

Correlation between Hydration Characteristics and Initial Cracking Time of Cement-based Materials at Early Ages

M.Z. Chen^{1*}, S. P. Wu¹, M.K. Zhou¹, Z. He²

¹*Wuhan University of Technology, Wuhan, China;* ²*Wuhan University, Wuhan, China*

1. Introduction

Recent advances in rapid construction overlay techniques, high early strength concrete technology, and new cement and admixture formulations have renewed concerns about volumetric stability of concrete. Cracks occurs easily in concrete structures, especially with the use of concrete characterized by a low water-to-cement ratio, an increased cement content, and the incorporation of silica fume (or other pozzolans) and a superplasticizer along with a quicker construction [1]. Early-age cracking influences directly the durability and serve life of concrete structures [2]. A lot of research results indicate that during the hydration, setting and hardening of cement-based materials at early ages, its microstructure, thermal properties, permeating quantity, diffusivity, compound impedance and the setting properties, can be some important parameters to describe mechanical properties and durability of concrete. Therefore, under the urgent need of the sustainable development and durable design of concrete structures, it's important to understand the mechanism of early age cracking and the relationship between early hydration and deformation of cement-based materials.

The structure of concrete is not a static property of the material. The properties of concrete depend on the cement hydration products, which continue to form for several years. The aim of studying the characteristics of the cement hydration is to understand the effect of the hydration on the structures and mechanical behaviors, not just to know the the chemical action or the hydration mechanism [3]. For quantifying the behavior of concrete in its early life, including its proneness to cracking, it has to know the evolution of the materials properties is related to the progress of the hydration process. Therefore, to better understand the hydration process on different sides is the precondition of effectively solving all problems of cement-based materials in service.

In order to explore the effect of early hdyration on dimensional stability of cement-based materials, initial time of cracking in mortar under drying restrained shrinkage and electrical resistivity of cement pastes at the early hydration were tested using a multicenter ellipse ring apparatus with an automatic monitoring system and a non contact resistivity meter,

*Corresponding author. Tel : +86-27-63002953; fax : +86-27-87641294; E-mail address: cmza@163.com

respectively. The hydration process revolved by resistivity measurement was used to compare the shrinkage cracking of corresponding mortars at the early ages. The results show that the lower the minimum value of resistivity during the very early hydration process, the shorter the initial cracking time. Between them, there existed a good linear correlation (the correlation coefficient >0.90). The mechanism investigation reveals that the liquid characteristic of initial hydration on cementitious materials is the key to influence the early shrinkage cracking at the same cement types and aggregate kinds, and the addition of chemical and mineral admixtures and soluble alkali affects the volume stability of cement-based materials via changing the liquid characteristics of hydration and corresponding the forming rate, pattern, dispersing, growth of hydrated products and so on.

2. Test methods

Initial cracking time of mortars is tested using a multicenter ellipse ring apparatus with an automatic monitoring system (see Fig.1). In this apparatus, five specimens can be measured at the same time, and a rigid ellipse is used to restrain the shrinkage of an ellipse-ring-shaped specimen surrounding it. It's well known that an elliptical shape generate a higher stress concentration than a circular shape does. Therefore, cracking of mortars will occur in a shorter time. More details regarding this apparatus can be found in Ref. [4, 5].

