



# Hydration of cement with retarder characterized via electrical resistivity measurements and computer simulation



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## HIGHLIGHTS

- Electrical resistivity method was applied to investigate hydration process of cement paste with retarder.
- This study correlated the results from electrical resistivity measurements to computer simulation.
- Electrical resistivity method investigation satisfactorily reflects the retarding effect of retarder.
- Computer simulation agrees with experimental results, well interpreting hydration process.

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## ABSTRACT

Development of the electrical resistivity with time was measured for cement pastes with the addition of citric acid monohydrate (0%, 0.03%, 0.05% and 0.07%) using a non-contact electrical resistivity measurement device. As the retarder content increases, the electrical resistivity becomes larger in the dissolution and precipitation period but smaller after the setting period because of the protective layer formed around the clinker grains. The setting-time test confirmed that the time of the second peak in the curve of the electrical-resistivity development rate can reflect the setting behavior of the pastes. The time of the third peak in the curve of the electrical-resistivity development rate reflects the transition from a phase-boundary mechanism to a diffusion-controlled mechanism during cement hydration, and thus it was treated as the critical time in a computer simulation of the cement hydration. The computer simulation enabled the visualization of the microstructural evolution and the development of the hydration degree and porosity with time. The simulated results demonstrate the strong retarding effect of citric acid on cement hydration in the early stage. The hydration degree determined by the simulation is in consistent with the results of a non-evaporable water test. The microstructural observations obtained via scanning electron microscopy (SEM) show that the retarder delays cement hydration during the early stage, which confirms the findings of the computer simulation.

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## 1. Introduction

The function of a retarder in a cement-based material is to offset its setting time to provide sufficient time for transportation and casting without any obvious loss of slump or workability. The most common method of measuring the setting time is the penetration resistance (Vicat) experiment. Aided by the development of novel technology and apparatus, Li et al. [1] have used the electrical-resistivity measurement as an alternative method of determining the setting time indirectly. The conventional methods of measuring the electrical resistivity of cementitious materials can be categorized into direct-current methods and alternating-current methods, both of which require electrodes for their measurements. Therefore, there is the potential for contact problems between the

electrodes and the matrix, which could seriously affect the accuracy of the measurement. In this study, a non-contact electrical resistivity measurement (NC-ERM) was applied. NC-ERM adopts a transformer principle that does not require the use of electrodes. Therefore, it avoids contact problems and offers simple procedures and more accurate measurements.

This study focuses on not only the setting time of a cement paste with a retarder but also its compressive strength, which is closely related to its microstructure, especially the porosity [2]. Therefore, it is of great significance to study the microstructural evolution during the cement hydration. Although NC-ERM can help to determine the setting time, it cannot directly offer insights into the microstructural evolution; for example, it cannot provide a visualization. Scanning electron microscopy (SEM) and small-angle X-ray scattering (SAXS) can provide information on the microstructural evolution, and mercury intrusion porosimetry (MIP) can measure the porosity. However, the measurements obtained via

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SEM and SAXS cannot be used to obtain quantitative results, and the procedures of MIP testing are very complicated. In this context, computer simulation not only can solve the aforementioned problems but also can be quite economical.

Computer simulations have been widely used in the field of cement-hydration research, including the HymoStruc model, the CEMHYD3D model [3], and the latest modeling platform ( $\mu\text{ic}$ ) [4]. Princigallo et al. [5] have conducted simulations using CEMHYD3D and HymoStruc to investigate the early development of properties in a cement paste, and they have reported good agreement between their simulation results and experimental data. Ye [6] has adopted a numerical simulation model to study the percolation of capillary pores in hardening cement pastes and has found a correlation between the pore structure and the permeability. However, these models did not incorporate NC-ERM. Therefore, this study correlated the results of NC-ERM with the results of a computer simulation to investigate the hydration process of cement pastes that contain a retarder.

## 2. Principles and methods

### 2.1. Mechanism of set-retardation

Citric acid monohydrate was used as the retarder in this study. According to Möschner et al. [7], the citric acid is almost completely removed from the pore solution within the first hours of cement hydration, as determined via the analysis of the pore solution, and the retarding effect of citric acid on cement hydration is associated with its ability to slow the dissolution of the clinker grains. Potassium may act as a counterion for the citrate  $\text{C}_6\text{H}_5\text{O}_7^{3-}$  to form K-citrate on the clinker surface, which forms a protective layer around the clinker grains and thus retards the dissolution. This retardation process has also been reported by Bishop et al. [8] as a ‘dissolution–precipitation’ mechanism for organic phosphonic acids.

