\text{C}$ ($42.8 - 46.4^{\circ}\text{F}$) for the EVA sample. This result suggests that all three latex samples can be applied in cementitious mortars because their MFFT is much lower than the usual working temperature.

Figure 1 displays the number-based particle size distributions of the latex dispersions. The commercial NRL samples contains the smallest particles with an average particle size (d_{50} value) of 150 nm. The particles of the deproteinized sample were significantly larger because the original NRL sample had been centrifugated. Consequently, the rubber parti

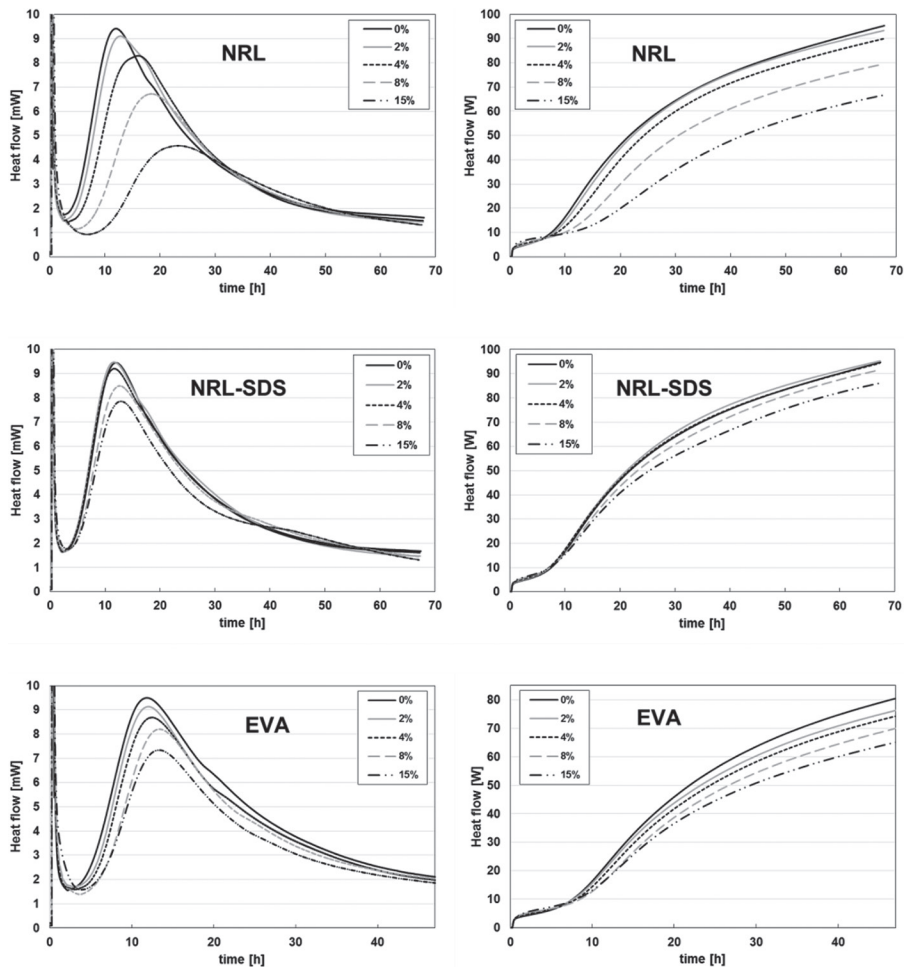


Fig. 2—Heat flow calorimetry of cement pastes containing 0-15% bmc of NRL (first row), NRL-SDS (second row) and EVA (third row); differential heat flow (left) and cumulative heat flow (right).

cles were highly concentrated in the supernatant which led to particle coagulation and the formation of bigger particles. The average particle size of this sample was 1,000 nm.

In comparison, the EVA polymer particles were even larger than those of the NRL-SDS sample and where in the range of 600 to 2,600 nm, with an average particle size of 1,500 nm.

To conclude, the properties of NRL as found so far allow its application in mortar.

Isothermal heat flow calorimetry

Isothermal heat flow calorimetry was used to investigate the influences of the latex dispersions on the kinetics of cement hydration at 20 °C (68 °F). **Figure 2** shows the isothermal heat flow curves of cement pastes prepared from CEM I 52.5 R in the absence and pres

Table 3—Final composition and properties of the mortars (w/c = 0.45) holding the different latex samples utilized in the strength tests

Latex sample	Latex dosage [% bmoc]	PCE dosage [% bmoc]	Defoamer type	Defoamer dosage [% bmoc]	Air content [vol.%]	Slump flow, cm (in.)
NRL	2	0.24	Tributyl phosphate	0.22	4.0	15.5 ± 0.3 (6.10 ± 0.12)
NRL-SDS	2	0.20	Dowfax	0.22	4.0	15.5 ± 0.4 (6.10 ± 0.16)
EVA	2	—	Surfynol	0.067	4.0	15.3 ± 0.2 (5.98 ± 0.08)

ence of 1, 2, 4, 8 and 15% bmoc latex dispersion. When the latex dispersion has a retarding effect on cement hydration, then three aspects can be observed in the heat flow curves: First, the induction period might be extended. Furthermore, the hydration rate during the acceleration period might be depressed and the total heat amount will be reduced.^{16,17} In **Fig. 2** it is clearly shown that the three different latexes show a different influence on cement hydration. Addition of the NRL latex dispersion delays the occurrence of the main hydration peak, decreases the height of the hydration peak and reduces the total heat generated which signifies a retardation effect. Higher dosages of the polymer cause stronger retardation. In comparison, the NRL-SDS modified cement paste has nearly no retarding effect on cement hydration. The heat flow curves of the neat cement paste (no NRL added) and that of the paste treated with NRL-SDS at different dosages are very similar. The reference EVA dispersion exhibits just a minor retarding effect on cement hydration; the delay of the heat release is minimal and increases at higher polymer dosage. Furthermore, the height of the hydration peak and the total heat generated is slightly reduced.