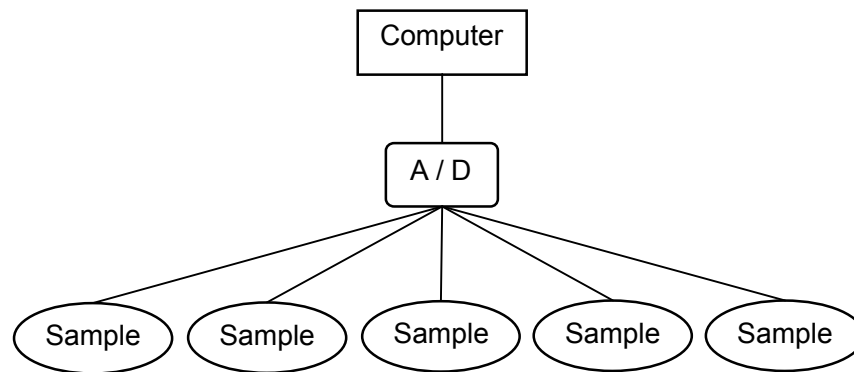


Fig. 1 Schematic of ellipse-ring shrinkage cracking tester with multi-channel

The mortar samples were prepared with three types of ordinary Portland cement (OPC), one dosage of fly ash, one dosage of silica fume, four types of alkali, three types of chemical admixtures and three w/b. Mortars were made of one part of cement and two parts of sand by mass. The fineness modulus of sand, conformed to China GB/T17671-1999 (ISO), is 2.65. Alkalinity was increased by adding to the mixing water as $\text{Na}_2\text{O}\%$, e.g. by mass of cement. Results of chemical analysis of OPC and mineral admixtures are shown in Table 1. Mix proportions of specimens are listed in Table 2.

Table 1 Chemical composition of materials (wt%)

Item	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LOI	Na ₂ O	0.64 K ₂ O
Hongkong Cement ()	20.83	6.28	2.47	63.12	1.16	2.04	1.03		0.64
Huaxin Cement ()	21.74	5.80	4.04	59.64	3.24	2.08	2.44		0.61
Lafarge Cement ()	18.21	3.10	3.08	67.48	1.76	3.05	2.00		0.52
Fly ash (FA)	54.07	29.82	6.81	4.73	1.16	0.48	0.99		1.12
Silica fume (SF)	91.56	1.00	1.22	0.34	1.31	0.40	2.33		1.70

Table 2 Mix proportions of specimens for cracking and resistivity test

No.	admixture	w/b	No.	admixture	w/b	No.	admixture	w/b
1-1	0	0.40	2-1	0	0.40	3-1	0	0.40
1-2	0.5%NaOH	0.40	2-2	1.0%NaOH	0.40	3-2	1.0%KOH	0.40
1-3	1.0%NaOH	0.40	2-3	1.0%KOH	0.40	3-3	1.0%Na ₂ SO ₄	0.40
1-5	0.5%NaOH	0.55	2-4	1.0%Na ₂ SO ₄	0.40	3-4	1.0% K ₂ SO ₄	0.40
1-6	1.0%NaOH	0.55	2-5	1.0% K ₂ SO ₄	0.40	3-5	0.6%JG-3	0.30
1-7	0.5%KOH	0.40	2-6	30%FA	0.40	3-6	0.6%JG-3 +1.0%Na ₂ SO ₄	0.30
1-8	1.0%KOH	0.40	2-7	30%FA+ 1.0%Na ₂ SO ₄	0.40	3-7	0.6%JG-3 +1.0%K ₂ SO ₄	0.30
1-9	0.53%SP	0.30	2-8	30%FA+ 1.0%K ₂ SO ₄	0.40	3-8	0.75%KDNOH- A+1.0%Na ₂ SO ₄	0.30
1-10	0.73%SP	0.30	2-9	10%SF	0.40			
1-11	0.73%SP +1.0%NaOH	0.30						

Note: 1-1~1-11: Hongkong cement (); 2-1~2-9 : Huaxin cement (); 3-1~3-9 : Lafarge cement ().

The specimens for cracking test were cured in a controlled environment chamber at 20±1 and over 95% of relative humidity until the age of 18h. Then, the outer molds of ring specimens were stripped off. After demolding, the top surface of the mortar ring was sealed using epoxy resin without hardener, so that drying would be allowed only from the lateral face. Then, the specimens were tested under a condition of 20±1 and 50% of relative humidity.

Resistivity of the cement pastes has been measured using a non contact resistivity meter (see Fig.2). This method adopts a transformer principle and eliminates electrodes. The measured resistivity curve can be used to interpret the hydration process as well as microstructure development



Fig.2 Photo of a non contact resistivity meter

of cement pastes. More details regarding the non contact resistivity measurement can be found in Ref. [5,6]. The dosage of admixtures and the w/b of specimens for resistivity test is the same of that of mortars for cracking test, which is listed in Table 2.