The aim of the research reported in this paper was to study the hydration of cement that has been added with a retarder using non-contact electrical resistivity measurement and computer simulation. The ‘dissolution–precipitation’ mechanism is assumed to be responsible for the set-retardation of citric acid monohydrate, and this mechanism is verified by the results of the non-contact resistivity measurements.

### 2.2. Computer simulation based on electrical resistivity measurements

According to the two dynamics concepts proposed by van Breugel [9] regarding cement hydration, in this study, a computer simulation was conducted based on electrical resistivity measurements to enable the visualization of the microstructural evolution

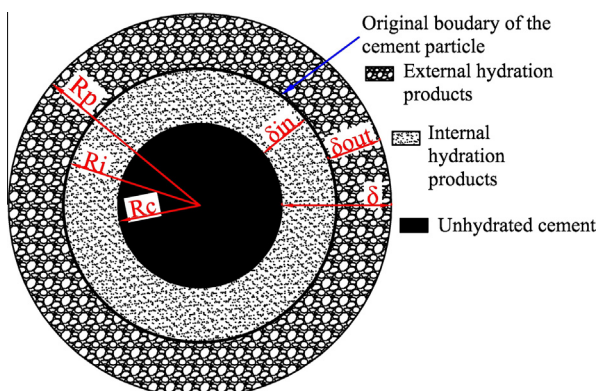


Fig. 1. Schematic representation of cement and hydration products with concentric circles.

of the hydration process and to study the influence of citric acid on the hydration process using this visualization and the quantitative results of the simulation.

The cement particles are assumed to be spherical and distributed randomly in the cement pastes. The cement hydration begins at the surfaces of the cement particles. As shown in Fig. 1, the hydration products outside the original boundary of the cement particle are called external products, and the products inside the boundary are called internal products.

Van Breugel proposed that the cement hydration process is primarily controlled by a phase-boundary mechanism and a diffusion-controlled mechanism, which can be expressed as follows:

$$\frac{d\delta_{in}}{dt} = K_b \quad t < t_{cr} \quad (1)$$

$$\frac{d\delta_{in}}{dt} = \frac{K_d}{\delta_{in} + \delta_{out}} \quad t \geq t_{cr} \quad (2)$$

$$K_b = \frac{K_d}{\delta_{cr}} \quad t = t_{cr} \quad (3)$$

where  $K_b$  and  $K_d$  are the rate coefficient and diffusion coefficient, respectively, in units of  $\mu\text{m}/\text{h}$ ;  $t$  is the cement hydration time, and  $\delta_{cr}$  (critical thickness) is the total thickness of the external and internal hydration products when the phase-boundary reaction transitions into the diffusion-controlled reaction at  $t = t_{cr}$ .

According to Eqs. (1)–(3), the rate of cement hydration during the period controlled by the phase-boundary mechanism is greater than that during the period controlled by the diffusion-controlled mechanism, and the rate during the second period decreases gradually with increasing hydration time. Therefore, the critical time ( $t_{cr}$ ) is of great importance for the cement hydration. According to the retardation mechanism of citric acid monohydrate described in Section 2.1, thicker protective layers form on the surfaces of the clinker grains as the retarder content in the cement pastes increases, thus resulting in a longer critical time. The rate coefficient decreases with increasing  $t_{cr}$ , thus slowing the cement hydration, which means that the cement hydration is delayed.

The addition of citric acid delays the main heat-release peak of the cement hydration, decreases the maximum heat release and broadens the peak, which indicates that citric acid retards the Portland cement hydration [7,10]. It can be observed that citric acid has the same impact on the electrical resistivity development rate curve, and thus the electrical resistivity development rate curve can be used to determine the cement hydration rate. The decrease in the electrical resistivity development rate after the third peak point means that the cement hydration slows from that point onward, which is consistent with  $t_{cr}$ , as described above. Therefore, in this study, the time of the third peak point was taken to be  $t_{cr}$ . NC-ERM offers an easy method of studying the hydration process and provides a more accurate critical time than do calorimetric measurements.

The computer simulation consisted of two steps [11]: the microstructure generation in two dimensions and the simulation over the hydration time. During cement hydration, the hydration products (calcium silicate hydrates and portlandite) are deposited on the surface of the cement, and hence the particles grow into contact with each other, thus reducing the rate of hydration. In this study, the effect of interparticle contacts was taken into consideration by computing influence coefficients using a numerical method in the program.

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