To conclude, isothermal heat flow measurements clearly demonstrate that original NRL has a strong retarding effect on cement hydration while the synthetic EVA dispersion retards only slightly. In contrast, the deproteinized natural rubber latex does not retard cement hydration at all.

Mortar formulations

Table 3 represents the final compositions and properties of the mortars used in the strength tests. It shows that for all mortar samples comparable consistency and air contents were adjusted.

All mortars contained 450 g (15.87 oz) cement, 1350 g (47.62 oz) norm sand and 9 g (0.32 oz) of latex dispersion (calculated as 2% bmoc in solid). The water to cement ratio for all mortar samples was set at 0.45 by adjusting the flow value of the mortar holding the reference dispersion EVA to 16.0 ± 0.5 cm (6.30 ± 0.20 in). For the mortars containing NRL or NRL-SDS, a PCE superplasticizer with the dosage of 0.24% bmoc or 0.20% bmoc respectively was added to achieve the slump flow of 16.0 ± 0.5 cm (6.30 ± 0.20 in). All mortar samples experienced serious air-entrainment. Consequently, application of defoamers was necessary. It was found that each latex dispersion required a different defoamer to achieve optimal results. For the NRL modified mortar, 0.22% bmoc of tributylphosphate was best to reduce the air content from 18% to $4 \pm 0.2\%$. The mortar with NRL-SDS required 0.22% bmoc of Dowfax to decrease the air content from 23% to $4 \pm$

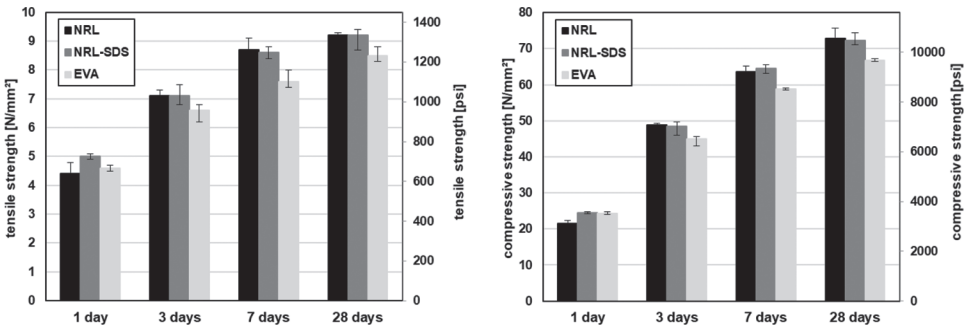


Fig. 3—Compressive (left) and tensile (right) strengths of the mortar specimens holding the three different latex polymers after 1, 3, 7 and 28 days respectively.

0.2% while for the mortar containing EVA, 0.067% bmoc of Surfynol were sufficient to change the air content from 13% to $4 \pm 0.2\%$.

The decreased air content reduced the slump flow values of all mortar samples to 15.5 ± 0.5 cm (6.10 ± 0.20 in). Thus, readjustment of the flow values was not necessary.

The results signify that the synthetic EVA latex is generally easier to defoam and that different emulsifiers / surfactants are contained in natural and synthetic latexes which then require different defoamer chemistries for optimum results. Furthermore, the industrial EVA does not require addition of a superplasticizer, different from the NRL-based latexes.

Compressive and tensile strengths of the mortars

Figure 3 displays the results for the compressive and tensile strengths of the polymer modified mortars after 1, 3, 7 and 28 days respectively.

Generally, the compressive and tensile strengths of the different mortars show the same trend. As expected, the values for both strengths of all samples increased with hydration time. After one day, the values for compressive strength of the mortar containing NRL (21.5 N/mm^2 (3118.31 psi)) as film-forming agent are slightly lower than for the mortar of the NRL-SDS and EVA dispersions which exhibit nearly the same values (24.5 N/mm^2 (3553.43 psi) and 24.3 N/mm^2 (3524.42 psi)). After 3, 7 as well as 28 days a difference can be observed. The mortars holding the NRL and NRL-SDS latexes performed slightly better than those containing EVA in respect to both compressive and tensile strength. The EVA modified mortars reached the values of 45.0, 58.9 and 66.8 N/mm^2 (6526.70 , 8542.72 and 9688.52 psi) for the compressive strength and of 6.6, 7.6 and 8.5 N/mm^2 (957.25 , 1102.29 , 1232.82 psi) and for the tensile strength after 3, 7 and 28 days. The strength values of the mortars containing NRL and NRL-SDS are very similar. After 3, 7 and 28 days the NRL modified mortars reached 48.9, 63.7 and 72.9 N/mm^2 (7092.35 , 9238.90 and 10573.25 psi) for the compressive strengths while the values for the mortars containing NRL-SDS were 48.5, 64.5 and 72.3 N/mm^2 (7034.33 , 9354.93 and 10486.23 psi). Regarding tensile strength, the values for the mortar holding NRL were 7.1, 8.7 and 9.2 N/mm^2 (1029.77 , 1261.83 , 1334.35 psi), thus similar to the values of the NRL-SDS modified mortars which were 7.1, 8.6 and 9.2 N/mm^2 (1029.77 , 1247.32 , 1334.35 psi).