3. Results

Resistivity measurement of a cement paste may reflect early hydration and microstructure formation of the cement paste [7]. The resistivity curves show the same trend for cement pastes with different mix proportions. As shown in Fig.3, the resistivity curve goes down first and climbs up when the lowest point is reached, then the curve changes the slope and starts to rise. The lowest point, $L(T_{min}, R_{min})$, might be regarded as the maximum conducting point.

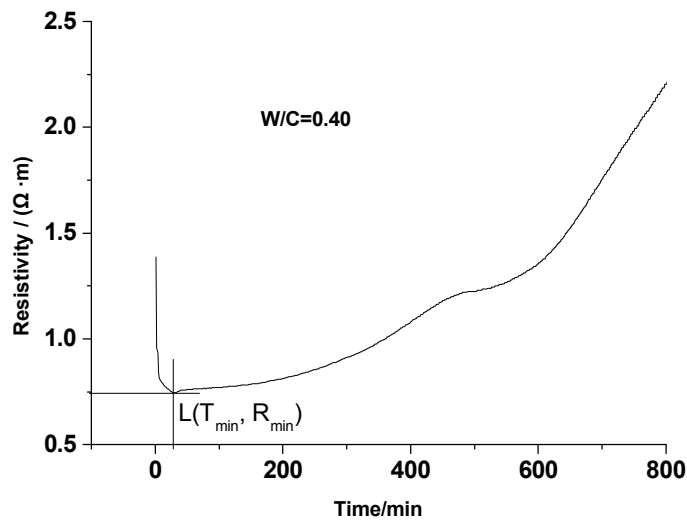


Fig.3 Development of resistivity vs. time for cement pastes during early hydration

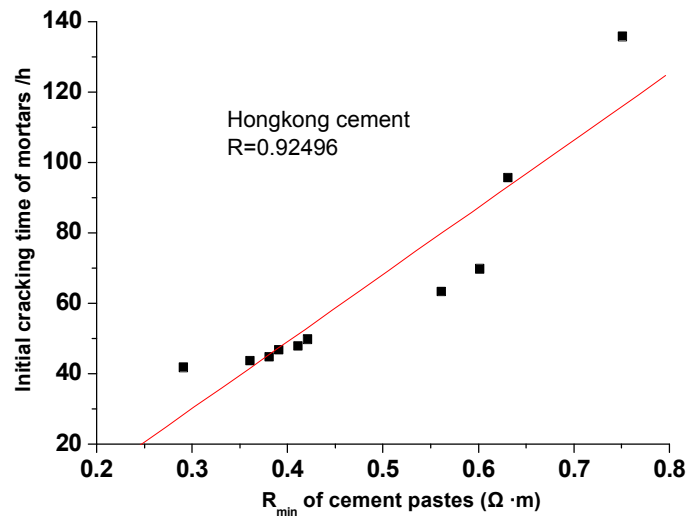


Fig. 4 Relationship between R_{min} and initial cracking time for cement

It was studied that the relationship between the minimum value (namely R_{\min}) of resistivity during the very early hydration process and the initial cracking time of corresponding mortars. The results show that the lower the minimum value of resistivity (namely R_{\min}) during the very early hydration process, the shorter the initial cracking time. Between them, there existed a good linear correlation (the correlation coefficient >0.90), as shown in Fig.4 ~ Fig.6.

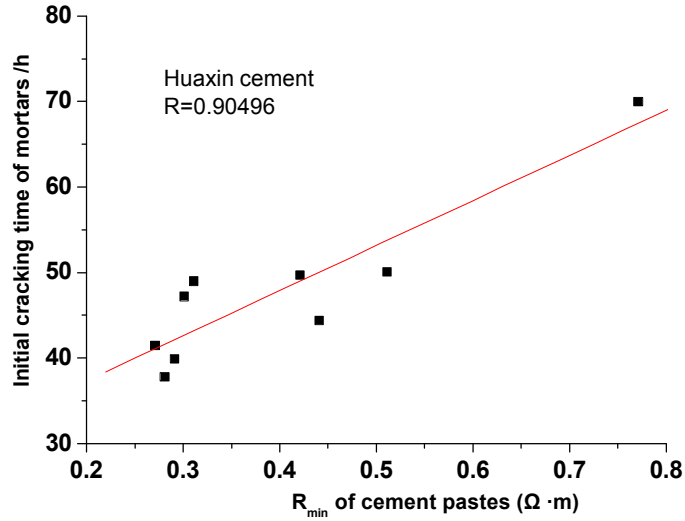


Fig. 5 Relationship between R_{\min} and initial cracking time for cement

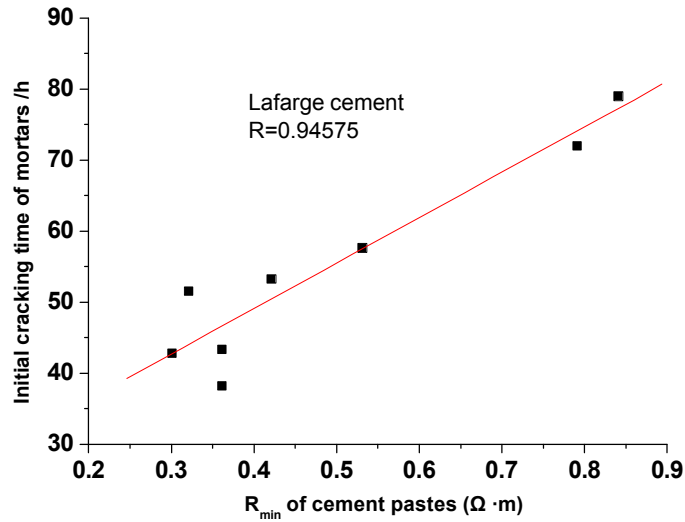


Fig. 6 Relationship between R_{\min} and initial cracking time for cement

4. Discussions

Hydration and microstructural development of cement-based materials are interdependent and materials properties are a function of the microstructure [8]. As yet, however, the relationship between microstructure and materials properties is not known quantitatively. For

practical purposes it is much easier to relate the evolution of materials properties to more easily accessible hydration parameters, like the degree of hydration, e.g. the amount of liberated heat. The electrical properties of cement pastes have proved to be rather sensitive to microstructure changes of cementitious materials. The resistivity measurement represents the global change of cement microstructure and ion concentration. And it is a more accurate index of microstructure development [6]. So, it should be acceptable to relate the cracking sensitivity to electrical resistivity. Schematically this is shown in Fig. 7.

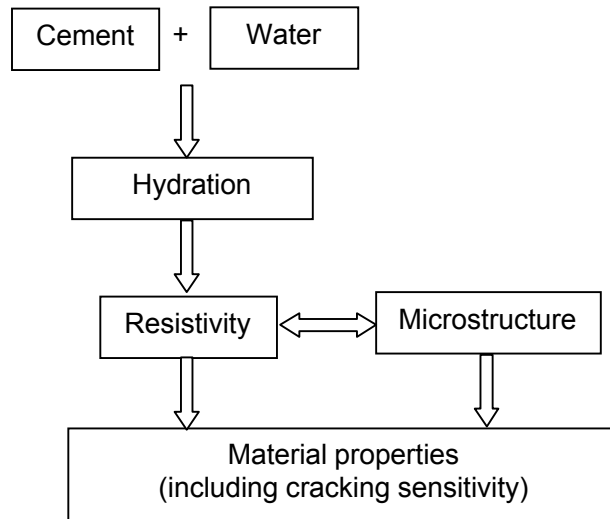


Fig. 7 Schematic representation of procedures for quantification of material properties in hardening cement-based materials

In the cracking test, each sample has the same moulding and curing methods, demoulding time, restrained degree (the same mold and aggregate) and environment, and therefore, the difference in initial cracking time for different samples is mainly related to the quality of cement pastes. However, the property of cement pastes depends on the performances of the new hydrated products in the system of cement-water. Many researches have indicated that the initial process of crystal formation during the hydration influences the structure formation of cement pastes and its hardening, and consequently influences the quality of cement pastes. Rebinder et al. [9] stated, that the ion concentration is important for the formation of C-S-H phase and subsequently its structure. The supersaturation degree of the liquid phase and its duration affect not only crystal nucleation and its growing rate but also crystallizing innerstress and inter-contiguity and the property and structure of new hydrated products [10], and further affect the property of cement pastes and finally influence shrinkage deformation of cement-based materials at early ages.

Therefore, the characteristic of the liquid phase during the initial hydration period of cementitious materials – water can be controlled through adjusting

its components, and consequently the concentration and its interaction of the ions in the liquid will be changed. So, the initial supersaturation, which decides the formation of crystal nucleus, will be influenced, and the formation rate, conformation, dispersivity and its growing of the hydrated products will be directly affected. As a result, it should be realized that the effective control of the formation process on cement pastes, and thereby it may be possible that the performance of cement-based materials will be forecasted and further controlled based on the “microstructure engineering”.

5. Conclusions

Based on the results in this paper, the following conclusions can be drawn.

- (1) The lower the minimum value of resistivity during the very early hydration process of cement pastes, the shorter the initial cracking time of the corresponding mortars. Between them, there existed a good linear correlation (the correlation coefficient >0.90).
- (2) The correlation between the resistivity and the initial cracking time provides the new method to appraise the cracking sensitivity of cement-based materials at early ages. That is to say, the minimum value of resistivity of cement-based materials during the early hydration may be an index for cracking sensitivity of cement-based materials at early ages.
- (3) The liquid characteristic of initial hydration on cementitious materials is the key to influence the early shrinkage cracking of cement-based materials with the same cement types and aggregate kinds. So, the micro control of the performance on cement-based materials may be really realized through adjusting material components and its proportion and controlling the characteristic of the liquid phase for the system of cementitious materials – water.

References

- [1] P.Y.Yan, H.Z.Lian. Analysis of early cracking of concrete by holistic methodology and countermeasure, *Architecture Technology*, 2003(1), 15~18
- [2] G.X.Huang, R.Y.Hui. Shrinkage of concrete, Beijing: China Railway Press 1990, 08: 5
- [3] P. Lu, Introduction of Cement-based Materials, Tongji University Press, Shanghai, 1991
- [4] Z. He, X.M. Zhou, Z.J. Li, New Experimental Method for Studying Early-age Cracking of Cement-based Materials, *ACI Materials Journal*, 101(1) (2004) 50-56
- [5] M.Z.Chen, Influence of Compositions on Hydration and Shrinkage Cracking in Cement-based Materials at Early Ages, Ph.D Thesis, Wuhan University, Wuhan, China, 2004
- [6] Z.J. Li, X. S.Wei, W. L.Li, Preliminary Interpretation of Hydration Process for Cement-based Materials at Early Ages, *ACI Materials Journal*, 100(3) (2003) 253-254
- [7] X.S. Wei, L.Z. Xiao, Z. J. Li, Study on Hydration of Portland Cement Using an Electrical Resistivity Method, *Journal of the Chinese Ceramic Society*, 32(1) (2004) 34-38
- [8] K.van.Breugel, Modelling of Strength Development in Hardening Concrete, Microstructure Features and Engineering Models, Published by Department of Civil & Mining Engineering, Division of Structural Engineering, TU Delft, The Netherlands, 2001
- [9] J. Skalny, J.F.Yong. Hydration Mechanism of Portland Cement, in: Symposium of The 7th International Congress on the Chemistry of Cement, China Building Industry Press, Beijing, China, 1985,pp. 169-194
- [10] M. Z. Chen, Y. W. Wang, Z. He, Relationship between Hydration Characteristics and Volume Stability of Cement-based Materials at Early Ages, *Journal of Wuhan University of Technology*, 28(2) (2006) 17-19, 69